We thank the reviewers for their constructive comments. Specific responses to each of the comments are provided below (reviews' comments in black, our responses in blue, and the manuscript text follows in italics with changes in bold).

Anonymous Referee #1:

This paper reports laboratory experiments aimed at understanding the formation of brown carbon (BrC) from various VOCs under different conditions. Studies on the evolution (aging) of the BrC formed are also presented. This work is a systematic analysis aimed at helping to interpret a number of ambient studies that showed BrC levels varied between cities with different mixtures of emissions.

The paper is highly relevant and interesting, it highlights the importance of anthropogenic SOA to BrC. I have only minor comments.

Are not many of the VOCs tested and attributed to anthropogenic SOA (eg, re discussions on urban SOA), also produced in biomass burning? If so, I would suggests the results have broader impacts than just what is discussed here.

The reviewer raises a good point. Other than primary BrC, which is directly emitted into the atmosphere from biomass burning, gas-phase emissions from burning are also exposed to sunlight and oxidants and can generate secondary products, including SOA. And as the reviewer suggested, nitrated aromatic compounds, identified in this work as strong light absorber in anthropogenic SOA, were also observed in some SOA samples produced from aging of biomass burning (e.g., Desyaterik et al., 2013; Iinuma et al., 2010). However, studies have also shown that SOA formation in biomass burning plumes is highly variable and dependent on factors such as fuel types, mass combustion efficiency, and aerosol aging, suggesting that the contribution of biomass burning SOA should be examined and parameterized carefully (Hennigan et al., 2011). To avoid "over selling" our results, we have carefully added some discussion regarding to the application of our results to biomass burning in lines 430-435, as shown below:

Similar light-absorbing compounds have been identified in certain SOA samples originating from biomass burning (Desyaterik et al., 2013;Iinuma et al., 2010); since substantial variations in SOA formation in biomass burning plumes have been observed both chemically and physically due to fuel types and fire aging conditions (Hennigan et al., 2011), we cannot simply assume similar effects of those parameters on SOA produced from biomass burning emissions.

References:

Desyaterik, Y., Sun, Y., Shen, X. H., Lee, T. Y., Wang, X. F., Wang, T., and Collett, J. L.: Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China, J Geophys Res-Atmos, 118, 7389-7399, Doi 10.1002/Jgrd.50561, 2013.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett Jr, J. L., Kreidenweis, S. M., and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, Atmos. Chem. Phys., 11, 7669-7686, 10.5194/acp-11-7669-2011, 2011.

Iinuma, Y., Böge, O., Gräfe, R., and Herrmann, H.: Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols, Environ Sci Technol, 44, 8453-8459, 10.1021/es102938a, 2010.

Line 179: Suggest changing: which likely explains, to: which could explain,…. I really don't know of ambient data supporting Lin et al (2014). For example, Washenfelder et al. (2015, Geophys. Res. Lett., 42, 10.1002/2014GL0624442015) saw no evidence that iepox (isoprene SOA) contributed to ambient BrC at a remote site in Alabama as part of SOAS where the aerosol is acidic (ie, papers show that it was acid catalyzed isoprene SOA, eg, see Xu et al, P. Natl. Acad. Sci., 112(1), 37-42, 2015).

We have changed Line 179 as suggested by reviewer.

We felt that the Lin study deserved citation because it is an example of SOA derived from isoprene producing light-absorbing SOA, which is in contrast to our study. We note that our experiments were conducted under conditions that are expected to inhibit formation of SOA from the IEPOX pathway, in contrast to the Lin study (i.e., no acidic seed particles were used in our experiments). We can say with certainty that the different reaction conditions relative to Lin et al will produce different types of SOA (Liu et al., 2016). Because we inhibited formation from IEPOX, we are unable to make any conclusions about optical properties of IEPOX SOA from our data. Evaluation of the real-world impact of IEPOX SOA formation on aerosol optical properties is beyond the scope of our study.

References:

Liu, J., D'Ambro, E. L., Lee, B. H., Lopez-Hilfiker, F. D., Zaveri, R. A., Rivera-Rios, J. C., Keutsch, F. N., Iyer, S., Kurten, T., Zhang, Z., Gold, A., Surratt, J. D., Shilling, J. E., and Thornton, J. A.: Efficient Isoprene Secondary Organic Aerosol Formation from a Non-IEPOX Pathway, Environ Sci Technol, 10.1021/acs.est.6b01872, 2016.

Last line of section 3.1, (lines 228-230) I think ambient data that includes actual light absorption coefficients are need to make this statement. The logic of the line is unclear.

We have edited the sentence as below:

Since fulvic acid is often cited as a surrogate of ***strong light-absorbing*** *atmospheric BrC* ***associated with biomass burning****, this comparison shows that light absorption by BrC produced from anthropogenic VOCs can be significant under certain photochemical condition****, consistent with high MAC values measured previously in urban environments when biomass burning impacts were low (e.g., Zhang et al., 2011, 2013; Liu et al., 2013)****.*

In section 3.4, the authors might also want to consider showing changes in the compete spectra, not just changes in absorption at 365 nm. This may prove useful when comparing to ambient data. This could go in supplementary material.

Complete spectra are now provided in supplemental materials as Figure S4. We have added a description in lines 331-332 that: complete spectra in the wavelength range of 300-700 nm are provided in Figure S4.

Line 372-373 regarding the discussion that alpha pinene and isoprene SOA produces little BrC. Again I would suggest the authors look at Washenfelder et al. As noted above, there is no evidence for isoprene SOA, but maybe pinene SOA from night-time reaction with NO3 radical.

Discussion on pinene SOA from night-time reaction with NO3 radical has been added to lines 385-386. We have also edited lines 372-373 to emphasize that our statement refers only to the conditions we investigated in our experiments (see below). We unfortunately did not conduct any experiments investigating BrC formation from NO_3 oxidation of pinene.

Sentence at lines 372-373 (now lines 380-382) is edited as:

*Although α-pinene and isoprene have large contribution****s*** *to the global SOA budget, they were shown to produce SOA with very small light absorption coefficients* ***under the photochemical conditions we investigated****, which agrees with literature data (i.e., Nakayama et al., 2010;Lang-Yona et al., 2010).*

Line 385, typo, ranged ?

The word “ranged” has been changed to “ranging”.

