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דיקן, פקולטה לכימיה
Prof. Yinon Rudich
Dean, Faculty of Chemistry

November 30, 2018

Prof. Ryan Sullivan – Editor

Dear Ryn,

We thank you for forwarding the Reviewers' comments to us. Overall, we find them very supportive of our work. We have replied to each one of the comments and changed the manuscript accordingly. Below please find our detailed responses to the 2 Reviewer's' comments and the manuscript and SI with the corrections also made in the text.

Finally, please note that we added Daphne Meidan as a co-author. Daphne contributed to the work and her name was omitted in the ACPD version by mistake.

We hope that we have supplied all the necessary information and that the paper can now be accepted for publication in ACP.

Thank you for handling this manuscript

Yours,

Yinon Rudich

1   *Interactive comment on* **"Dynamic changes of optical and chemical properties of tar ball aerosols by**

2   **atmospheric photochemical aging"** *by Li et al.*

3   **Li et al.**

4   yinon.rudich@weizmann.ac.il

5

6   **Anonymous Referee #1:** Generally speaking, this is an interesting paper where 'tar ball aerosol particles' were

7   produced and photochemically aged in an OFR. I am not sure whether tar balls in atmospheric aerosol particles

8   are an important topic. As they are mentioned in the title, the reader expects tar balls to be central for this paper,

9   but it seems to me, the real topic of the paper is BrC formed after wood combustion, and tar balls have been

10   identified with that BrC. Maybe the authors can straighten this out with regard to the title and the focus of the

11   introductory text part. The specific tar ball aerosol generation is interesting. However, this is a laboratory method

12   to obtain as much as possible tar balls in the generated aerosols. How realistic is this aerosol for the environment?

13   I wonder if some key parameters of the 'tar ball aerosol' generated in the lab should be given in the experimental,

14   or, at the latest, early in the results section: Give the particle size distribution, give a rough chemical composition,

15   OC/EC, WSOC, weight fraction of tar balls. Do these particles still contain inorganic constituents? How much?

16   When this is not done, the reader starts into the results section without knowledge about what has actually been

17   generated and is now undergoing heterogeneous oxidation in the OFR. Much of this information is available,

18   but scatter through the manuscript. I would strongly recommend to introduce a section 'Initial tar ball aerosol

19   characteristics after generation'. Maybe the chemical information and the optical measurement results should

20   be separated. Overall, the manuscript call for a better organization. The obtained results are interesting but their

21   atmospheric relevance should be discussed in view of realistic fraction of tar balls over EC or over OC. Some

22   statements in the conclusion section are very broad , line 676 ff.

23   **Authors' reply**: We appreciate the Reviewer's general comments. Tar balls are abundant carbonaceous

24   particles produced by incomplete burning of biofuels. Tar balls contribute a significant number concentration

25   and mass loading in fire emissions. These ubiquitous particles have strong absorption and present potential light

26   absorption across the entire solar spectrum. Due to the strong absorption and high concentrations, they can alter

27   local photochemistry and perturb the radiative balance in the atmosphere on regional and global scales (Pósfai

28   et al., 2004; Hand et al., 2005; Alexander et al., 2008; Chen et al., 2017; Sedlacek III et al., 2018). In ambient

29   biomass burning emissions, tar ball particles coexist with other types of pyrolysis particles (e.g., inorganic salts,

fly ashes, amorphous carbonaceous aerosol, soot, etc.) as both internal and external mixtures, and they can undergo rapid atmospheric processes (dilution due to transport, mixing, removal by precipitation, photochemical and nocturnal oxidation, etc.) once they are released from the fires. Therefore, there are many practical difficulties in intensive investigation of the chemical and optical properties of ambient wood tar aerosols.

New methods for laboratory generation of tar ball particles from wood pyrolysis have recently been suggested, and the laboratory-produced tar ball aerosols resemble atmospheric tar balls in most of their observed properties, including the signature feature of spherical morphology and light absorption, elemental ratio, and similar chemical compositions (Tóth et al., 2014, 2018; Hoffer et al., 2016, 2017). These laboratory-generated tar balls are with the similar size range of atmospheric tar ball aerosols (Sedlacek III et al., 2018; Girotto et al., 2018). This opens up the possibility to conduct detailed laboratory experiments on proxies of tar ball aerosols to understand their basic physical and chemical processes. In this study, we followed the reported production protocol (Tóth et al., 2014; Hoffer et al., 2016) to produce liquid wood tar from pyrolysis of wood under high temperature (dry distillation over 500 ^{o}C to mimic a smoldering process), then tar ball droplets were generated via aerosolization from these tar solutions. The generated tar droplets underwent subsequent dehydration and heat shock to produce tar ball particles. To study the extensive optical and chemical properties of wood pyrolysis tar materials, polar and nonpolar tar materials were further separated and concentrated to produce polar and nonpolar tar ball particles (Hoffer et al., 2016, 2017).

Before starting the photochemical aging studies, the laboratory-generated fresh tar ball particles were extensively characterized and compared with previous studies on ambient biomass burning organic aerosols (BBOA). As shown in Figure S3 of their morphology (supporting information, SI), the lab-generated tar balls are amorphous, carbonaceous spherules with major carbon and minor oxygen content. The O/C ratio in the bulk tar balls was 0.2~0.4 (Figure 2, Table S1 in SI), which is consistent with ambient tar balls and BBOA (Sumlin et al., 2017, 2018; Aiken et al., 2008; Li et al., 2012; Zhou et al., 2017). The detailed chemical information of fresh tar balls was obtained using high resolution time-of-flight aerosol mass spectrometer (HR-Tof-AMS) and by single-particle laser desorption/resonance enhanced multiphoton ionization mass spectrometry (SP-LD-REMPI-MS). The mass spectra for typical polar and nonpolar tar balls are shown in Figure 2, Figure 3, and Table S2 (SI). It is clear that the tar balls contain significant fractions of aromatic hydrocarbons and methoxy-phenolic compounds. These results are consistent with the finding that BBOA or wood tar aerosols consist of major poly-aromatic hydrocarbons (Tóth et al., 2018, Li et al., 2017; Tivanski et al., 2007; Chen and Bond, 2010). In the manuscript, the mass spectra of these atmospherically-relevant tar balls are extensively described and compared with previous studies on field and domestic released BBOA.

We observed weak signals of inorganic ions (e.g., NO_3^-, Cl^-, SO_4^{2-}, and NH_4^+) in the AMS mass spectra of the tar balls, and the mass fractions of these inorganics contributed less than 1.5 wt.% of the bulk aerosols in total (see below Figure R1, pie chart of tar ball chemical composition from AMS measurement), indicating that the generated wood tar particles are dominantly carbonaceous aerosols, the result has been verified by many studies (Pósfai et al., 2004; Hand et al., 2005; Adachi and Buseck, 2011).
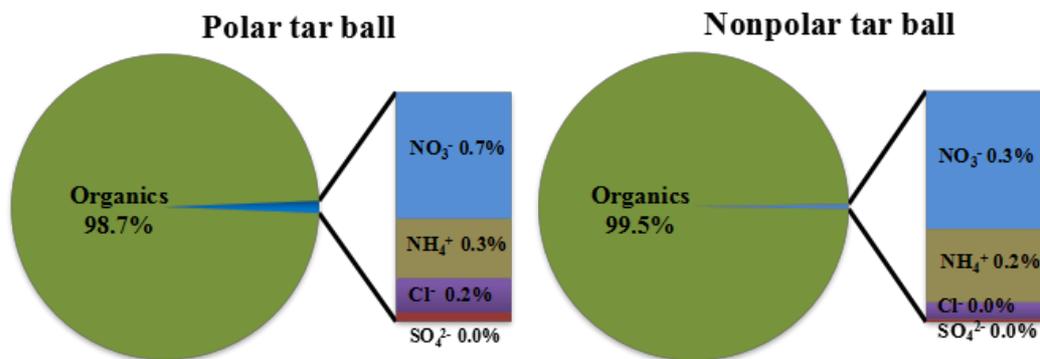
Figure R1. Chemical composition of polar and nonpolar tar ball aerosols obtained from AMS measurement

Following the Reviewer's suggestion, we measured the OC-EC-TC fractions (total carbon, TC = OC+EC) in the tar ball aerosols using carbon analyzer based on thermal-optical reflectance (TOR) based on the IMPROVE protocol. It is clear that the EC content was almost below detection limit for both polar- and nonpolar-tar balls, the slight EC fraction in nonpolar tar ball is less than 0.7% of the TC content and resides in EC1, which can be termed as non-refractory char-EC, empirically defined as EC1－PC. Char-EC is stripped from some OC under oxygen-free heating during OC/EC measurement, which has much weaker absorption, and thus can be classified as brown carbon rather than black carbon (Andreae and Gelencsér, 2006; Arora et al., 2015; Kim et al., 2011; Han et al., 2008, 2009). Many other studies on biomass burning emissions from wildfires and domestic burning have also reported negligible EC content in tar ball aerosols (Chakrabarty et al., 2010; Tivanski et al., 2007; Hand et al., 2005; China et al., 2013). These results further support the finding that the composition of the wood tar we generated is dominated by carbonaceous material.

Table R1. Raw blank corrected elemental carbon composition in polar and nonpolar tar ball samples from thermal-optical measurements

Tar ball Carbon ($\mu g\ cm^{-2}$)	OC1	OC2	OC3	OC4	PC	EC1	EC2	EC3	OC	EC
Polar	7.3	6.1	3.5	0.0	2.0	2.0	0.0	0.0	18.9	0.0
Nonpolar	10.8	9.6	6.0	2.9	7.9	8.1	0.1	0.0	37.2	0.3

Note: OC1, OC2, OC3, OC4 are four organic fractions determined at 140, 280, 480, and 580 ^{o}C pyrolysis temperatures, respectively, in a helium (He) atmosphere. EC1, EC2, and EC3 are three EC fractions being oxidized at 580, 740, and 840 ^{o}C, respectively, in a 2% O_2/98% He atmosphere. OC=OC1+OC2+OC3+OC4+PC, EC=EC1+EC2+EC3-PC.

The light absorption properties of laboratory-generated tar balls were also characterized, see Figure 4 and Table 2. The wavelength-dependent refractive index (RI) was retrieved over the UV-Vis range (365~425nm) for fresh tar ball aerosols and are reported for the first time and compared with reference values from environmental tar balls and BBOA (Sedlacek III et al., 2018; Sumlin et al., 2017, 2018; Chakrabarty et al., 2010). The identical

89 values at some discrete wavelength and the spectral-dependence trends of the RI further justify the use of the

90 laboratory-generated tar balls for studying the optical and chemical behavior of ambient tar ball and/or BBOA

91 in atmospheric process. The RI of tar balls were retrieved based on Mie-Lorenz scattering theory from size- and

92 wavelength-resolved extinction cross section measurements of 200~350 nm tar ball aerosols (see the method in

93 manuscript and tar ball size distribution in Figure S1, SI).

94 This manuscript focuses on the changes in absorption by tar ball aerosols upon photochemical aging. It was

95 found that OH oxidation bleached the tar balls by depleting of absorbing moieties, while addition of NOx during

96 aging inhibited the bleaching and even restored the absorption of tar balls by forming nitrogen-containing

97 functional groups. The changes in the broadband optical properties of the tar balls under different oxidation

98 conditions are presented in the paper, and the chemical mechanisms attributing to the optical changes were

99 discussed. The entire manuscript follows the following scheme:

Laboratory generation of polar and nonpolar tar ball: 2. Experimental setup in Figure 1 and parameter summarized in Table 1

Characterization of **fresh** polar and nonpolar tar ball: 3.1 Chemical composition and optical properties of fresh tar ball aerosols

Chemical information of the fresh, polar and nonpolar tar ball aerosol: AMS and LD-REMPI-MS results. Comparison with reference
Figure 2 and 3, Table S1 and S2

Optical properties of the fresh polar and nonpolar tar ball aerosols: BBCES and UV-Vis results. Comparison with reference, mixing rules were discussed
Figure 4 and Table 2, Figure S4 and S6

explain absorption: Figure S5

Photochemical oxidation of **nonpolar tar ball** (mentioned in abstract): 3.2

Optical/chemical changes of nonpolar tar ball aerosols upon OH photooxidation with different aging extent: bleaching in BBCES and UV-Vis, chemical changes following oxidation, photobleaching mechanism
Figure 5, 6, and 7, Table S5 and S8, Figure S12 and S19

NOx-dependent photochemical oxidation of **nonpolar tar ball** (mentioned in abstract): 3.3

Optical/chemical changes of nonpolar tar ball aerosols upon NOx-dependent OH photooxidation under different NOx addition: increased absorption BBCES and UV-Vis results, chemical changes following oxidation, attribute the absorption enhancement mechanism to organic nitrate formation
Figure 8 and 9, Table S5 and S8, Figure S21 and S22

Atmospheric implications of tar balls due to changes induced by photochemical aging: 3.4

light **extinction/absorption efficiency** and **radiative forcing** changes from tar ball aerosols following NOx-dependent photochemical aging
Figure 10 and 11, Figure S23 and S24

100 To summarize: this study probed for the first time changes in the optical and chemical properties of proxies

101 for tar ball aerosols due to OH radical aging with different oxidation extent from 0.7 to 6.7 atmospheric

102 equivalent days in the presence/absence of NOx. We also assessed pristine photolysis under different photon

103 fluxes and O_3 oxidation of tar balls in the OFR. Finally the atmospheric and climatic implications of tar balls

104 were discussed using a simple radiative transfer model.