Anonymous Referee #2:

BrC has raised attention over the past decade because of its important contribution to light absorption and climate forcing. The authors aimed to unravel the complex links between SOA light absorption and chemical composition. To achieve this goal, biogenic VOCs (isoprene, alpha-pinene) and anthropogenic VOCs (TMB, toluene) were exposed to varying NOx levels in a chamber. The results show BrC formed from anthropogenic VOCs; specifically, the toluene SOA has the highest absorption under high-NOx level and 30-80% RH conditions. They found a nearly 50% underestimate of the MAC values based on a partitioning model, which is usually the case for current climate models. They also discussed the effect of RH and aging on the optical properties of aromatic BrC. In the end, the authors calculated the imaginary refractive indices and compared them with previous literature values. Overall, the experiments are described well and the results provide new insights into the BrC light absorption. I favor its publication in ACP with the following minor revisions.

-in section 3.3, why is there no absorption enhancement when RH was increased from 30% to 80%?

That is a good question that we are unfortunately unable to definitively answer. In the second paragraph of section 3.3 (lines 297-317), we discuss possible reasons for this observation, though we can only present hypotheses that need further testing. We hypothesize that observations are related to particle-phase reactions because it is difficult to identify any gas-phase reactions involving water vapor that produce BrC chromophores. We assume that the modest to high RH serves as an on/off “trigger” in the production of light-absorbing compounds. We presume that water is not directly involved in these reactions so that additional condensed phase water provided by increasing RH from 30% to 80% does not further enhance reaction rates. Further investigations, including molecular analysis on SOA products formed under various RH conditions, would help answer this specific question.

-fig 1, the alpha-pinene SOA has a higher absorption than the isoprene SOA over the 300-350 nm wavelength range. It might be appropriate to comment on this. It will also be useful to list the MAC values in the supplement.

The text in lines 182-183 has been edited as:

Compared to isoprene SOA, *SOA formed from photochemical oxidation of* α-pinene ~~***also***~~ *showed* ***slightly higher absorption in the 300-350 nm wavelength range, though the absolute MAC values are still small***.

The MAC values of isoprene, α-pinene, TMB and toluene SOA formed under NO_x-free and high-NO_x conditions at 30% RH, i.e., data shown in Figure 1, are now listed in Table S1 in supplemental materials. A description has been added into Figure 1 caption:

Figure 1. MAC values for SOA formed under NOx-free and high-NOx conditions, from isoprene, α-pinene, TMB, and toluene. Note the 10× difference in scale between the terpene and aromatic precursors. ***The MAC values shown in this figure are tabulated in the supplementary material (Table S1).***

-fig 6, it's interesting that the authors observed a decline in the MAC values within 10 hours. I wonder whether the authors tried the 80% condition. And I suggest listing the change in MAC values over time in the supplement.

We did conduct toluene SOA aging experiments at 80% RH though these experiments were conducted with a different experimental protocol. To be specific, UV lights were turned off after several hours of aging to distinguish between the effects of photolysis and hydrolysis. Results were shown in Figure 7. It is clear that the MAC values started to decrease in the first several hours, consistent with what we observed for the 30% RH condition shown in Figure 6.

In response to this comment and a similar comment from Reviewer 1, we added spectra showing the spectral changes as a function of time in Figure S4. We also added a table showing the MAC values in the 300-700 nm spectral range over time as Table S3.

-please add a column in table 1 to label the high-NOx, low-NOx and NOx-free levels.

We have added this column to Table 1.

-line 178, delete (Lin et al., 2014b). Citation already given in line 176, be careful about repeating the citation, line 194, 220, 240, 242: : :: : :

Repeating citations have been deleted.

-line 242 and line 412, there is some ambiguity. Is biomass burning anthropogenic or non-anthropogenic? In line 242 the authors see it as anthropogenic, in line 412, however, it is treated as non-anthropogenic.

The discussion at line 242 was mainly focused on the impacts of biogenic VOCs, specifically isoprene. To avoid confusion, lines 243-246 have been edited as:

Hecobian et al. (2010) measured the light absorption of water-soluble organic carbon (WSOC) in Atlanta in different seasons and found that the winter WSOC has a ~3 times higher MAC than summer, due to ~~***biomass burning influence in winter***~~ ***a higher fraction of organic aerosols formed from biogenic VOCs in summer*** *(Hecobian et al., 2010).*

-line 273 to line 275: I would suggest rephrasing the sentence.

The sentence is rephrased as:

A third possibility is that organic peroxides and alcohols, which were shown to be the dominant component of isoprene SOA (Krechmer et al., 2015), may react with toluene SOA components to produce oligomers capable of absorbing in the UV/VIS that are not present in the single-precursor SOA particles.

Optical Properties and Aging of Light Absorbing Secondary Organic Aerosol

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Keywords: Secondary Organic Aerosol, Brown Carbon, Light Absorption

Abstract

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

1. Introduction

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

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

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

2. Experimental methods

Experiments were performed in the indoor 10.6 m^3 Teflon chamber at the Pacific Northwest National Laboratory (PNNL) operating in batch mode where a discrete quantity of a VOC is introduced into the chamber and allowed to react with the gas-phase oxidants (Liu et al., 2012). The Teflon chamber was flushed continuously with dry purified air until particle concentrations were less than 5 cm^{-3} prior to all experiments. For each experiment, a measured amount of VOC was injected into a glass bulb with a syringe, evaporated with gentle heating, and transferred to the chamber in a flow of purified air. After the VOC injection, 0.5 mL of H_2O_2 solution (Sigma-Aldrich, 50 wt% in H_2O) was injected into the chamber in the same manner. Humidity was controlled by passing pure air at a variable flow rate through pure water (18.2 MΩ cm, <5ppbv TOC) with a HEPA filter downstream of the bubbler to remove any contaminant particles. In experiments in which NO_x were present, NO was injected from a gas cylinder containing a known NO concentration (500 ppm, Matheson Tri-Gas®) with flows regulated by mass flow controllers. After all components were injected and well-mixed in the chamber, UV lights were turned on to initiate photooxidation. The UV flux in the chamber, averaged J_{NO2}=0.16 min^{-1}, was measured continuously by a radiometer that is calibrated to an equivalent photolysis rate of NO_2 and suspended in the center of the chamber. Measurements of J_{NO2} using the photostationary state method were in agreement with the radiometer measurements (Leighton, 1961).

During the experiments, a suite of online instruments were used to characterize the gas- and particle-phase composition. The mixing ratios of the hydrocarbons were continuously monitored with an Ionicon proton-transfer-reaction mass spectrometry (PTR-MS). The mass loading of the aerosol particles was measured using an Aerodyne high-resolution time of flight mass spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006), while the number and volume concentrations were measured with a TSI scanning mobility particle sizer (SMPS). An NO/NO_2/NO_x analyzer (Thermo Environmental Instruments model 42c) was used to measure the concentration of NO and NO_x. A UV absorption O_3

analyzer (Thermo Environmental Instruments model 49C) allowed for the measurement of O_3 concentration.

SOA samples were collected on filters to measure their light absorption. Photooxidation products were collected onto PTFE filters (Pall Life Sciences, 47 mm, 1 μm pore size) at a flow rate of 9 L min^{-1} for a collection period of 60-120 minutes. Typically at least 20 μg of organic mass is required for accurate measurement of light absorption. As described in previous studies (Hecobian et al., 2010;Zhang et al., 2011), filters were extracted in high purity water (> 18.2 MΩ cm), filtered through a 25mm diameter 0.45 μm pore syringe filter (Fisher Scientific, Fisherbrand^{TM} Syringe Filters) and transferred into a long-path (100 cm pathlength) UV-Visible spectrometer (Ocean Optics) to determine the light-absorption spectra. After water extraction, filters were also sonicated in methanol (VWR International, A.C.S. Grade) to extract non-water soluble mass (Liu et al., 2013;Liu et al., 2015a). Total absorption due to BrC (Abs(λ)) is determined as the sum of water-soluble and methanol-extracted absorption from the sequential extraction processes. An extraction efficiency test was performed with 6 filters, in which filters were cut in halves, one half extracted with methanol only and the other half processed with the sequential extraction. Results show that the sum of light absorption from the sequential extraction is comparable to methanol extraction alone, with a slope within 8% of 1 (Figure S1). Studies have shown that the extraction efficiency of organic mass is >90% using methanol as the solvent (Chen and Bond, 2010;Updyke et al., 2012). Thus, it is reasonable to assume that total light absorption determined from the sequential extraction procedure closely approximates the “true” optical properties of the SOA samples. The limit of detection (LOD) was 0.081 Mm^{-1} in the 300-700 nm wavelength range with an estimated uncertainty of 21%. The mass absorption coefficient (MAC) was then estimated using equation 1:

$$MAC(\lambda) = \frac{Abs(\lambda)}{OM} \tag{1}$$

in which Abs(λ) is the light absorption from filter-collected aerosol samples at a wavelength λ, and OM is the SOA mass concentrations on the filter estimated from AMS measurements and the sampled air volume. Wall-loss corrections were not applied to either measured SOA mass concentrations or light absorption determined from filter-collected aerosol samples for consistency. Based on lowest SOA mass concentrations during all experiments, the LOD of the MAC is estimated as 0.004 $\mathrm{m}^2\ \mathrm{g}^{-1}$.

2.1 Description of the SOA two-product model

Ambient studies have shown that SOA produced from urban emissions in isoprene-rich environments tend to have much lower BrC absorption compared to that in anthropogenic emission dominant environments (Zhang et al., 2011). In our study, two mixed precursor experiments were conducted to investigate the changes in aromatic BrC due to addition of isoprene reaction products. We employ a two-product model to describe the partitioning of organic mass between aromatic- and isoprene-derived SOA (Pankow, 1994;Odum et al., 1996). SOA yield parameters for pure compounds are determined by fitting real-time batch mode data as described in the literature (Presto and Donahue, 2006). In the mixed precursor experiments, the PTR-MS data is used to determine the amount of each precursor reacted during the filter collection periods. Then, the pure compound yield parameterizations are used to calculate the relative fractions of the isoprene- and aromatic-derived SOA collected on the filter. The calculation assumes that all SOA components are mutually miscible and reproduced the measured SOA mass with the difference less than 10% (Table ~~S1~~S2). These fractions are then used along with the optical properties of the single-precursor SOA to predict the optical properties of the mixed aerosol.

3. Results and Discussion

3.1 Effects of VOC types and NO_x levels

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

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

Compared to isoprene SOA, SOA formed from photochemical oxidation of α-pinene ~~also~~ showed ~~very limited light~~slightly higher absorption~~. However, we~~ in the 300-350 nm wavelength range, though the absolute MAC values are still small. We observe a slight increase in the MAC values at wavelengths below 450 nm for the α-pinene SOA formed under high-NO_x conditions relative to that formed in the absence of NO_x. These observations are consistent with other studies that have found minimal light absorption for α-pinene SOA, again indicating that the compounds partitioning to the condensed phase do not have extended conjugation (Henry and Donahue, 2012;Nakayama et al., 2010;Laskin et al., 2014).

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

For both toluene and TMB SOA, high NO_x products show substantially higher light absorption than low NO_x. Shown in figures 1 and 2, aromatic SOA formed under high NO_x conditions have much higher MAC values, both in the UV and in the visible. Several studies, based upon both chamber and field observations, have suggested that nitrogen-containing molecules are strong light absorbers (i.e., Nakayama et al., 2013;Liu et al., 2015b;Zhang et al., 2011;Lin et al., 2015b). In a companion study, we reported detailed characterization of the most prominent BrC chromophores in toluene-SOA formed under both NO_x-free and high-NO_x conditions by deploying liquid chromatography combined with a UV/vis detector and high-resolution mass spectrometry (LC-UV/Vis-ESI/HRMS) (Lin et al., 2015b). Samples of toluene-SOA produced under high-NO_x and NO_x-free conditions have substantially different chemical compositions. In high-NO_x SOA, we identified 15 nitro-aromatic compounds, including nitrocatechol, dinitrocatechol and nitrophenol, the total absorbance of which accounts for 60% and 41% of the overall absorbance in the wavelength ranges of 300-400nm and 400-500nm, respectively (Lin et al., 2015b). In contrast, photooxidation products observed in NO_x-free SOA are dominated by non-aromatic compounds with high degree of saturation, which did not show substantial light absorption in the UV/Vis range. Similar to toluene SOA, TMB SOA produced under high-NO_x conditions contains nitrogen-containing compounds in contrast to NO_x-free SOA, which explains the difference in light-absorbing properties (Liu et al., 2012).