105 The particulate inorganic and OC-EC composition have been discussed and added in the manuscript and in the

106 supporting information:

107 Page 11, Line 272 in manuscript: "as no other refractory elemental carbon (EC) content was detected in our

108 samples with a thermal-optical analysis method (details see in SI)."

109 Page 4 in supporting information: Part 2. OC-EC content of fresh polar and nonpolar tar ball aerosols

Page 11, Line 297 in manuscript: "Negligible fractions of inorganics (e.g., sulfate, nitrate, chloride, and ammonium) in tar balls were obtained from AMS measurement as shown in Fig. S2 (SI), and these results further confirm that tar ball aerosols are dominated by carbonaceous compounds with minor amounts of N, S, and Cl (Pósfai et al., 2004; Hand et al., 2005; Adachi and Buseck, 2011). Thereafter, only organics in tar balls are considered,"

Page 5 in supporting information: Part 3.Fresh tar ball composition from HR-Tof-AMS measurement

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Zhou, S., Collier, S., Jaffe, D. A., Briggs, N. L., Hee, J., Sedlacek III, A. J., Kleinman, L., Onasch, T. B., and Zhang, Q.: Regional influence of wildfires on aerosol chemistry in the western US and insights into atmospheric aging of biomass burning organic aerosol, Atmos. Chem. Phys., 17, 2477-2493, doi:10.5194/acp-17-2477-2017, 2017.

Anonymous Referee #2: This manuscript describes the systematic study of how the chemical and optical properties of laboratory-generated tar ball aerosols change upon reaction with OH, exposure to 254 nm light and oxidation in the presence of NOx. What is really interesting about this study is that the authors extracted the polar (water-soluble) and non-polar fractions and found significant differences in both chemical composition and the responses to oxidation. The formation of organic-nitrates was found to increase absorption, which at least partially offsets the decrease in absorption ("bleaching") observed upon photolysis and oxidation by OH radicals. By using a range of EADs (Equivalent daytime Atmospheric oxidation Days) of ~0.5-7 days, the authors explore atmospherically relevant extents of oxidation. The use and description of a controlled method for obtaining reproducible tar ball extract samples in the laboratory is also important. This procedure allows the authors to make systematic studies of semi-authentic aerosol samples that appear to be consistent with ambient tar ball samples. Overall, this manuscript is well written, and the data are interpreted carefully. Given the growing evidence of the importance of tar balls in atmospheric aerosols and the open questions about brown carbon's molecular composition, this manuscript is an important contribution in this area and is appropriate for ACPD.

Specific comments:

1. Since the photolysis was carried out at only one wavelength, 254 nm, statements about increases in absorption from the formation of organic-nitrates offsetting bleaching from photolysis should be highly qualified.

Authors' reply: We thanks the Reviewer for the thoughtful comments. Tar ball particles underwent photochemical aging in the OFR. This included NOx-dependent OH photooxidation and photolysis at 254 nm. We suggest that NOx-dependent OH radical aging should be the dominant photochemical pathway that bleach, darken and oxidize tar balls (Sumlin et al., 2017). The role of photolysis in tar ball chemical and optical changes were investigated, and the results are discussed in detail in the Supporting Information Part 12 (**Optical and chemical changes for tar ball aerosols due to photolysis from UV light irradiation in the OFR**). Specifically, we exposed the tar balls to the same aging condition without O_3 and NOx addition, where the actual UV flux is higher without O_3, RO_2/HO_2 radicals and NOx that absorb some of the photons. However, no significant chemical and RI changes were observed in the tar balls even under maximum UV flux in the OFR. On the experimental time scale (residence time ~144s in the OFR), the small observed changes during photolysis can be neglected compared to the extensive bleaching and oxidation observed under the same conditions in presence of OH radical. We have clarified these points in the paper (Page 18, Line 496-504).

It was also found that addition of NOx restored absorption and counteracted the OH photochemical bleaching of the tar balls to facilitate absorption under high NOx concentration. We suggest that the formation of organic nitrates offsets the bleaching from photolysis and from OH photooxidation to eventually enhance light absorption of the tar balls. It is correct that 254nm UV photolysis in the OFR does not represent the solar irradiation in the atmosphere, it is arbitrary to state that increases in absorption from the formation of organic-nitrates offset bleaching from photolysis. We corrected this statement (Page 2, Line 35-36), and we will quantify the photolysis and OH radical oxidation effect in a following

44   study, and study the chemical process of some related organic-nitrates during their lifetime in
45   the atmosphere.

46   Page 2, Line 35-36 in manuscript: "These observations suggest that secondary organic nitrate
47   formation counteracts the bleaching by OH radical photooxidation to eventually regain some
48   absorption of the tar balls aerosols."

49   2. Equation 4: How is the mass concentration of the solution, C, determined in calculating the
50   MAC (mass absorption cross section)?

51   **Authors' reply**: The mass concentration of BrC extracted in methanol solution was calculated
52   to be in the range of 0.01~0.02 g L^{-1}. The BrC concentration was calculated from filter mass
53   loading of tar ball aerosol (100~150 μg), methanol volume (7.5 mL) assuming hundred
54   percent extraction efficiency, and OM/OC ratio from AMS measurement. The mass loading
55   for each filter sample was estimated from the aerosol volume distribution measured by SMPS,
56   particle density measured from AAC-SMPS (~1.24-1.33 g cm^{-3}), and the total sampling
57   volume. The BrC mass concentration can be calculated by the function shown below:

$$C_{BrC} = \frac{V_{tar} \times \rho_{eff} \times t \times v}{V_{methanol}} \times r$$

58   Where V_{tar} is the tar ball aerosol volume concentration measured by SMPS between 14 and
59   670 nm, ρ_{eff} is effective density calculated from aerodynamic and electric-mobility
60   distribution for fixed monodispersed tar ball, t is the filter sampling time, v is filter sampling
61   flow, $V_{methanol}$ is the total volume of solvent used to extract the filter sample, r is organic
62   carbon (OC) fraction in tar ball aerosol, which can be derived from AMS measurement of
63   OC/OM with the assumption that the EC content can be neglected in tar ball aerosol (as
64   discussed above).

65   We added this information in the methods part of the manuscript:

66   Page10 Line 270 in manuscript: "C is the extracted organic carbon mass concentration in
67   solvent (g m^{-3}), which can be determined directly by normalizing the extract concentration
68   and OC mass fraction for tar balls as OC/OM obtained from AMS data, as no other refractory
69   elemental carbon (EC) content was detected in our samples (details see in SI)."

70
71   3. Line 597: "EAD" should be "EDA".

72   **Authors' reply**: Thanks. "EAD" has been corrected in Page 22, Lin 620.

73
74   4. What fraction of the mass and/or the absorption is attributable to the polar vs. the non-polar
75   fractions?

76   **Authors' reply**: In this study, light absorbing properties of polar and nonpolar chemical
77   matrix from wood pyrolysis were characterized. We found that the refractive index for the
78   mixture of polar and nonpolar organic fractions fit both volume and molar mixing rules (see
79   supporting information of prediction of mixture tar ball optical properties based on different
80   mixing rules). However, the actual fractions of the polar and nonpolar compounds

81 contributing to the mass/absorption of ambient tar ball or BBOA are still under study, as they
82 vary with biofuel, burning conditions, atmospheric processes, and also the method/efficiency
83 used to classify the polar and nonpolar materials from the sample (Sengupta., et al., 2018; Lin
84 et al., 2017; Chen and Bond, et al., 2010; Sumlin et al., 2017) (Page 6, Line 133-137).
85 According to most previous studies, the nonpolar or less polar fractions have higher
86 absorption properties compared with the polar fraction from BBOA. Sengupta et al. (2018)
87 reported that the fuel mass normalized nonpolar fraction is 2-3 times more absorbing than the
88 polar fraction, and complex fuel-dependence and atmospheric aging dependence were
89 observed for absorption changes of both fractions. Lin et al. (2017) and Bluvshtein et al.
90 (2017) tracked the absorption changes of BBOA with respect to different solvent extraction
91 during a whole fire episode, and found distinct different absorbing features for the
92 water-extracted fraction compared to the organic solvent extracts, while acetonitrile and
93 orgmix (acetonitrile: dichloromethane: hexane = 2:2:1, v/v) extracts exhibited similar
94 absorption. According to Lin et al. (2017), from the beginning to the end of the fire event,
95 organic extracts showed higher light absorption at shorter wavelength (λ<380 nm). In contrast,
96 higher light absorption with an absorption feature around 450 nm (attributed to nitro-phenols)
97 hump was observed for water extracts.

98 Rajput et al. (2014) classified the mass fractions of polar and nonpolar organic matter from
99 agricultural-waste burning emissions. Nearly 85 wt.% of the burning organic emissions was
100 attributed to a polar fraction, and this fraction from wheat residue burning was much lower
101 than from paddy burning. Asa-Awuku et al. (2008) suggested that relative molar proportion of
102 nonpolar (hydrophobic) to polar (hydrophilic) compounds in original biomass burning aerosol
103 is 1:3 from Köhler Theory Analysis (Page 6, Line 133-137; Page 17, Line 451-456).

104 In short, the polar fraction dominates the bulk organic aerosol from biomass burning.
105 However, the real polar fraction in the tar balls is undefined, as tar balls belong to BBOA but
106 from specific burning condition with special physicochemical properties. The topic raised in
107 the Reviewer's question will be part of our following research topic to investigate the exact
108 contribution of both the polar/nonpolar matrix and to identify specific chromophore
109 molecules to tar ball aerosol absorption/mass. We have sent the samples of the fresh and aged
110 laboratory-generated polar/nonpolar tar ball for extensive molecular chemical analysis using
111 HPLC/PDA/HRMS (high performance liquid chromatography platform coupled to
112 photo-diode array and high resolution mass spectrometry detectors) and other common MS
113 techniques (e.g., ESI/APPI-MS, electrospray ionization/atmospheric pressure photo ionization
114 mass spectrometry), the results will be published in a different manuscript.

115 We have added the discussion of polar and nonpolar fractions contribution to tar ball
116 aerosols mass and absorption in the manuscript:

117 Page 6, Line 133-137: "The actual fractions of the polar and nonpolar compounds
118 contributing to the mass of ambient tar ball or biomass burning organic aerosol (BBOA) can
119 vary with biofuel sources, burning condition, atmospheric process, and also method/efficiency
120 to classify the polar and nonpolar materials from the sample (Sengupta., et al., 2018; Lin et al.,
121 2017, 2018; Chen and Bond, et al., 2010; Rajput et al., 2008),"

122 Page 17, Line 451-456: "As mentioned above, the real fractions of polar and nonpolar BrC
123 contributing to the mass/absorption of BBOA are undefined, some investigations report that

124   the polar BrC dominate the tar balls' mass (50~85%), but contribute less to the absorption in

125   BBOA (less than 40%) (Asa-Awuku et al., 2008; Bluvshtein et al., 2017; Lin et al., 2017,

126   2018; Rajput et al., 2014; Sengupta et al., 2018). The "linear mixing rule" confirmed in this

127   study should be helpful in the mathematical modeling to assess the climatic impacts of

128   biomass burning related BrC aerosol, when their chemical composition is classified."