For similar reaction conditions, the TMB-derived SOA are less absorptive than the toluene SOA. The difference in the light absorption properties between toluene SOA and TMB SOA may be explained by the difference in the production of nitrophenols. Sato et al. (2012) showed that nitrophenols were not detected in the TMB SOA, possibly due to the fact that NO_2 addition to the phenoxy radical formed in reaction of TMB with OH is inhibited~~ (Sato et al., 2012).~~. Our measurement is consistent with this hypothesis and infers that nitro-aromatics such as nitrophenols are the main sources of light absorption for the aromatic SOA.

The MAC values of SOA produced from aromatic VOCs are comparable to those of other light-absorbing material relevant to atmospheric aerosol particles, such as fulvic acid. Shown in Figure 3a, the blue shaded area represents the measured MAC range of SOA produced in the toluene+NO_x experiments, with the MAC of Suwannee River fulvic acid as a reference. Over the wavelength range 380-480 nm, toluene SOA has higher MAC values than fulvic acid. Since fulvic acid is often cited as a surrogate of strong light-absorbing atmospheric BrC associated with biomass burning, this comparison shows that light absorption by BrC produced from anthropogenic VOCs can be significant under certain photochemical condition~~.~~, consistent with high MAC values measured previously in urban environments when biomass burning impacts were low (e.g., Zhang et al., 2011, 2013; Liu et al., 2013).

3.2 Mixed precursor experiments

Results from laboratory studies have shown that the addition of isoprene reduced the BrC absorption of aerosols formed from toluene+α-pinene mixtures(Jaoui et al., 2008). The lower absorption was attributed to decreased organic aerosol yields (e.g., lower amounts of light-absorbing SOA were formed) (Jaoui et al., 2008). From ambient observations, Zhang et al. (2011) reported contrasting light absorption properties in two urban environments. Fresh SOA in LA displayed much higher light-absorption presumably because of the anthropogenic-dominated environment, while Atlanta aerosols formed from a mix of anthropogenic and biogenic (isoprene) VOC precursors had a 4-6 times lower MAC value~~ (Zhang et al., 2011).~~. Hecobian et al. (2010) measured the light absorption of water-soluble organic carbon (WSOC) in Atlanta in different seasons and found that the winter WSOC has a ~3 times higher MAC than summer, due to ~~biomass burning influence in winter (Hecobian et al., 2010).~~a higher fraction of organic aerosols formed from biogenic VOCs in summer. Using summer-time samples collected in Atlanta, Liu et al. (2013) reported a significantly higher BrC MAC value that was associated with primary anthropogenic emissions, compared to the lower MAC value observed at sites with local anthropogenic emissions on top of regional biogenic-dominant emissions~~ (Liu et al., 2013).~~. To investigate whether isoprene photooxidation products enhance or inhibit absorption of aromatic SOA, we conducted two mixed-precursor experiments. Figure 4 shows the comparison of MAC values at 365 nm of SOA formed from single precursor and from mixed isoprene and aromatic VOCs, under high-NO_x conditions. In both isoprene/toluene and isoprene/TMB experiments, the SOA formed has lower MAC values than those formed from the pure aromatics alone. Qualitatively, this is the behavior that one would expect, since non-absorbing isoprene SOA will “dilute” the chromophores from the aromatic-derived SOA. To determine whether the total aerosol absorption can be described quantitatively, we first estimate the mass of aromatic- and isoprene-derived SOA (Table ~~S1~~S2) using a partitioning model described in section 2.1. We then calculate predicted aerosol MAC values as the mass-weighted average of the MAC values measured for the pure isoprene- and aromatic- derived SOA species. Figure 4 shows a comparison of the measured and predicted mixed-precursor SOA optical properties. The predicted MAC values are 31%-55% lower than the measurements, a difference that is likely outside of the measurement uncertainty. There are several potential explanations for the difference between the predicted and observed MAC values. First, it is possible that SOA formation is not well-described by partitioning theory. One potential source of error in our calculation is that we assume isoprene and aromatic SOA are fully miscible in one another; however, we note that the total predicted SOA mass is within 10% of the observed SOA mass and hence the underprediction of the MAC values cannot be explained by this error. A second possibility is that the partitioning model underestimates the mass of aromatic SOA that has condensed into the mixed-phase particles. Studies have shown that gas-phase wall loss of toluene reaction products can be significant under certain conditions in batch-mode experiments (Zhang et al., 2014). The SOA yield parameterizations are based on data collected in the absence of seed particles, in which case gas-phase wall loss could be significant. However, isoprene reacts much more quickly than toluene (Figure S2); therefore isoprene SOA should form first and provide surface area which should mitigate gas-phase wall loss of the toluene reaction products. Because no seed particles were present in the pure toluene experiments, we would expect those yield values to be biased low relative to the toluene yield in the mixed precursor experiments, thus potentially explain the underprediction of MAC values. A third possibility is that ~~reactions between~~ organic ~~peroxide~~peroxides and ~~alcohol functionalities known~~alcohols, which were shown to be the dominant component of isoprene SOA (Krechmer et al., 2015~~)~~), may react with toluene SOA components to produce oligomers capable of absorbing in the UV/VIS that are not present in the single-precursor SOA particles. Examination of the AMS spectra in the mixed experiments and comparison to the spectra of the pure aromatic- and isoprene- SOA were inconclusive in providing evidence of this hypothesis. Samples were not collected for detailed analysis by LC-UV/Vis-ESI/HRMS. Therefore, at this time we can’t conclusively explain the apparent absorption enhancements we observe.

3.3 Effect of Relative Humidity on Light Absorption by aromatic SOA

In order to investigate the effect of RH on SOA light absorption, both toluene and TMB photo-oxidation experiments were conducted at fixed VOC and NO_x values but variable RH levels (Table 1). Figure 5 illustrates the light absorption spectra of toluene- and TMB-derived SOA as a function of experimental RH. The data shown here were from samples collected at a photolysis time of 200 minutes which corresponds to the time when light absorption reached its highest value. In both TMB and toluene experiments, SOA generated under dry conditions (RH <5%) displayed significantly lower MACs than SOA formed at RH>30%. SOA formed at 30, 50 and 80% RH have similar light absorption to one another. Thus moderate RH enhances the MAC values by a factor of 1.33 at 365 nm and further increases in RH have no effect. An overview of toluene-SOA molecular compositions was analyzed by nano-DESI/HRMS(Lin et al., 2015b), and showed that a large number of nitrogen containing compounds (CHON) were produced under moderate RH condition (Figure S3). The difference in molecular compositions suggest that low RH inhibited the formation of nitrogen-containing compounds, which have been shown to be major light absorbers in toluene-SOA formed in the presence of NO_x(Nakayama et al., 2013;Liu et al., 2015b;Zhang et al., 2011;Lin et al., 2015b).

We are unable to identify any gas-phase reactions in the toluene photolysis mechanism directly involving water vapor. Thus, we conclude that RH must be affecting particle-phase reactions that enhance chromophore formation. Several studies have investigated the effect of RH on various particle-phase SOA chemistry and optical properties. Song et al. (2013) found that SOA produced from α-pinene+NO_x+O_3 in the presence of acidic seed aerosols at elevated RH was less light-absorbing than SOA formed under dry conditions~~ (Song et al., 2013) ~~, which is opposite of our observations. They suggested that the change in light-absorbing properties might be triggered by evaporation of water, which may have enhanced the acidity of aerosol seeds (Nguyen et al., 2012), thererby promoting oligomerization reactions. Zhong ~~et al.~~and Jang (2014) investigated the light absorption of BrC formed from wood burning and observed a faster decay of chromophores at higher RH, which they attributed to the decomposition of chromophores by H_2O_2 that is produced by aqueous-phase photooxidation in the presence of elevated water content level~~ (Zhong and Jang, 2014).~~. Moderate to high RH may promote heterogeneous reactions, which aids in the reactive uptake of volatile compounds into aerosols. Cao and

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

3.4 Effect of photochemical aging on light absorption of aromatic SOA

Atmospheric aerosols have a wide range of lifetimes, ranging from hours to days (i.e., Wagstrom and Pandis, 2009). Previous studies have observed a decrease in aerosol absorption with aging in BrC from various sources including biomass burning and SOA formed from aromatics (Forrister et al., 2015;Zhong and Jang, 2011;Lee et al., 2014). We therefore performed several experiments to study the effect of aging on BrC absorption. Figure 6 shows the MAC values at 365 nm as a function of photolysis time for toluene and TMB SOA produced in the presence of NO_x at 30% RH~~.~~ (complete spectra in the wavelength range of 300-700 nm are provided as Figure S4 in SI, with values tabulated in Table S3). We observe a clear decrease in aerosol absorption with aging with MAC values decreasing by ~35% after 400 minutes and >50% after 800 minutes.

Laboratory studies have suggested that photo-bleaching was due to degradation of BrC chromophores (Lee et al., 2014;Zhong and Jang, 2011;Zhong and Jang, 2014). In our observations, the decrease of MAC with aging is accompanied by a decreasing ON-to-OM ratio, shown in Figure 6. Here we define the term ON as the sum of NO, NO_2 and $C_xH_yO_zN_w$ families measured by AMS, to represent organic nitrates formed during the experiments. NO and NO_2 come exclusively from organic nitrates in these experiments. Ammonium is below the instrument detection limit, and the ratio of m/z 30:46 (around 5-6) is indicative of organic nitrate, thus ruling out formation of ammonium nitrate (Farmer et al., 2010). Therefore, the decrease in the aerosol ON:OM with time indicates the loss of ON groups (Figure 6). ON groups have been identified as the strong light absorbers in aromatic SOA formed under high-NO_x conditions, thus the relative decrease in ON fraction relative to OM is consistent with the observed evolution in OA light absorption.

This observed loss of ON could be caused by photolysis and/or hydrolysis of ON groups. Lee et al. (2014) has observed a substantial decline in the double bond equivalent (DBE) values upon photolysis of aromatic SOA, and suggested that the decrease in SOA light absorption and chemical composition was due to photolysis~~ (Lee et al., 2014).~~. On the other hand, Liu et al. (2012) suggested that particle-phase hydrolysis could substantially reduce ON group concentration, which they also related to a decrease in BrC light absorption~~ (Liu et al., 2012).~~. To distinguish between the effects from photolysis and hydrolysis, SOA was allowed to age in the chamber with UV lights off but at elevated RH in several experiments. Shown in figure 7, the MAC values of toluene and TMB SOA are approximately constant with aging despite the elevated RH. Therefore, we conclude that decrease in MAC values are driven primarily by photolysis (i.e., photobleaching), which is correlated with loss of ON groups that have been shown in many studies, including our sister study, to be BrC chromophores (Lin et al., 2015b;Liu et al., 2015b;Zhang et al., 2013). The effect of RH is less clear, with the dark experiments suggesting the net effect of water-related processes, such as hydrolysis and oligomerization, is either negligible or tends to slightly enhance BrC light absorption, while comparison of experiments with and without RH (section 3.3) suggesting moderate RH enhances the SOA MAC values.

3.5 Imaginary refractive indices

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

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

where *Abs(λ)* is the solution absorption at a given wavelength, OM is the organic mass extracted in solution, and ρ_p is the density of organic aerosols. The density of organic aerosols was calculated by comparing the volume-weighted mobility size measured by SMPS and the mass-weighted aerodynamic size distribution measured by AMS (DeCarlo et al., 2004). A density of 1.25±0.3 g cm^{-3} was obtained for SOA produced under NO$_x$-free conditions, while a density of 1.41±0.2 g cm^{-3} was estimated for SOA produced in high-NO$_x$ experiments. Those density values were employed in equation 2 to estimate *k* values at 365 nm for various types of SOA, which are summarized in Table 2 (k values for the 300-700 nm range are listed in Table ~~S2~~S4).

Although α-pinene and isoprene have large ~~contribution~~contributions to the global SOA budget, they were shown to produce SOA with very small light absorption coefficients under the photochemical conditions we investigated, which agrees with literature data (i.e., Nakayama et al., 2010;Lang-Yona et al., 2010). The SOA compounds produced are dominated by carbonyl, carboxyl, and hydroxyl functional groups, which do not have strong electronic transitions in the UV/Vis range. As a result, those biogenic SOA particles are expected to have a mostly cooling effect on global radiative balance. However, studies have shown that biogenic SOA can be converted into BrC via reactions with dissolved ammonia (Updyke et al., 2012;Laskin et al., 2014~~).~~), or by monoterpene SOA formed from nighttime reactions with NO_3 radical (Washenfelder et al., 2015). Furthermore, it has been demonstrated that reactive uptake of IEPOX into acidic aerosols produce BrC (Lin et al., 2014b), which may have substantial impacts on specific regions with elevated ammonia levels and/or active IEPOX chemistry.