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158

Dynamic changes of optical and chemical properties of tar ball aerosols by atmospheric photochemical aging

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Abstract. Following wood pyrolysis, tar ball aerosols were laboratory generated from wood tar separated into polar and nonpolar phases. Chemical information of fresh tar balls was obtained from a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and single-particle laser desorption/resonance enhanced multiphoton ionization mass spectrometry (SP-LD-REMPI-MS). Their continuous refractive index (RI) between 365 and 425 nm was retrieved using a broadband cavity enhanced spectroscopy (BBCES). Dynamic changes of the optical and chemical properties for the nonpolar tar ball aerosols in NOx-dependent photochemical process were investigated in an oxidation flow reactor (OFR). Distinct differences in the chemical composition of the fresh polar and nonpolar tar aerosols were identified. Nonpolar tar aerosols contain predominantly high-molecular weight unsubstituted and alkyl-substituted polycylic aromatic hydrocarbons (PAHs), while polar tar aerosols consist of a high number of oxidized aromatic substances (e.g., methoxy-phenols, benzenediol) with higher O:C ratio and carbon oxidation state. Fresh tar balls have light absorption characteristics similar to atmospheric brown carbon (BrC) aerosol with higher absorption efficiency towards the UV wavelengths. The average retrieved RI is $1.661+0.020i$ and $1.635+0.003i$ for the nonpolar and polar tar aerosols, respectively, with absorption Ångström exponent (AAE) between 5.7 and 7.8 in the detected wavelength range. The RI fits a volume mixing rule for internally mixed nonpolar/polar tar balls. The RI of the tar ball aerosols decreased with increasing wavelength under photochemical oxidation. Photolysis by UV light (254 nm), without strong oxidants in the system, slightly decreased the RI and increased the oxidation state of the tar balls. Oxidation under varying OH exposure levels and in the absence of NOx diminished the absorption (bleaching), and increased the O:C ratio of the tar balls. The photobleaching via OH radical initiated oxidation is mainly attributed to decomposition of chromophoric aromatics, nitrogen-containing organics, and high-molecular weight components in the aged particles. Photolysis of nitrous oxide (N_2O) was used to simulate NOx-dependent photochemical aging of tar balls in the OFR. Under high NOx condition with similar OH exposure, photochemical aging lead to the formation of organic-nitrates, increased both oxidation degree and light absorption for the aged tar ball aerosols. These observations suggest that secondary organic nitrate formation counteracts the bleaching by OH radical photooxidation to eventually regain some absorption of the aged tar balls aerosols. The atmospheric implication and climate effects from tar balls upon various oxidation processes are briefly discussed.

1 Introduction

Organic aerosol (OA), which represent a ubiquitous and dominant burden of the tropospheric particulate pollutants, play important roles in atmospheric chemistry and balance of regional and global radiation (Jimenez et al., 2009; Kanakidou et al., 2005; Seinfeld and Pandis, 2016; Shrivastava et al., 2017). An indirect climate influence of OA relies on their interaction with water thus acting as cloud condensation nuclei (CCN) that may alter the hydrological cycle (cloud formation and perception) and modify Earth's albedo (Forster and Taylor, 2006; IPCC, 2013; Seinfeld and Pandis, 2016). The direct climate effect of OA is through extinction of incoming solar radiation and outgoing longwave radiation. Of particular importance is the warming effect due to light-absorbing carbonaceous aerosol commonly termed as brown carbon (BrC) (Andreae and Gelencsér, 2006). BrC is an important yet poorly understood OA component due to its complex physical properties, undefined chemical composition, and also its dynamic evolution under atmospheric processes (Adler et al., 2010; Moise et al., 2015; Laskin et al. 2015). It has been estimated that BrC accounts for 10-40% of the total light absorption in the atmosphere and when deposited on snow pack (Bahadur et al., 2012; Park et al., 2010), and contributes to global forcing of 0.10-0.25 W m^{-2}, with even higher values on regional scales (Feng et al., 2013).

The origin of BrC can be either primary (i.e., directly emitted) or secondary (i.e., generated by reactions of aromatic or carbonyl compounds in clouds or particles) (Laskin et al., 2015). On a global scale, biomass burning releases over two-thirds of primary BrC and also contributes substantially to overall secondary OA formation (Jacobson, 2014; Jo et al., 2016). Better understanding of the optical properties of biomass burning BrC aerosols is crucial for constraining its atmospheric and climatic implications and Earth's energy balance. Unlike black carbon that absorbs light strongly throughout the entire UV-visible range, different chromophores that may also be coupled via charge transfer complexes enable BrC absorption in a much more pronounced and complicated wavelength-dependence manner (Phillips and Smith, 2004; Reid et al., 2005; Lin et al., 2016, 2017).

Tar balls are a specific type of particles produced from wood combustion (especially from biomass smoldering burning) which are abundant in the troposphere (Pósfai et al., 2004; Hand et al., 2005; Chen et al., 2017). Tar ball particles have been collected and identified in many biomass burning plumes (Pósfai et al., 2004; Fu et al., 2012; Li et al., 2017). Microanalysis has found that tar balls are homogeneous spherical carbonaceous particles with sizes ranging from tens to hundreds of nanometers. These particles contribute a considerable fraction of the biomass burning BrC (Pósfai et al., 2004; Hand et al., 2005; Li et al., 2017). The estimated burden of tar balls on regional and global climatic forcing has been emphasized (Chung et al., 2012; Jacobson, 2012, 2014).

Tar balls from different burning conditions and bio-fuels coexist with many other types of particles (e.g., inorganic salts, soot, and other carbonaceous aerosols in form of internal or external mixing), and these smoke particles undergo rapid atmospheric processing once they are released from the fire (Pósfai et al., 2004; Hand et al., 2005; Li et al., 2015, 2017). However, *in situ* determination of the optical properties of these particles during their lifetimes in the air has seldom been reported due to inherent difficulty in selective tar balls sampling out of complex particle ensembles typical of field burning emissions.

The complex refractive index ($RI=n+ki$, n and k are real and imaginary parts, corresponding to scattering and absorption, respectively) is an intrinsic optical property of aerosols. Quantifying the RI of OA is highly needed for evaluating the related radiative forcing influence (Moise et al., 2015). Recently, several studies have investigated the optical properties of tar ball particles (Chakrabarty et al., 2010; Hoffer et al., 2016; Sedlacek et al., 2018). The optical measurements reported for tar balls or other biomass burning BrC, were discrete over several wavelengths that were constrained by instruments measuring particle light coefficients, or indirectly inferred from calculations based on their electron energy-loss spectra or from UV-Vis absorption of solutions containing dissolved tar balls (Alexander et al., 2008). Hand et al. (2005) measured light scattering coefficients of tar balls-dominated fire plumes using a nephelometer, and reconstructed the scattering coefficients with simplified organic carbon (OC) and elemental carbon (EC) data to get an average RI of 1.56+0.02i for tar balls at $\lambda = 632$ nm. Chakrabarty et al. (2010) measured the RI of tar ball particles from smoldering biomass combustion at 405, 532, and 780 nm, they observed a clear wavelength-, biofuel-, and even burning condition-dependent RI. The light absorption by tar balls was similar to humic-like substance (HULIS) with an imaginary part (0.002~0.015) that increased exponentially towards the near UV wavelengths. Recently, Hoffer et al. (2016) generated tar ball particles from flameless wood pyrolysis in the laboratory. They reported a higher RI value of 1.84+0.20i at 550 nm, which fell closer to RI of soot than to that of HULIS. Large discrepancies reside in these results and discrete RI values make it difficult to decipher the complicated wavelength-dependence character of tar balls optical properties, which finally constrains the assessment of its radiative forcing effect.

Freshly emitted smoke BrC contain chromophores with diverse chemical structures, polarity, and volatility (Lin et al., 2016, 2017). After emission into the atmosphere, smoke particles undergo dynamic changes as a result of dilution, precipitation, and chemical processing on scales of seconds to days, which eventually affect the physiochemical properties of BrC particles during their lifetimes in the atmosphere (Reid et al., 2005; Li et al., 2015; Laskin et al., 2015). Sumlin et al. (2017) simulated atmospheric photooxidation of biomass burning BrC, and reported that photooxidation diminishes their light absorption. Zhong and Jang (2014) investigated the

97 influence of humidity and NOx presence in photochemical aging of biomass burning BrC. They found that

98 sunlight faded the color of BrC, and humidity facilitated the decay of light absorption by BrC, while presence of

99 NOx delayed the fading. Overall, they concluded that light absorption by BrC is governed by chromophores

100 formation and bleaching by sunlight in the atmosphere. Therefore, evaluating the climatic impacts of tar ball

101 particles requires more extensive investigation of its optical properties, and understanding of the dynamic

102 transformations of the optical properties during atmospheric aging.

103 In this study, we generated proxies for tar ball particles by flameless wood pyrolysis (Tóth et al., 2014; Hoffer

104 et al., 2016). This method allows consistent and continuous generation of tar ball proxy aerosols for studying their

105 properties and processes. The RI of the tar aerosols as a function of wavelength in the ultraviolet-short visible

106 region (365~425nm, 0.5 nm resolution) was determined using a broadband cavity enhanced spectrometer

107 (BBCES). A high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) and a single-particle mass

108 spectrometer applying laser desorption/resonantly enhanced multiphoton ionization (SP-LD-REMPI-MS) were

109 used for probing the chemical profile of tar ball aerosols under NOx-dependent multiple-day photochemical

110 oxidation. Specifically, the dynamic changes of their optical properties in correlation with their chemical

111 composition were investigated. The atmospheric implications and climate forcing due to atmospheric aging of tar

112 aerosols and evolution of their optical properties were also explored.

113 **2 Experiment**

114 **2.1 Tar ball particle generation**

115 Following the formation mechanism in biomass burning process, polydisperse tar ball particles were generated

116 from droplets of wood tar in the laboratory (Tóth et al., 2014; Hoffer et al., 2016). In this study, a similar procedure

117 was applied for producing tar ball aerosols. In brief, commercial wood pellets (Hallingdal Trepellets, water content

118 of 6.55 wt.%, size of 2~3 cm in length, 0.2-0.3 cm in diameter) were smashed, heated and dry-distilled in absence

119 of air (25°C min^{-1} increase to 530 $^{\circ}$C from room temperature, and held for 20 min at 530 $^{\circ}$C) to produce liquid tar-

120 water emulsions (~25 mL per hundred grams of used wood pellets). The emulsions were filtrated using 0.45 μm

121 pore size filters (PTFE membrane, diameter 47 mm, Pall Corp.) to remove particulate matter or solid precipitation.

122 After overnight static stabilization, the wood tar solution was phase-separated into water soluble and non-soluble

123 oily phases at an initial 3:1 volume ratio. Herein, we will term these two fractions as 'polar' and 'nonpolar' phases,

124 respectively. The phase-separated solution was further concentrated using a heating plate at 300 $^{\circ}$C with N$_2$ purge

125 flow to prevent oxidation. A final 1:1 volume ratio of polar to nonpolar phase was obtained; then the concentrated

5

126   solutions were sealed and stored in the dark under 2 °C for following experiments. With respect to their potential

127   reactivity and instability, the distillation products were used within a few days.

128   For particle optical measurement, tar balls were produced from aerosolization of above predefined wood tar

129   diluted in methanol (Gradient grade for HPLC, purity≥99.9 wt.%, Merck) using a constant output atomizer (Model

130   3076, TSI) with high-purity N_2 as a carrier gas. As the actual fractions of the polar and nonpolar compounds

131   contributing to the mass of ambient tar ball or biomass burning organic aerosol (BBOA) can vary with biofuel

132   sources, burning condition, atmospheric process, and also method/efficiency to classify the polar and nonpolar

133   materials from the sample (Sengupta., et al., 2018; Lin et al., 2017, 2018; Chen and Bond, et al., 2010; Rajput et

134   al., 2008), tar ball aerosols in this study were generated from polar, nonpolar, and mixtures of two phase tar

135   solutions at volume mixing ratio of 2:1, 1:1, and 1:2, respectively. Activated charcoal denuders and quartz heating

136   tube (150 °C, residence time ~0.7s for particles at a nitrogen flow of 1.0 LPM) were used after the atomizer to

137   outgas the methanol from the gaseous and particulate phases. Mesh filters (TSI) downstream were used to filter

138   out some ultrafine (less than 100 nm) particles.