In the present study, the SOA generated from the photooxidation of aromatic VOC precursors, particularly toluene, were found to have significant absorption in the UV/Vis range when formed in the presence of NO_x. Toluene-SOA formed under high-NO_x conditions has a *k* value ~~ranged~~ranging from 0.019 to 0.047 at 365 nm, and 0.011-0.033 at 405 nm. Shown in Figure 3b, the k values are in good agreement with the measurement by Nakayama et al. (2010), where reported k values were 0.047 at 355 nm and 0.007 at 532 nm~~(Nakayama et al., 2010).~~. The k values reported by Zhong and Jang (2011) and Liu et al. (~~2015~~2015b) are close to the lower limit from this work, the former reported a k value of 0.0214 at 350 nm, and the latter reported a range of 0.022-0.033 at 320 nm~~(Zhong and Jang, 2014;Liu et al., 2015b).~~. However, the *k* values derived in this work are substantially higher than those in Nakayama et al. (2013), which reported *k* values ranging from 0.0018 to 0.0072 at 405 nm. A possible explanation is the difference in NO_x levels among the experiments; Zhong and Jang (2011) and Nakayama et al. (2013) studies were conducted at NO_x levels lower than 1 ppmv~~(Zhong and Jang, 2014;Nakayama et al., 2013),~~, which are lower than employed in our study. Nakayama et al. (2013) has reported that light absorption of SOA has a dependence on NO_x, that MAC increases with NO_x ~~(Nakayama et al., 2013),~~, which likely also explains the higher k values reported by earlier work from the same group (Nakayama et al., 2010). Another potentially important difference among the experiments is the RH, with Nakayama 2013 and the Liu studies conducted under dry conditions(Nakayama et al., 2013;Liu et al., 2015b). From what we have observed, moderate RH could enhance the light absorption of BrC.

4. Conclusions and Atmospheric Implications

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

BrC observed in urban environments has large variations in reported MAC values, and our mixed-precursor experiments may provide some explanations for the observed variation. From our measurements, SOA formed from mixtures of isoprene+aromatic VOC have lower MAC values than those formed from the pure aromatics, suggesting that isoprene photooxidation products dilute light-absorbing compounds. Therefore, it is possible that some of the variance in BrC properties between urban sites can be explained by the presence or absence of biogenic emissions. In addition, our results suggested that NO_x concentration, RH level, and photolysis time have considerable influences on the formation and decay of light-absorbing compounds. ~~The~~Similar light-absorbing compounds have been identified in certain SOA samples originating from biomass burning (Desyaterik et al., 2013;Iinuma et al., 2010); since substantial variations in SOA formation in biomass burning plumes have been observed both chemically and physically due to fuel types and fire aging conditions (Hennigan et al., 2011), we cannot simply assume similar effects of those parameters on SOA produced from biomass burning emissions. Thus the result suggests that we should revisit how SOA is treated in climate models, especially in urban areas. Several current regional and global models include NO_x-dependent SOA yield (Lane et al., 2008;Farina et al., 2010;Ahmadov et al., 2012); accurately parameterizing BrC formation from SOA will require a similar strategy.

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

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

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

	NO_x-free	High-NO_x
Isoprene	0.029	0.196
α-pinene	0	1.15
TMB	0.967	6.028-9.899
toluene	0.461	19.48-46.87

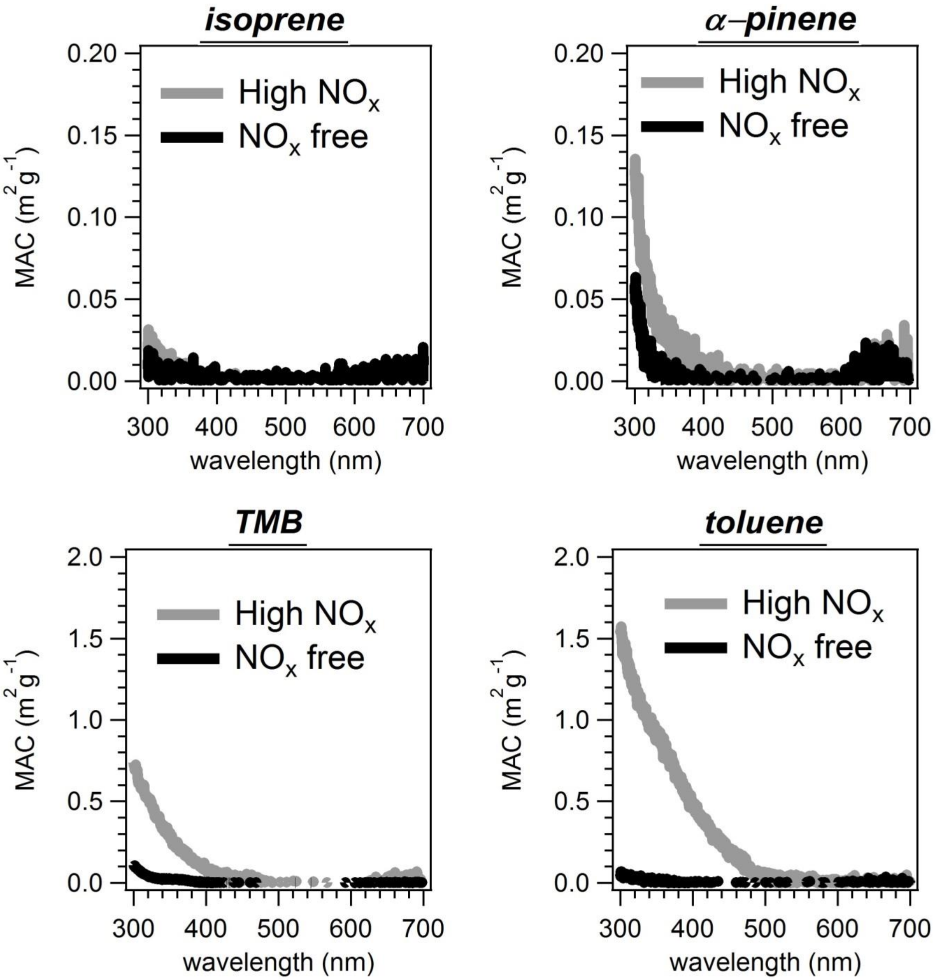

Figure 1. MAC values for SOA formed under NO$_x$-free and high-NO$_x$ conditions, from isoprene, α-pinene, TMB, and toluene. Note the 10× difference in scale between the terpene and aromatic precursors. The MAC values shown in this figure are tabulated in the supplementary material (Table S1).