2.2 NOx-dependent OH oxidation of tar ball aerosols

140   Heterogeneous oxidation of tar ball aerosols was simulated using an oxidation flow Reactor (OFR), shown

141   schematically in Fig. 1. The OFR has been characterized (Kang et al., 2007; Peng et al., 2015, 2016) and the

142   operational procedures have been described previously (He et al. 2018). Briefly, the OFR consists of a horizontal

143   13.3 L aluminum cylindrical chamber (46 cm long × 22 cm ID) operating in continuous flow mode. The chamber

144   is equipped with two power controllable ozone-free mercury-lamps with peak emission at λ= 254 nm (82-934-08,

145   BHK Inc., CA, USA). The two UV lamps are surrounded by Pyrex sheath tubes that are continuously purged with

146   N_2 to cool the lamps and remove outgassing compounds. OH radicals in the OFR are produced through photolysis

147   of externally introduced O_3 under 254 nm illumination and the further reaction of singlet oxygen (O^1D) with water

148   vapor:

149    $$O_3 + hv(254nm) \rightarrow O^1D + O_2 \qquad\qquad R1$$

150    $$O^1D + H_2O \rightarrow 2OH \qquad\qquad R2$$

151   External O_3 was produced by irradiation of 0.2 LPM high purity O_2 using a mercury lamp (λ=185nm, 78-2046-

152   07, BHK Inc., CA). The O_3 concentration downstream of the OFR was measured by an O_3 monitor (2B

153   Technology). A Nafion membrane humidifier (Perma Pure LIC, NJ) was used to supply water vapor to the OFR.

154   Tar ball aerosols carried by 1.0 LPM N_2 flow from the atomizer were introduced into OFR. The initial aerosol

155   concentrations in the OFR were mediated by controlling the concentration of the wood tar solution to be atomized

156   until the number of 350 nm particles was above 100 cm^{-3}, as shown in Fig. S1 of tar ball aerosols size distribution

157   (SI, supporting information). Finally, a total flow of 5.5 LPM with 36~38% RH, initial 27~28 ppm O$_3$, and

158   200~250 μg m^{-3} tar ball particles (assuming material density of 1.0 g cm^{-3}) was maintained, with a corresponding

159   plug flow residence time (RT) of 144s for aerosols in the OFR.

160   The extent of simulated daytime oxidation by OH exposure was varied by changing the UV light intensity. Here,

161   OH exposures in the OFR were inferred by measuring the decay of added SO$_2$ (monitored by Thermo SO$_2$ analyzer,

162   model 43i) due to reaction with OH radicals at specific UV lamp intensity. A low concentration (~60ppb) of SO$_2$

163   was used to minimize its influence on the OH radical reactivity. Typical total OH exposures ranged from

164    $(8.7\pm2.3)\times10^{10}$ to $(8.6\pm1.7)\times10^{11}$ molec cm^{-3} s or 0.5~7 equivalent daytime atmospheric oxidation days (EAD)

165   were maintained, taking typical ambient average OH concentration as 1.5×10^6 molec cm^{-3} (Kang et al., 2007;

166   Peng et al., 2015, 2016).

167   In addition to reactions with oxidants, organic aerosols may change their chemical and physical properties by

168   photolysis (Epstein et al., 2014; Lee et al., 2014; Wong et al., 2014). Therefore, the influence of light irradiation

169   during tar ball photochemical aging was assessed at the short exposure time in the OFR. Here, tar balls aging was

170   repeated at the same conditions (e.g., RT, RH, N$_2$/O$_2$ flow, tar balls concentration, UV lamp power) without O$_3$

171   supply in the OFR. The 254 nm photon flux at specific to maximal UV lamp power was calculated by fitting the

172   OH exposure estimated from SO$_2$ decay and by the Aerodyne OFR Exposure Estimator (v3.1,

173   https://sites.google.com/site/pamwiki/hardware/estimation-equations).

174   Under polluted conditions, nitrogen oxides (NOx) are often involved in the atmospheric transformations of

175   organic aerosol and alter their physiochemical properties (Rollins et al., 2012; Ng et al., 2007; Lin et al., 2015).

176   Therefore, NO$_x$ influence on tar ball aerosol aging was also investigated. Due to rapid conversion of NOx

177   (NO+NO$_2$) into nitric acid (HNO$_3$) under high O$_3$ and OH concentrations, simple addition of NOx into OFR cannot

178   sustain NOx levels that compete with HO$_2$ radicals in the reaction with organic proxy (ROO). NOx generated via

179   N$_2$O reaction with O^{1}D has been modeled and tested to suit the characterization of NOx-dependent SOA formation

180   pathways using OFR (Peng et al. 2017; Lambe et al., 2017). In this study, N$_2$O (99.999%) addition of 0.5 vol.%

181   and 2.0 vol.% were used during tar ball aerosol photochemical oxidation in the OFR, and equivalent OH exposure

182   of about 4.0 EAD was maintained. NO$_x$ (NO and NO$_2$) concentrations downstream of the OFR was measured

183   using a NO/NO$_2$ analyzer (Ecotech, Serinus 40 NOx). Experimental parameters including initial O$_3$ and N$_2$O

184   concentrations, NOx, moisture ratio, maintained OH exposures and the corresponding photon flux at 254 nm are

185   presented in Table 1.

2.3 Online optical and chemical characterization

187   Prior to the optical and chemical measurements, excess ozone and NOx were removed from the sample air stream

188   following the OFR using two diffusion denuders packed with Carulite (Carus Corporation, Peru, IL) and one

189   activated charcoal tube. The stream flow was further dehydrated with two silica gel diffusion dryers. Afterward,

190   the tar ball aerosols were characterized by a combination of on-line chemical and optical instruments.

191   Bulk chemical fragments and organic elemental ratios of tar ball aerosols were monitored in real time by the

192   HR-ToF-AMS (Aerodyne Research Inc., Billerica, MA, USA) in alternating high sensitivity V and high-resolution

193   W modes. The working principles of the AMS have been described in details elsewhere (DeCarlo et al., 2006). In

194   short, aerosol particles are separated from the gas phase through an aerodynamic lens system and then transferred

195   into the vacuum system, where they are impacted onto a vaporizer at about 600 $^{\circ}$C, thus vaporizing the particles.

196   The analyte vapors are ionized with 70 eV electron impact ionization (EI). A time-of-flight mass spectrometer is

197   used for high-resolution analysis of the ions. SQUIRREL v1.16 and PIKA v1.57 codes

198   (http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/) were used to process the collected

199   AMS data. Four ion groups were classified as $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$ (z>1), and $C_xH_yO_iN_p^+$(i≧0, p≧1) based

200   on fragment features. The ions O^+, OH^+, and H_2O^+ were included in the $C_xH_yO_z^+$ group, as concentrations of these

201   species were calculated from the organic CO_2^+ ion abundance using the method in Aiken et al (2008). The ambient

202   improved (AI) atomic ratios of oxygen to carbon (O:C), hydrogen to carbon (H:C), nitrogen to carbon (N:C), and

203   organic mass to organic carbon (OM/OC) were generated from the measured ion fragments.

204   Particle-bound organic molecules were measured using a custom single-particle time-of-flight mass

205   spectrometer. This instrument features laser desorption and resonantly enhanced multiphoton ionization (SP-LD-

206   REMPI-ToF-MS), allowing for the detection of aromatic substances on individual particles. Detailed description

207   and application of the instrument in LD-REMPI ionization mode is given by Bente et al. (2008) and Passig et al.

208   (2017). Briefly, aerodynamically accelerated particles are individually sized using laser velocimetry, and heated

209   by a pulsed CO_2 infrared laser (10.6 μm) to desorb organic molecules. Aromatic substances in the gas plume are

210   selectively ionized via REMPI by a KrF-excimer laser pulse (248 nm) and detected in the positive MS flight tube.

211   The REMPI-MS technique is very sensitive and selective for aromatic substances (Boesl et al., 1978; Grotemeyer

212   et al., 1986; Rettner and Brophy, 1981) and suitable for studies on pyrolysis and (wood) combustion processes

213   (Heger et al., 1999; Czech et al., 2017). For the tar ball aerosols it provides complementary information to the

214   HR-ToF-AMS spectra. A custom software on LabView basis records and calculates the aerodynamic size and

215   individual mass spectra of the particles.

216   For optical measurements, tar ball aerosols were size-selected using an Aerosol Aerodynamic Classifier (AAC,

217   Cambustion, UK). AAC has significant advantages over the commonly used Differential Mobility Analyzer

218   (DMA) classifier. The AAC classifies particles based on the aerodynamic size without charging and hence it

219   avoids the contribution of multiply charged particles, thus generating real monodisperse size-selected particles

220   distribution, reducing the errors associated with multiply charged large particles. In addition, the AAC has higher

221   particle transmission efficiency at the relevant size range (Tavakoli and Olfert, 2013, 2014). Aerodynamic size-

222   classified particles after the AAC were further scanned by a scanning mobility particle sizer (SMPS, classifier

223   Model 3080, DMA Model 3081, CPC model 3775, TSI) to derive their mobility size distribution. The effective

224   density of tar balls can be estimated from Equation 1 with assumptions of homogeneous composition and particle

225   shape factor of 1.0, which was verified later in this study:

226      $\rho_{eff} = \dfrac{D_{aero}}{D_m} \rho_0$ [1]

227   Where ρ_{eff} is an effective density, D_{aero} and D_m are aerodynamic and mobility diameters, respectively. ρ_o is unit

228   density of 1.0 g cm^{-3}.

229   Based on the derived effective density, size-specific tar ball aerosols covering mobility diameters between 175

230   to 350 nm with an interval of 25 nm were size-selected via AAC, and monodisperse tar balls were introduced into

231   a dual-channel broad-band cavity enhanced spectrometer (BBCES) for light extinction (α_{ext}) measurements in the

232   wavelength of 360~395 nm and 385~435 nm (at resolution 0.5 nm). A detailed description of the instrument can

233   be found elsewhere (Washenfelder et al., 2013; Flores et al., 2014a, b). With the combination of a condensation

234   particle counter (CPC, Model 3575, TSI) to measure particle concentration (N) in series, size-specific particle

235   extinction cross section (σ_{ext}) can be calculated by Equation (2):

236      $\sigma_{ext}(\lambda, Dp, RI) = \dfrac{\alpha_{ext}(\lambda, D_p, RI)}{N(D_p)}$ [2]

237   Where λ is the wavelength of incidence light, D_p is the particle mobility diameter.

238   Using the Mie-Lorenz scattering theory, the wavelength-dependent complex refractive index of spherical

239   homogeneous particles was derived (Pettersson et al. 2004; Abo Riziq et al. 2007). The retrieval algorithm was

240   limited to search for n≧1 and k≧0 as their physical boundaries. Thereafter, spectral dependent extinction,

241   scattering, and absorption cross sections (σ_{ext}, σ_{sca}, and σ_{abs}) were calculated from the complex RI at specific

242   particle size. Using these parameters, the single scattering albedo, indicating the scattering fraction of light

243   extinction (SSA = $\sigma_{sca}/\sigma_{ext}$), was calculated.

244   The absorption and extinction Ångström exponents ($\mathring{A}_{abs}$ and $\mathring{A}_{ext}$) describe the spectral dependence of aerosol

245 light properties, and are widely used in climate modeling (Russell et al., 2010). It is customary to extrapolate the

246 optical spectral absorption and extinction fitting to the range of wavelengths using a power law $\propto \lambda^{-\mathring{A}abs}$ and $\propto \lambda^{-}$

247 $^{\mathring{A}ext}$, respectively. In this work, we determined $\mathring{A}_{ext}$ and $\mathring{A}_{abs}$ with a linear regression of $\ln(\sigma_{ext})$ and $\ln(\sigma_{abs})$ against

248 $\ln(\lambda)$ over the range of 365 to 425 nm:

249
$$\mathring{A}_{ext} = -\frac{\ln(\sigma_{ext})}{\ln(\lambda)} \qquad \mathring{A}_{abs} = -\frac{\ln(\sigma_{abs})}{\ln(\lambda)} \qquad\qquad [3]$$

250 Here $\mathring{A}_{ext}$, $\mathring{A}_{abs}$, and SSA were calculated for tar ball aerosols with a median diameter of 150 nm.

251 **2.4 Offline optical characterization**

252 In addition to the *in-situ* measurements, tar ball particles were also collected quantitatively onto Teflon filters (47

253 mm diameter, 0.45 μm porosity, Pall Corp.) at sampling flow rate of 2 LPM and then extracted using methanol

254 (HPLC grade, purity≥99.9%, Merck) for offline UV-Vis absorption measurement (Cary 60 UV-VIS spectroscopy,

255 Agilent). Methanol extraction of organic compounds has been commonly performed in various studies (Hoffer et

256 al., 2006; Laskin et al., 2009; Yee et al., 2013; Finewax et al., 2018; Xie et al., 2017). Here we verified the

257 completeness of the extraction by extracting each filter twice with methanol. Moreover, vortex shaking (Vortex

258 Genie-2, Scientific Industries) rather than sonication was applied to avoid chemical degradation of the extracts

259 upon ultrasonic irradiation (Miljevic et al., 2014; Mutzel et al., 2013). The methanol extractable BrC mass

260 absorption cross section (MAC, m^2 g^{-1}) and refractive imaginary k of the tar balls were estimated based on

261 following relations (Chen and Bond, 2010; Laskin et al., 2015):

262
$$MAC_{(\lambda)} = \frac{Abs_{(\lambda)} \times \ln(10)}{C \times b} \qquad\qquad [4]$$

263
$$k_{(\lambda)} = \frac{\lambda \times \rho \times MAC_{(\lambda)}}{4\pi} \qquad\qquad [5]$$

264 $Abs_{(\lambda)}$ is the base-10 absorbance result from UV-VIS spectroscopy (unitless), b is the optical length of the solution

265 (1 cm), C is the extracted organic carbon mass concentration in solvent (g m^{-3}), which can be determined directly

266 by normalizing the extract concentration and OC mass fraction for tar balls as OC/OM obtained from AMS data,

267 as no other refractory elemental carbon (EC) content was detected in our samples (details see in SI). λ is the

268 incident light wavelength, and ρ is material density (g cm^{-3}). Here, the derived effective density ρ_{eff} was used. The

269 absorption Ångström exponent based on MAC was also derived as $\mathring{A}_{abs-UV-Vis}$ over the 365-425 nm spectral range.

270   In addition, particles were impacted at a flow of 2.5 L min^{-1} onto cyclopore track-etched polycarbonate

271   membrane (47 mm, 0.1μm porosity, Whatman Inc.) to investigate the morphology of tar balls using Scanning

272   Electronic Microscopy (SEM, JEOL JSM-7000F).

2.5 Radiative impacts of tar ball aerosols

274   To assess the climatic influence of tar ball aerosols, a wavelength-dependent direct shortwave aerosol simple

275   radiative forcing efficiency (SRF, W g^{-1}) was estimated using the clear sky air mass global horizontal solar

276   spectrum (AM1GH), assuming that tar ball aerosols form a uniform, optically thin aerosol layer at the lower

277   troposphere or on ground (Bond and Bergstrom, 2006; Levinson et al., 2010):

278    $$\frac{dSRF}{d\lambda} = -\frac{1}{4}\frac{dS_{(\lambda)}}{d\lambda}\tau_{atm(\lambda)}^2(1-F_c)[2(1-R_{sfc})^2\beta_{(\lambda)}MSC_{(\lambda)} - 4R_{sfc}\cdot MAC_{(\lambda)}] \quad\quad [6]$$

279   Where $dS(\lambda)/d\lambda$ is the solar irradiance (photons s^{-1} cm^{-2}), τ_{atm} is the atmospheric transmission (taking 0.79 for

280   simple calculation), F_c is the cloud fraction (approximately 0.6), R_{sfc} is the surface albedo (approximate 0.19 for

281   urban area ground and 0.8 for snow) (Chen and Bond, 2010), β is the average up-scatter fraction (the fraction of

282   scattered sunlight that is scattered into the upward hemisphere), and $MSC(\lambda)$ is wavelength-dependent mass

283   scattering cross section, respectively. We simply calculated radiative forcing of particles with atmospheric relevant

284   size of 50 to 500 nm, and SRF was estimated and integrated over the measured range of 365~425nm. The actinic

285   flux over 365~425 nm was obtained from the "Quick TUV Calculator", available at

286   http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/ using the following parameters: SZA (solar zenith

287   angle) of 0 degree, noon time, June 30, 2000, 300 Dobson overhead ozone column, surface albedo of 0.19 for

288   urban area and 0.8 for snow, and 0 km altitude.

3 Results and discussion

3.1 Chemical composition and optical properties of fresh tar ball aerosols

291   Negligible fractions of inorganics (e.g., sulfate, nitrate, chloride, and ammonium) in tar balls are obtained from

292   AMS measurement as shown in Fig. S2 (SI), and these results confirm again that tar ball aerosols contain

293   dominated carbonaceous compounds with minor amounts of N, S, and Cl (Pósfai et al., 2004; Hand et al., 2005;

294   Adachi and Buseck, 2011). Thereafter, only organics in tar balls are considered, and the high-resolution bulk

295   organic mass spectra for polar and nonpolar tar ball particles are given in Fig. 2. The mass spectra features and

296   particle effective densities are summarized and compared in Table S1 (SI). Distinct differences in the chemical

297   composition were observed between polar and nonpolar tar ball aerosols. The alkyl fragments ($C_xH_y^+$, e.g., $C_nH_{2n-1}^+$,

298    $_1^+$, $C_nH_{2n+1}^+$) dominate the signals for nonpolar particles (accounting for ~56% of total fragments), implying that

1

299 the nonpolar tar balls have compositional similarity with common hydrocarbon organic aerosol (HOA). The

300 $C_xH_yO^+$ fragments are the primary ions for the polar tar balls, contributing ~42% of their mass spectrum,

301 suggesting that most of the organic constituents in the polar tar balls are substantially oxygenated. Both spectra

302 exhibit significant intensity at m/z 28 (CO^+), m/z 29 (CHO^+), and m/z 43 ($C_2H_3O^+$), indicating the presence of

303 carbonyl ions. The strong signal at m/z 31 (CH_3O^+) results from methoxy species that preferably partition into the

304 polar tar fraction. In addition, the significant signals at m/z 50-52 ($C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$), m/z 65 ($C_5H_5^+$), m/z 77-

305 78 ($C_6H_5^+$, $C_6H_6^+$), m/z 81 ($C_6H_9^+$), and m/z 91 ($C_7H_7^+$), which are characteristic of aromatic compounds, indicate

306 that tar balls, especially from the nonpolar phase, contain a considerable amount of aromatic organics or present

307 high aromaticity. Ion peaks at m/z 77-78, 81, and 91 are typical for monocyclic aromatics such as alkyl-substituted

308 benzene (for m/z 77-78, 91) and heterocyclic aromatics (for m/z 81) (Li et al., 2012). While the relative higher

309 signal at m/z 128 ($C_{10}H_8^+$) in the nonpolar tar ball mass spectra can be assigned to molecular ion of naphthalene

310 (Herring et al., 2015). Moreover, signals at m/z 55 and 57 ($C_3H_3O^+$, $C_3H_5O^+$) are signature fragments of aliphatic

311 and non-acid oxygenated organics that are used to trace cooking emissions (He et al., 2010), and these two

312 fragments were also observed in the tar ball aerosols. Similar to ambient biomass burning emissions, $C_2H_4O_2^+$

313 (m/z 60) and $C_3H_5O_2^+$ (m/z 73), two characteristic fragments from levoglucosan and similar cellulose pyrolyzed

314 species (e.g., mannosan, galactosan) were detected in all the tar ball aerosols, and these fragments were more

315 prominent in the polar aerosols due to the solubility of levoglucosan and analogs in water. Weimer et al. (2008)

316 reported the percentage of m/z 60 and 73 for the burning of various woods to be 0.6-4.1% and 0.1-2.0%,

317 respectively. The percentage of these two fragments in our tar ball aerosols (0.7-1.6% for m/z 60 and 0.5-0.9% for

318 m/z 73) are comparable to the literature data, although the fuel and the pyrolysis procedure are different. The m/z

319 137 peak is dominated by fragments of $C_8H_9O_2^+$ and $C_7H_5O_3^+$, and these fragments have been determined in

320 biomass burning emissions and were assigned to lignin-related ions with methoxy-phenolic structures (Li et al.,

321 2012; Li et al., 2014). Phenols and methoxy phenols are prominent compounds, accounting for 41% of the

322 identified organic species, in primary BBOA (Schauer et al., 2001). The signal at m/z 137 is much higher in the

323 nonpolar phase tar ball aerosols (1.0% and 0.5% for nonpolar and polar tar balls, respectively), and the fraction

324 of fragment m/z 137 is consistent with reference values of 0.3-2.0% (Li et al., 2012). m/z 44 (CO_2^+), a marker

325 fragment of carboxylic acids has been parameterized as $f44$ (fraction of mass spectrum signal at m/z 44) to present

326 the oxidation degree of organic aerosols (Aiken et al., 2008; Ng et al., 2010). Higher $f44$ values indicate more

327 oxidized OA (OOA), while less oxidized OA is characterized by lower $f44$ (Schauer et al., 2001). Peroxides can

328 also produce CO_2^+ signal via extensive fragmentation in the AMS (Aiken et al., 2008). $f44$ has also been shown

329   to be linearly correlated with the elemental O:C ratio of OA (Aiken et al., 2008). In this study, $f44$ for the nonpolar

330   and polar tar ball aerosols are 1.9% and 2.4%, and the corresponding O:C ratios are 0.25 and 0.44. The higher

331   O:C and H:C ratios explain the polarity of the polar tar ball aerosols. The simplified average carbon oxidation

332   state ($\overline{OSc} \approx 2$O:C-H:C) describe the oxidation level of particulate complex organic mixtures (Kroll et al., 2011).

333   The calculated $\overline{OSc}$ for the tar ball aerosols are -1.05~-0.76, which agrees well with reference values of -1.0~-0.7

334   for primary BBOA (Kroll et al., 2011). These values are in the broad range of -1.7~-1.6 for HOA and -0.5~0 for

335   semivolatile OOA (Aiken et al., 2008). In addition, a small fraction of nitrogen-containing organic compounds

336   (NOC) was detected, with the $C_xH_yO_iN_p^+$ group contributing 1.6~3.6% of the tar ball mass spectra with estimated

337   N:C ratio below 0.01, which agrees with previously reported N:C values of 0.008~0.018 for biomass burning

338   emissions (He et al., 2010). Biomass burning is an important source of NOC in the atmosphere, alkaloid and nitro-

339   aromatic constituents were detected to be abundant constituents of the NOC (Laskin et al., 2009; Lin et al., 2017).

340   Nitroaromatic compounds were also identified in urban fire emissions (Bluvshtein et al., 2017; Lin et al., 2017).

341   Although these compounds constitute a small fraction of the BBOA mass, these chromophoric NOC species

342   accounted for 50~80% of the total visible light absorption by the extractable BrC (Lin et al., 2017).

343   Fragments larger than 100 amu ($f_{m/z>100}$) contribute a large fraction of the total organic signals for tar ball

344   aerosols, consistent with biomass burning emissions that contain a large fraction of high-molecular weight

345   compounds (Ge et al., 2012; Zhou et al., 2017). $f_{m/z>100}$ is 32% for the nonpolar tar ball aerosols, which is higher

346   than that of the polar particles (15%), demonstrating that the nonpolar tar balls consists of more high-molecular

347   weight organics. The measured effective densities for polar and nonpolar tar balls are 1.33 and 1.24 g cm^{-3}.

348   Chemical characteristics from AMS and densities for internal mixture tar balls follow the volume-linear mixing

349   of polar and nonpolar tar solutions.