742

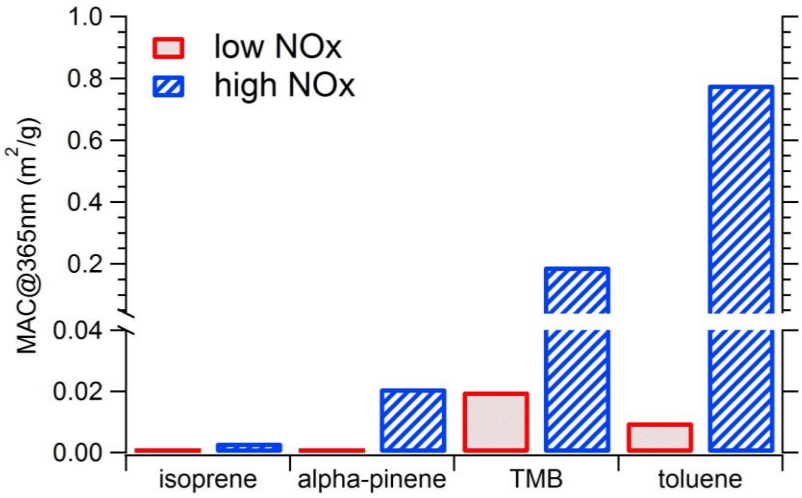

Figure 2. Comparison of MAC from various types of SOA, at a wavelength of 365 nm.

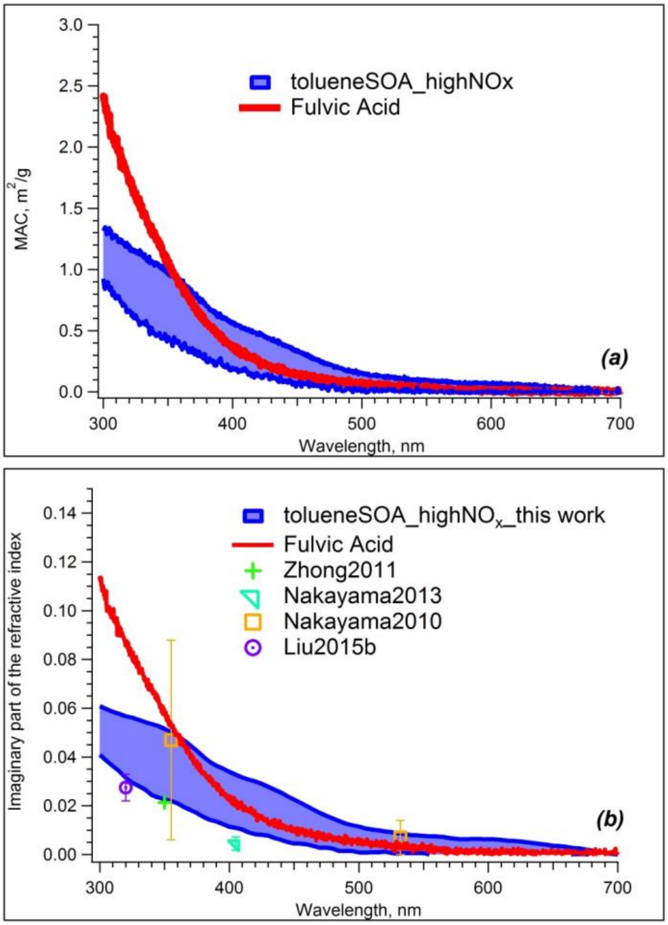

Figure 3. (a) MAC values of Suwanee River fulvic acid (SRFA), and toluene-SOA formed at different high-NO$_x$ conditions. (b) Imaginary part of the refractive index, k, derived from toluene high-NO$_x$ SOA measurements through the 300-700 nm range, with SRFA and literature data as references (Nakayama et al., 2010;Nakayama et al., 2013;Liu et al., 2015b;Zhong and Jang, 2011). SRFA k values were estimated assuming a density of 1.47 g cm^{-3} (Dinar et al., 2006).

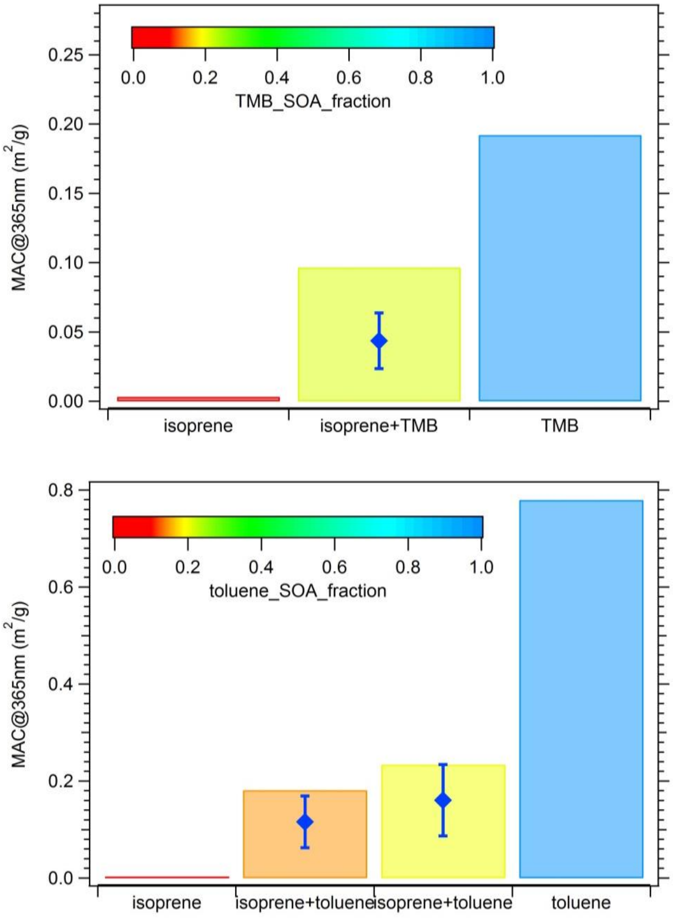

Figure 4. Comparison of MAC values from single-precursor and mixed precursor experiments. Bars represent the MAC values at 365 nm from measurements, and are color-coded by the mass fraction of aromatic SOA. The blue diamonds represent the predicted MAC values based on the modeled fraction of isoprene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