350   A considerable aromatic fraction in the tar ball aerosols was confirmed by the LD-REMPI-MS measurement.

351   Fig. 3 presents the mass spectra of aromatic substances obtained for each one exemplary polar and one nonpolar

352   particle, respectively. Aerodynamic size distributions for the detected tar ball aerosols are given in Fig. S3, and

353   substances identified in the mass spectra are listed in Table S2 (SI). The features in the mass spectra are consistent

354   with the polarity of examined tar ball aerosols and ambient BBOA (Lin et al., 2018). The complex REMPI-

355   spectrum shows rows of intense unsubstituted and partially alkylated PAH peaks in the nonpolar tar balls,

356   including naphthalene, acenaphthylene, phenanthrene, pyrene, and in particular, the softwood combustion marker

357   retene at m/z 234 and some possible derivatives (oxidized-retene at m/z 250 with one oxygen addition, methyl-

358   retene at m/z 248 with one methyl addition) (McDonald et al., 2000; Shen et al., 2012). Retene and some of the

359   aforementioned PAHs are also observed in the polar tar ball aerosols' mass spectra with lower intensities. In

360   contrast, the polar tar ball REMPI mass spectra shows strong peaks from oxidized aromatics, more specifically,

361   benzenediol and methoxy-phenols (e.g., catechol, guaiacol, acetovanillone, syringaldehyde, conifery aldehyde,

362   etc.). These results are also verified in ambient BBOA, of which the nonpolar BrC consists of primary

363   unsubstituted PAHs, while the polar fraction includes major aromatic acids and phenols (Lin et al., 2018). The

364   REMPI mass spectra corresponds to the large fractions of CHO^+ and CH_3O^+ fragments and high O:C ratios

365   observed for the polar tar aerosols via HR-ToF-AMS, and keep in consistence with the strong signals of typical

366   aromatic fragments observed in the nonpolar tar aerosols in Fig. 2. The dominance of aromatic compounds in tar

367   ball chemical composition agrees well with previous work on BBOA (Schauer et al., 2001; Wei et al., 2015; Bente

368   et al. 2008, 2009; Czech et al. 2017). Biomass burning is a major source of environmental PAHs (alkylated PAHs,

369   oxygenated-PAHs, phenols, nitrogen-substituted PAHs, etc.) in both particulate and gaseous phases, and extensive

370   emissions of PAHs from incomplete combustion pose a great threat to ecosystem and human health due to their

371   carcinogenic toxicity (Li et al., 2017; Shen et al., 2013; Sigsgaard et al., 2015; Shrivastava et al., 2017). Moreover,

372   the primary PAHs can act as precursors that substantially contribute to ambient SOA or BrC aerosol when involved

373   in atmospheric photochemical aging, leading to profound climatic influence (Yee et al., 2013; Yu et al., 2014; Lu

374   et al., 2011; Zhang et al., 2012).

375   The complex refractive index (RI) of tar ball aerosols was retrieved under the assumption that the particles have

376   similar chemical composition and a spherical shape. The SEM images shown in Fig. S4 (SI) confirm the spherical

377   morphology and homogeneous composition of the tar ball particles generated in this study. Electron energy-loss

378   spectroscopy (EELS) spectra indicates that the tar ball particles contain major C and minor O, which fits the AMS

379   result and previous work (Pósfai et al., 2004; Chakrabarty et al., 2010). Continuous spectral-dependent RI and

380   SSA for tar balls were derived and are presented in Fig. 4, RI results for tar ball aerosol at mixing ratio of 2:1 and

381   1:2 are presented in Fig. S5 (SI). Although scattering dominates the light extinction, absorption in the UV and in

382   the visible ranges was unambiguously identified for the tar ball aerosols, with characteristic absorption similar to

383   atmospheric BrC and HULIS (Hoffer et al., 2006; Bluvshtein et al., 2017; Lin et al., 2017). The imaginary part, k,

384   increases towards the UV range, presenting 0.02~0.03 difference over the measured spectra range. The real part,

385   n, for the nonpolar tar balls decreased from 1.673 at 365nm to 1.647 at 425nm, which is almost parallel to the

386   descending n for the polar tar balls ranging from 1.651 at 365nm to 1.625 at 425nm. k is 0.029~0.013 for the

387   nonpolar tar ball over light wavelength of 365~425nm, while the imaginary part for nonpolar aerosols is 0.007 at

388   365nm and zero at wavelength longer than 410 nm, indicating that there is no detectable absorption or k is lower

389 than our detection limit. The overwhelming imaginary part for the nonpolar tar aerosol agrees with many reports

390 that nonpolar or less polar organics have higher absorption compared with the polar BrC in BBOA (Lin et al.,

391 2018; Sengupta et al., 2018). The stronger absorption and relative higher scattering abilities, resulting in a lower

392 SSA compared with the polar tar ball aerosols. The SSA increases towards the visible wavelength from 0.86 at

393 365nm to 0.90 at 425nm for nonpolar tar ball, and the corresponding values are 0.95 to 1.0 for the polar tar balls.

394   The optical properties of aerosols relate to their chemical composition. Evidently, most of the PAHs identified

395 in the tar ball aerosols with high intensity have strong absorption between 350 and 450nm (Samburova et al., 2016;

396 Lin et al., 2018), as shown in Fig. S6 (SI), which coincide the range of tar ball absorption measured here, implying

397 that PAHs could be a dominate contributor to the absorption of fresh tar balls. Higher imaginary k can be explained

398 partly by the larger proportion of PAHs as well as more high-molecular-weight organics present in the nonpolar

399 tar ball particles, as conjugated aromatic rings and phenols contribute to the major chromophores in the wood

400 smoke (Laskin et al., 2015; Lin et al., 2017, 2018). High-molecular weight organics may resemble HULIS that

401 can form charge transfer complexes (Phillips and Smith, 2004), that can absorb light at a longer wavelength range.

402 The result is consistent with the finding that higher molecular weight and aromaticity result in stronger absorption

403 for atmospheric BrC (Dinar et al., 2008). Moreover, the higher NOC content may also contribute to the

404 chromophores in the nonpolar tar aerosols (Lin et al., 2017, 2018).

405   The average RIs at 375 and 405 nm are 1.671+0.025i and 1.659+0.017i for nonpolar tar ball aerosols. The

406 corresponding RIs are 1.647+0.005i and 1.635+0.04i for the polar tar ball aerosols. The imaginary part k retrieved

407 from the BBCES data, though low, agrees well with k values calculated from UV-Vis absorption of the bulk

408 solution. The MAC for the methanol extracted BrC in tar ball aerosol is shown in Fig. S7 (SI). The absorption

409 may be different for complex materials in the particulate and in the aqueous phases since parameters such as shape

410 factor, mixing state, together with artifacts from the optical instruments detection and data retrieval methods can

411 all affect the final optical results, while solvent-dependent extraction/dissolving efficiency of chromophores or

412 solvent effect (e.g., pH in water solution) may impact the solution absorption coefficient (Huang et al., 2018; Lin

413 et al., 2017). The light absorption coefficient of particulate BrC has been reported to be 0.7~2.0 times that of bulk

414 BrC extracts by Liu et al. (2013).

415   The absorption Ångström exponent (Å$_{abs}$) is often used to describe the wavelength-dependence of aerosol light

416 absorption with a value of nearly 1 for BC particles and values substantially larger than 1 indicating the

417 contribution from BrC (Reid et al., 2005; Chen and Bond, 2010). In this work, Å$_{abs}$ for the nonpolar and polar tar

418 ball particles ranges from 5.9 to 6.8 between 365 and 425 nm, which is consistent with values of 5.7~7.8 calculated

from the bulk absorption <u>in solution</u>. The nonpolar tar balls have a lower Å_{abs}. The difference in Å_{abs} reflects the different chemical composition of chromophores in the particles, as inferred also from the AMS data. Bluvshtein et al. (2017) reported relative low values of Å_{ext} (2~3) and Å_{abs} (4~6) over 300~650 nm for ambient fire plume, which are likely affected by BC in the smoke aerosol and also due to lower wavelength dependence of aerosol absorption and scattering over the longwave visible range. Overall, the broadband optical results for fresh tar ball aerosols are consistent with limited discrete measurements of atmospheric BBOA as summarized in Table 2. It has also been found that the biomass fuel type, combustion conditions, and atmospheric processing eventually affect the optical properties of BBOA. Lack et al. (2012) modeled core-shell absorption for primary organic matter (POM) and BC from biomass burning. They found that the imaginary part of the RI and BrC MAC of POM at 404 nm were 0.007±0.005 and 0.82±0.43 m^2 g^{-1}, respectively. Charkey et al. (2010) compared the optical properties of tar balls from smoldering combustion of different biomass. Fuel-dependent imaginary RI for tar ball at 405 nm was 0.008~0.015 and Å_{abs} over 405~532 nm was 4.2~6.4, which is in line with the Å_{abs} value of 6~7 reported for BBOA derived HULIS (Hoffer et al., 2006). Sedlacek et al. (2018) observed a weak absorption for wildfire produced tar balls with RI of 1.56 +0.02i. Sumlin et al. (2018) simulated BrC formation under different pyrolysis temperatures. The BrC produced from over 300 $^\circ$C combustion has imaginary part k of 0.05~0.09 and real part n of 1.59~1.68 at 375 nm, and RI at 405 nm is 1.57+0.03i, corresponded Å_{abs} over 375~405 nm is 6.4~7.4.

Optical mixing rules can be used to estimate or explain the refractive indices of internally mixed substances, and three mixing rules are commonly applied in climate models: molar refraction of absorption (Jacobson, 2002), volume-weighted linear average of the refractive indices (d'Almeida et al., 1991), and the Maxwell-Garnett rule (Chýlek et al., 2000). The "linear mixing rule" and molar refraction mixing rules were tested in this work for mixtures of tar ball particles against the retrieved optical data. Relevant data analysis details are provided in the supporting materials (Table S3-S4, <u>Fig.</u> S<u>8</u>-S1<u>2</u>). It was found that both mixing rules can predict the index of refraction for the polar/nonpolar tar balls, and values calculated based on "linear mixing rule" fit better with the experimental data. <u>As mentioned above, the real fractions for polar and nonpolar BrC contributing to the mass/absorption of BBOA are undefined, some investigations report the dynamic polar BrC dominate in mass loading (50~85%), but contribute less to the absorption in BBOA (less than 40%) (Asa-Awuku et al., 2008; Bluvshtein et al., 2017; Lin et al., 2017, 2018; Rajput et al., 2014;Sengupta et al., 2018). The "linear mixing rule" confirmed in this study should be helpful in the mathematical modeling to assess climatic impacts of biomass burning related BrC aerosol, when their chemical composition is classified.</u>

3.2 Photooxidation of tar ball particles

Aerosols have a wide range of atmospheric lifetimes from hours to days, during which they are involved in various atmospheric processes, resulting in changes of properties (Reid et al., 2005; Rudich et al., 2007; Jimenez et al., 2009). Therefore, we studied the effects of photochemical oxidation of the nonpolar wood-pyrolyzed tar ball aerosols to investigate the physiochemical changes that can occur during tar balls' atmospheric lifetime. Fig. 5 presents the evolution of the wavelength-dependent RI and SSA as a function of the aerosols' O:C ratio following NO_x-free photochemical aging in the OFR. The oxidation covers 0.7-6.7 EAD. Substantial decrease of the RI and an increase of the SSA are correlated with an increase of the O:C ratio, these specific parameters are summarized in Table S5 (SI). Light scattering as well as the absorption by the tar balls aerosol decrease with increasing OH oxidation. The tar aerosols lose their scattering and absorption significantly up to 3.9 EAD aging. The average RI decreased from initial 1.661+0.020i to 1.632+0.007i, and the corresponding average SSA increased from 0.89±0.01 to 0.96±0.02. Then, the RI by tar balls persisted with enhanced oxidation, so that the MAC values remained stable after 3.9 days oxidation (Fig. S13, SI), suggesting that all the photochemical-labile chromophores were largely eliminated, while the remaining fraction still presented some light absorption. Forrister et al. (2015) also observed a stable fraction of biomass burning BrC that had persistent absorption even after long photochemical evolution time in the ambient environment. They suggested that the remaining persistent fraction determines the background BrC levels. In our study, the O:C ratio for tar ball aerosols increased continuously with photochemical oxidation, implying production of oxygenated constituents (carboxylic, carbonyl compounds, etc.), and the interaction between these increasingly oxidized species coupled with the relative stable intrinsic chromophoric structures (e.g., fused aromatic rings in Fig. 3) in some supermolecular structure that may explain the persistent absorption for aged tar ball aerosols (Dewar and Lepley, 1961; Desyaterik et al., 2013; Samburova et al., 2016). In addition, a balance between photobleaching of intrinsic chromophores and photochemical formation of BrC via gas-particle transfer, as well as dynamic gas-particle partitioning of chromophores and products of their photo-degradation should also be considered in the overall absorption behavior for BBOA during photochemical processes.

The observed photooxidation bleaching is consistent with previous studies on atmospheric processes of BrC. Sumlin et al. (2017) conducted multiple-day photochemical oxidation on primary biomass burning BrC aerosols and observed that BrC losses its light absorption and scattering in the near-UV wavelengths by aging. Their derived RI at 375 nm decreased from 1.59+0.03i for fresh emission to 1.50+0.02i after 4.5 EAD oxidation with a

477 corresponding O:C ratio increase from 0.34 to 0.40. Decrease in the overall BBOA absorption and scattering was

478 also detected *in-situ* following a one day evolution by Adler et al. (2011). They monitored an average RI of

479 1.53+0.07i and 1.54+0.04i for aerosols dominated by open fire and smoldering emissions, respectively, while the

480 RI decreased to 1.49+0.02i of the aged aerosols during the following day. Zhong and Jang (2014) reported that

481 light absorption of wood smoke BrC was modified by the photochemical process, owing to the production of BrC

482 from SOA formation and loss of BrC from photochemical bleaching of the chromophores. The total MAC for the

483 BrC eventually decreased by 19~68% within one day of aging. They proposed that bleaching occurred by

484 excitation of electrons through the absorption of sunlight via π-π^* (UV and near UV illumination) or n-π^* (visible

485 wavelengths irradiation) transitions. Then, the excited electrons disrupted the conjugated structure of

486 chromophores, leading to the fading of wood smoke color.

487 When tar ball aerosols were illuminated merely by 254 nm UV light at residence time of 144s, photolysis

488 occurred and weakly diminished their light absorption in line with the extent of photon flux exposure. UV

489 irradiation similar to the O_3.9 condition slightly decreased the average RI to 1.649+0.018i, indicating that

490 photolysis played a minor role in tar ball aerosols bleaching and contributed to less than 15% of imaginary k

491 changes in NOx-free photochemical aging process. Even at full power of UV lamps in the OFR, the average RI

492 decreased by 0.012 and 0.005i for maximum photolyzed tar balls (Table S6-S7, Fig. S14-S17, SI). As we also did

493 not observe detectable optical changes in blank tests upon exposure to O_3 under dark (SI, Fig. S18-S19), the

494 bleaching of the tar balls in the OFR is mainly attributed to OH-initiated chromophores decomposition via

495 heterogeneous reactions, rather than to O_3 oxidation or photolysis.

496 These results indicate a fundamental relationship between photochemical processes and impairment of light

497 absorbing and scattering abilities in tar ball aerosols. The optical behaviors of tar balls are a consequence of their

498 chemical composition changes, which are very sensitive to photochemical process, and even one daytime

499 atmospheric aging resulted in significant oxidation and bleaching of tar balls. In Fig. 6a, the H:C, OM/OC, $\overline{OSc}$,

500 and particle effective density versus O:C ratio are shown. Fig. 6b presents the contributions of $C_xH_y^+$, $C_xH_yO^+$,

501 $C_xH_yO_z^+$, and $C_xH_yO_iN_p^+$ groups to the tar balls composition under a range of OH exposure conditions. Mass

502 spectra features and densities of the tar ball aerosols under various oxidation processes are summarized in Table

503 S8 (SI). Increasing the OH exposure leads to continuous increase of O:C and H:C ratios, leading to higher $\overline{OSc}$

504 for the tar ball aerosols. This result is consistent with Sumlin et al. (2017), who reported that the O:C and H:C for

505 BBOA increased by ~0.08 and ~0.03 after 4.5 EAD photochemical oxidation, respectively. In this work, the

506 measured O:C ratio increased from 0.25 to 0.38 after maximum aging, while the H:C ratio increased by 0.07 from

507   initial value of 1.55.

508   Other previous studies also depicted dynamic change of elemental ratios for SOA upon aging (Aiken et al.,

509   2008). The H:C ratio may either increase or decrease, depending on the precursor type and oxidation conditions.

510   Overall, O:C and H:C ratios changes relate to specific chemical processes or/and to gas-particle mass transfer

511   during aging of aerosols (Heald et al., 2010; Kim et al., 2014). The tar ball aerosols consist of mostly reduced

512   species ($\overline{OSc}$ <0), which can be oxidized primarily via oxidative formation of polar functional groups to the carbon

513   skeletons. In OH-initiated oxidation, functionalization includes OH/OOH function group addition and

514   COOH:Carbonyl groups formation that increase the net oxygen content in SOA (Kroll et al., 2011). Hydration or

515   polar functional groups addition to unsaturated C-C bonds may also increase the H:C ratio. Moreover,

516   fragmentation or evaporation also mediate the O:C and H:C ratios of SOA in further aging (Zhang and Seinfeld,

517   2013; Kim et al., 2014). We attribute the increase in H:C ratio to such oxidation mechanisms that involve bulk

518   species in the particles. As shown in Table S8 (SI), $f_{m/z>100}$ decreased monotonically with aging. After 6.7 EAD

519   photooxidation, $f_{m/z>100}$ contributed only 21% of the total organic signals. The decrease of $f_{m/z>100}$ indicates that

520   fragmentation reactions are involved in the photochemical evolution, and decomposition of high-molecular weight

521   compounds, thereby, reduced the size of the conjugated molecular system. The persistent high value of $f_{m/z>100}$

522   after 6.7 EAD photooxidation imply that some high molecular weight compounds remained in the tar ball aerosols,

523   and continue to contribute to light absorption ether as individual chromophores or as charge transfer complexes.

524   From Fig. 6b, $C_xH_y^+$ fragments deplete with OH exposure, while $C_xH_yO^+$ and $C_xH_yO_z^+$ fragments increase,

525   implying the formation of oxygenated moieties in the tar ball aerosols. In addition, a decrease in the $C_xH_yO_iN_p^+$

526   fraction was measured from initial 3.6% to 1.9% after the maximum oxidation. Ng et al. (2010) suggested to use

527    $f44(CO_2^+)$ *vs.* $f43(C_2H_3O^+)$ triangle space as indication of OA sources and for estimation of their degree of

528   oxidation and volatility. The $C_2H_3O^+$ (less oxidized fragments) is a indicative fragment from aldehydes or ketones.

529   High $f44/f43$ ratio indicates low volatility and high oxidation level of SOA. Moreover, high $f44/f43$ and O:C ratio

530   are associated with increased hygroscopicity and possible CCN activity of OA (Hennigan et al., 2011; Lambe et

531   al., 2011). The $f44$ *vs.* $f43$ in this study varied with photochemical aging and fell within the expected range for

532   ambient OOA, as shown in Fig. 7. Increase of $f44/f43$ ratio with OH oxidation in Fig. 6b depicted the increase of

533   carboxylic and/or peroxide compounds compared to carbonyl species in the tar balls, which is consistent with the

534   atmospheric evolution of ambient biomass burning plumes (Hennigan et al., 2011; Canonaco et al., 2015).

535   To infer the possible chemical processes, detailed mass spectras were compared between fresh and 6.7 EAD

536   photochemical oxidized tar balls (Fig. S20, SI). We found that decrease of alkyl/alkenyl chains (e.g., $C_nH_{2n-1}^+$,

537 $C_nH_{2n+1}^+$) and aromatic ring structure fragments (e.g., $C_6H_5^+$, $C_6H_9^+$) contributed the prominent changes in the

538 $C_xH_y^+$ group, and relative higher CO_2^+ increment relative to $C_2H_3O^+$ explained the increase in the $f44/f43$ ratio.

539 The decrease in the abundance of $C_2H_4O_2^+$ (*m/z* 60) and $C_3H_5O_2^+$ (*m/z* 73) is consistent with recent studies that

540 levoglucosan or similar species can decay in the atmosphere due to photochemical oxidation (Hennigan et al.,

541 2010). The pronounced decrease of intensity at *m/z* 137 ($C_8H_9O_2^+$ and $C_7H_5O_3^+$) suggests that the methoxy-phenol

542 components were dissipated substantially in the aged tar balls .

543   In summary, photochemical oxidation by OH radicals destructed the aromatic rings and methoxy phenolic

544 structures, which are expected to be the primary chromophores in the tar balls. The NOC content and high-

545 molecular weight species were also depleted via OH oxidation. These chemical changes upon OH oxidation may

546 explain the observed diminishing in light scattering and absorption upon photochemical aging.

547 **3.3 NO$_x$-dependent tar ball particles oxidation**

548 N_2O was recently introduced for simulating NO$_x$-dependent SOA formation pathways in OFR under high O_3

549 concentration, as $O(^1D)+N_2O$ reactions can be applied to systematically vary the branching ratio of the RO_2+NO

550 reactions relative to the RO_2+HO_2 and/or RO_2+RO_2 reactions over a range of conditions relevant to atmospheric

551 SOA formation (Lambe et al., 2017). Here we introduced 0.5 and 2.0 vol.% N_2O to investigate NOx-involved

552 daytime aging of tar ball aerosols in the OFR. The OH exposures were maintained for all these tests at about 4

553 EAD. The corresponded NO_2 concentrations downstream of the OFR was measured to be 96.1±1.3 and 528.3±6.2

554 ppbv. The concentration of static NO can be neglected under these severe oxidation conditions. Fig. 8 shows the

555 mass spectra features for fresh and aged tar balls reacted in the absence/presence of NO$_x$. Parameters including

556 organic elemental ratios and densities are summarized in Table S8 (SI). In general, tar balls oxidized under N_2O

557 addition exhibit higher O:C and relative lower H:C ratios. NO_y^+ (NO^+ and NO_2^+) signals appear in the mass spectra

558 and the intensities of NO_y^+ display a positive trend with N_2O concentration, together with an increase of

559 oxygenated fragments ($C_xH_yO^+$ and $C_xH_yO_z^+$) and decrease of hydrocarbon fragments ($C_xH_y^+$). The signal ratio of

560 NO^+ (*m/z* 30) to NO_2^+ (*m/z* 46) is used to distinguish organic nitrate from inorganic nitrate. The signal from

561 standard inorganic nitrate (e.g., NH_4NO_3) has a typical NO_2^+/NO^+ ratio of 0.485 obtained from our AMS data

562 (detailed mass spectra is shown in Fig. S21, SI). The ratio and standard mass spectra are similar to previous studies

563 (Zhou et al., 2017). The fraction of NO_y^+ (NO^+ and NO_2^+) signals in the aged tar balls increased from 0% to 0.7%

564 and 1.5% at 0.5 vol.% and 2.0 vol.% N_2O additions, respectively. The corresponding values of NO_2^+/NO^+ ratio

565 are 0.162 and 0.174, which are much lower than that for inorganic nitrates. Furthermore, the contribution of

566 $C_xH_yO_iN_p{}^+$ fragments increased from 1.9% to 4.4% and 4.5% over the course of aging. Therefore, we can conclude

567 that NOC rather than inorganic nitrate formed in the NO_x-dependent photooxidation process, resulting in an

568 overall increase of N:C ratio from 0.010 to 0.012 and 0.015. Additionally, the density of tar balls slightly increased

569 from 1.24 for the fresh tar balls to 1.26 for the one aged in presence of 2 vol.% N_2O.

570   Detailed changes in the mass spectra over the course of the experiment are shown in Fig. S22 (SI). Indicative

571 ions of cyclolakyl fragments (e.g., $C_2H_3{}^+$, $C_3H_5{}^+$, $C_4H_7{}^+$) decreased, while NO_x addition increased the CO^+ and

572 $CO_2{}^+$ intensities relative to $C_2H_3O^+$, leading to higher $f44/f43$ ratio. Ng et al. (2007) observed a similar change for

573 photooxidation of terpenes in presence of NO_x. Changes in AMS spectra with NO_x addition may mark differences

574 between the dominating reaction pathways in tar ball photooxidation as RO_2+NO verses RO_2+HO_2 and/or

575 RO_2+RO_2 reactions.

576   Photochemical oxidation with NO_x addition enhances the oxidation level and increases both the absorption and

577 scattering of tar ball aerosols. Dynamic changes of the complex RI are shown in Fig. 9 and summarized in Table

578 S5 (SI). The RI of tar ball aerosols increased from an average of 1.632+0.007i for pure OH-initiated

579 photooxidation to 1.635+0.015i with the addition of 0.5 vol.% N_2O, and a greater increase up to 1.648+0.019i

580 with 2.0 vol.% N_2O. The increase of RI is therefore primarily attributed to NOC formation. Zhong and Jang (2014)

581 observed that higher NO_x level slowed photo-bleaching of wood smoke BrC, and they suggested that NOx-

582 modified reaction pathways produce secondary NOC chromophores (i.e., nitro-phenols). Liu et al. (2016)

583 simulated daytime chemistry of various VOCs in the presence of NOx and found that light absorption of produced

584 SOA, especially aromatic ones, increased with NOx concentration. These findings were also corroborated by

585 experimental study of Lin et al. (2015), where the chemical composition and the light absorption properties of

586 laboratory generated toluene SOA were reported to have strong positive dependence on the presence of nitro-

587 phenols formed at high NOx oxidation conditions. The color of the BrC diminished with photolysis, correlated

588 with a decline of the NOC fraction. Nitration of aromatic species via $NO_x/N_2O_5/NO_3$ has been proposed as one

589 of the main mechanisms to produce secondary BrC in the atmosphere (Lu et al., 2011; Lin et al., 2015, 2017;

590 Bluvshtein et al., 2017).

591   The imaginary part at 2.0 vol. % N_2O addition was almost comparable with that of the fresh tar ball aerosols

592 (average value: RI=1.661+0.020i), although the real part was lower, suggesting that photooxidation in the

593 presence of NO_x promote the formation of N-containing chromophores via secondary processes. In our

594 experiments, formation of the N-containing chromophores overweighed the bleaching from OH photooxidation

595 to eventually regain the absorption of the aged tar balls. The average SSA calculated for 150 nm particles

596   decreased from 0.96 to 0.91 and 0.89 with N_2O addition. Absorption enhancement with N_2O addition for tar balls

597   upon photooxidation can also be seen in the MAC changes shown in Fig. S23 (SI), where MAC at 375 nm for

598   fresh tar ball was 0.854 $m^2 g^{-1}$, it decreased to 0.416 $m^2 g^{-1}$ via OH photo-bleaching, then MAC increased to 0.459

599    $m^2 g^{-1}$ at 0.5 vol.% N_2O addition, and up to 0.598 $m^2 g^{-1}$ at 2.0 vol.% N_2O addition due to chromophores formation.