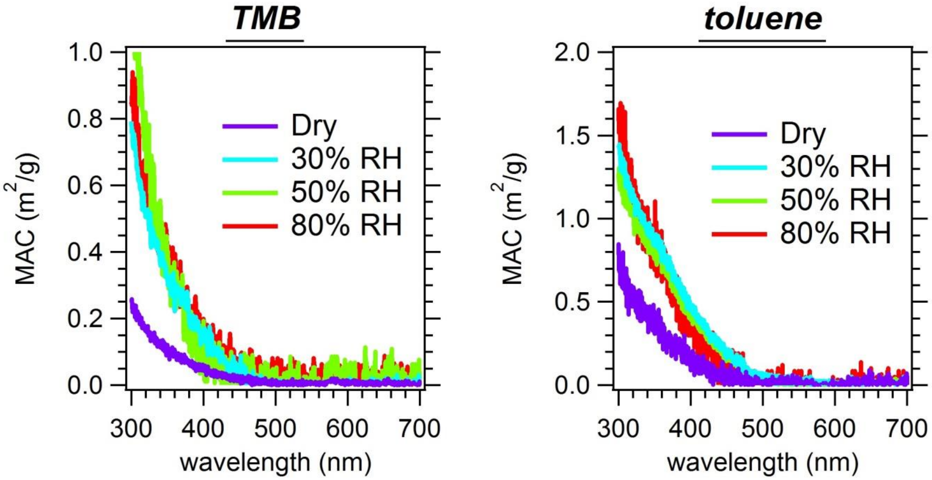

Figure 5. MAC spectra of TMB and toluene SOA formed at <5%, 30%, 50% and 80% RH.

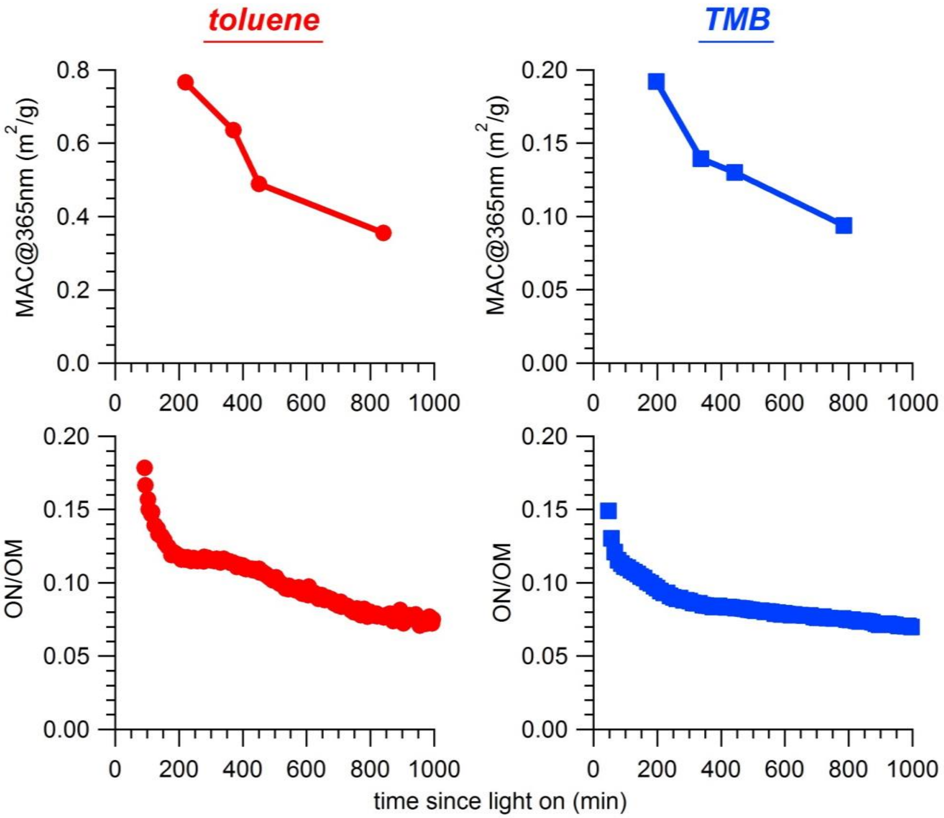

Figure 6.Measurements of the MAC values (at 365 nm) of toluene and TMB SOA formed at 30% RH in the presence of NO_x as a function of photochemical age (top panels). The bottom panels show the AMS-measured ON-to-OM ratio.

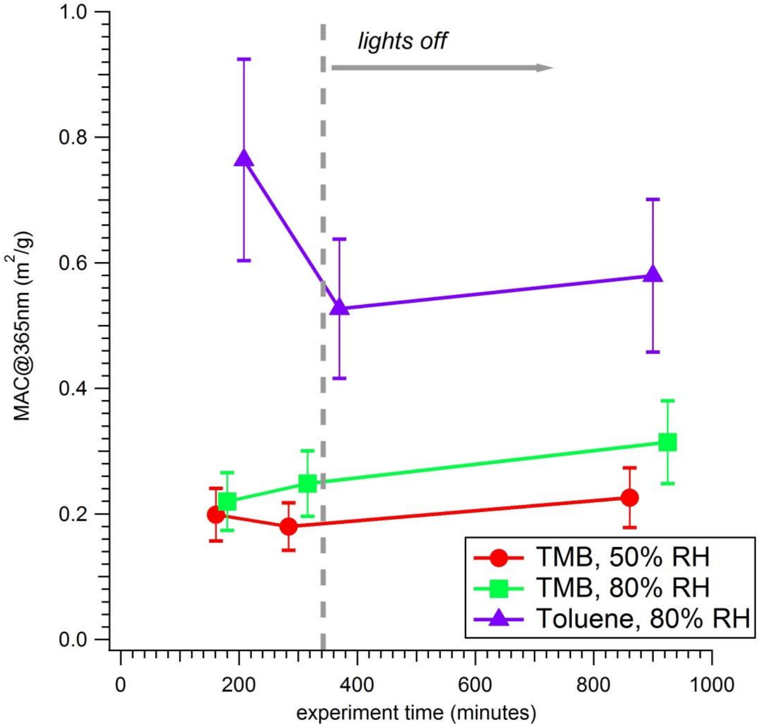

Figure 7. MAC values of aromatic SOA formed under high NO_x conditions and aged in the chamber with the lights off at different RH levels.