600   **3.4 Atmospheric and Climate implication**

601   Atmospheric aging alters the RI of SOA, and the dynamic changes of RI depend on complicated reaction pathways

602   (Liu et al., 2016). OH-initiated photochemical oxidation and photolysis decrease the RI of laboratory proxies of

603   tar balls under NOx-free condition, while photooxidation under high NOx has an opposite effect on the RI of tar

604   balls. We investigated the relationship between the dynamic RI values of tar ball particles and their possible

605   climatic implications, including the change of light extinction/absorption efficiency and the clear-sky direct

606   radiative forcing. For clarity, light extinction/absorption efficiencies were calculated and compared at wavelength

607   of 375 and 405 nm, while radiative forcing was estimated over all the measured wavelengths from 365 to 425 nm.

608   Atmospheric and climatic implications were assessed for fresh and oxidized tar ball upon NOx-dependent ~3.9

609   EAD photooxidation (O_3.9, N_0.5, and N_2.0), in which fresh tar balls were taken as reference.

610   As shown in Fig. 10, photochemical oxidation under NOx-free condition (O_3.9) diminished light extinction

611   and absorption efficiency of tar ball aerosols in the atmospheric relevant size of 50-300 nm, causing about 5~40%

612   decrease in extinction at 375 and 405 nm wavelength. For aerosols larger than 400 nm, the extinction efficiency

613   of tar ball aerosols increased instead after photochemical aging. The light extinction efficiency presented higher

614   size-dependence than absorption, and extinction changes were more sensitive to particle size, especially in the

615   smaller sizes. The decreased absorption was more pronounced with ~60% decrease at 375 nm and over 75% at

616   405 nm. Previous studies have confirmed the relationship between biomass burning emissions and acute regional

617   visibility deterioration (Huang et al., 2012; Chen et al., 2017). Our results demonstrate that OH radical initiated

618   daytime aging may play an important role in improving visibility degradation caused by primary biomass BrC.

619   However, photochemical evolution under high NOx conditions may compensate effects of the photooxidation

620   bleaching of tar ball aerosols via the formation of NOC chromophores. At N_0.5 conditions, the light extinction

621   decreased by 4 to 20% at 375 nm and 5 to 24% at 405 nm, respectively. The corresponding absorption decrease

622   was 20~27% at both wavelengths. With more N_2O addition, formation of secondary N-containing chromophores

623   almost completely offsets light extinction/absorption decrease caused by photooxidation. Under the N_2.0

624   conditions, enhancement of light absorption efficiency for tar ball was about 0~9% at 405 nm in the entire size

625   range of 50-500 nm.

626   Radiative forcing from aerosols over both ground and snow is vital to climate models (Barnett et al., 2005;

627   Kanakidou et al., 2005). Integrated radiative forcing for tar ball aerosols as a function of particle size under various

628   oxidation conditions is shown in Fig. 11. Size-/wavelength-resolved SRF are also shown in Fig. S24 and S25 (SI).

629   Integrated SRF over ground has negative values for tar balls over almost all the atmospheric relevant sizes,

630   indicating a radiative cooling effect by tar ball aerosols except at 195~210 nm, where fresh tar ball particles present

631   warming effect with SRF up to ~0.48 W g^{-1}. In practical fire emissions, the size of tar balls depends on the burning

632   and environment conditions and biomass fuel types with typical values between tens to hundreds of nanometers

633   (Reid et al., 2005; Pósfai et al., 2004). The complicated size-dependence character of SRF makes it difficult to

634   assess the real climatic effect of tar ball particles without extensive calculations. Fig. 11a suggests fresh tar balls

635   have SRF values of -7.46 W g^{-1} at 150 nm and 0.45 W g^{-1} at 200 nm, respectively. The SRF decreased for all size

636   ranges due to photochemical oxidation to -7.93 W g^{-1} at 150 nm and -1.37 W g^{-1} at 200 nm for tar ball aerosols

637   under O_3.9 condition. At N_0.5 conditions, SRF was -7.37 W g^{-1} at 150 nm and 0.16 W g^{-1} at 200 nm, and the

638   corresponding values at N_2.0 conditions increased to -7.20 W g^{-1} at 150 nm and 0.31 W g^{-1} at 200 nm.

639   In contrast, tar ball particles contributed to positive forcing (warming effect) over the bright terrain throughout

640   the atmospheric aging, as shown in Fig. 11b. Radiative forcing over the snow showed a simple increasing trend

641   with particle size, indicating that larger BrC aerosol with identical mass loading in the air have a higher warming

642   effect. The changes of snow-based radiative forcing upon photochemical aging followed the same trends as in the

643   ground-based cases. Fresh tar ball at size of 200 nm has SRF of 20.12 W g^{-1} over the incident solar wavelength of

644   365~425 nm on the snow terrain. With photochemical oxidation under NO_x-free condition, radiative forcing

645   decreased significantly. After 3.9 EAD atmospheric aging, snow-based radiative forcing for tar ball decreased by

646   65~73% over the size range of 50~500 nm, the value of 200 nm tar ball became 6.99 W g^{-1}. When NOx was

647   involved in the photochemical oxidation of tar balls, the decrement of radiative forcing was weakened. At N_0.5,

648   SRF for 200 nm tar ball was 14.01 W g^{-1}, while at N_2.0 condition, size-dependent SRF from the aged tar ball

649   was almost comparable with that from fresh tar ball, and SRF for 200 nm tar ball was 18.56 W g^{-1}.

650   Although less than 10% of the solar spectrum's energy is distributed between 365 and 425 nm, the radiative

651   forcing over this range represents a significant warming or cooling potential over the arctic terrain. In conclusion,

652   photochemical oxidation under NO_x-free conditions can decrease radiative forcing of tar ball aerosols, resulting

653   in enhancement in the cooling effect over ground and decreased in warming effect over the snow. However, NOx

654   involvement in photooxidation inhibits the decrease in radiative forcing of tar ball aerosols. Overall, the complex

2

655 changes in optical properties of tar balls at long aging times impose great uncertainties in traditional model-based

656 estimation of BBOA. Our study emphasizes the importance of taking this atmospheric process into consideration

657 to refine the understanding of the climatic and atmospheric influences from these aerosols.

4 Conclusions

659 In this study, proxies for tar ball aerosols were generated in the laboratory following a flameless wood pyrolysis

660 process. The optical and chemical properties of the generated tar balls were constrained using BBCES and HR-

661 Tof-AMS/SP-LD-REMPI-MS and were shown to have many similarities to ambient biomass burning aerosols.

662 Laboratory generated fresh tar ball aerosols have light absorption characteristics similar to atmospheric BrC with

663 higher absorption efficiency towards the UV. The average complex refractive indices between 365 and 425 nm

664 are $1.661+0.020i$ and $1.635+0.003i$ for nonpolar and polar tar ball aerosols, respectively.

665 Atmospheric evolution for tar ball aerosols was experimentally simulated using an oxidation flow reactor. The

666 study focused on dynamic changes in the optical and chemical properties due to NOx-dependent photochemical

667 oxidation. Furthermore, the relationship between oxidation level and the resulting RI of the tar ball aerosols was

668 explored. We found a substantial decrease in the scattering and absorption properties of tar balls, with a

669 corresponding increase in SSA with OH oxidation in the absence of NOx. A correlation between the RI decrease

670 and increase in the O:C and H:C ratios was observed. The decrease in light scattering and absorption is attributed

671 to the destruction of aromatic/phenolic/NOC and high-molecular weight species chromophores via OH-initiated

672 photooxidation of tar balls. Over longer aging times, the average RI of the tar ball aerosols decreased from

673 $1.661+0.020i$ to $1.632+0.007i$ upon atmospheric equivalent to 3.9 days aging, and the corresponding O:C and H:C

674 ratio increased from initial 0.25 and 1.55 to 0.35 and 1.59, respectively.

675 Our results suggest that OH oxidation rather than photolysis or ozone reactions plays the dominate role that

676 determine the optical and chemical properties in tar balls aging. The observed decrease in absorption results from

677 depletion of chromophores such as aromatic rings, phenolic compounds and high molecular weights species.

678 Simulations under high NO_x environment enhanced the aerosol oxidation state and increased the scattering and

679 absorption of tar ball aerosols relative to OH photooxidation in the absence of NOx. At ~3.9 EAD, addition of 0.5

680 and 2.0 vol.% N_2O increased the organic elemental ratios (O:C, H:C, and N:C ratios) and doubled the organic

681 nitrates fraction in the particles from 1.9 % to ~4.4 %. The formation of NOC chromophores overweigh the

682 intrinsic depletion of chromophores, leading to higher RI of $1.635+0.015i$ and $1.648+0.019i$.

683 The atmospheric and climatic implications from tar ball aerosols under various oxidation conditions were

684 assessed using a simple radiative forcing model in terms of extinction/absorption efficiency changes and ground-

685 /snow-based radiative forcing. These results demonstrate that the optical and chemical properties of tar ball

686 particles are dynamically related to atmospheric aging, and optical changes are governed by both photobleaching

687 and secondary chromophores formation. Therefore, the atmospheric process should be emphasized in model

688 predictions for evaluating biomass burning BrC aerosol radiative forcing as well as climate change.

689

Acknowledgments

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1054

Caption of Table and Figure

Table 1. Experimental conditions for tar balls photochemical oxidation

Table 2. Comparison of tar ball particle optical parameters with reference values of BBOA (mean ± standard deviation)

Figure 1. Experimental setup for laboratory generation and aging of tar ball aerosol: including generation setup, OFR photochemical aging, gaseous-particulate chemical monitoring, particle size distribution and optical properties measurements.

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Figure 6. Dynamic changes for the chemical characteristics of tar ball particle under NOx-free OH photochemical oxidation: a) OM/OC, H:C ratio, particle density, and average carbon oxidation state ($\overline{OSc}$) changes as a function

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1087   biomass burning organic aerosol.

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1090   different oxidation conditions in term of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, and $C_xH_yO_zN_p^+$ fragment groups. $C_xH_yO_zN_p^+$

1091   include all nitrogen-containing fragments, (e.g., $C_xH_yON^+$, $C_xH_yO_zN_i^+$, $C_xH_yN^+$, etc.), NO_y^+ include NO^+ and NO_2^+.

1092   O_3.9 represents 3.9 days equivalent atmospheric photochemical aging in absence of NOx, N_0.5 and N_2.0

1093   indicate photochemical oxidation with 0.5 and 2.0 vol.% N_2O addition at ~4.0 days atmospheric oxidation.

1094   **Figure 9.** Changes of retrieved spectra-dependent RI as a function of O:C ratio for tar ball particles upon NOx-

1095   dependent photochemical oxidation: a) real part, b) imaginary part, and c) SSA calculated from 150 nm particles.

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1100   **Figure 10.** Size-resolved light extinction and absorption efficiency ratio of NO_x-dependent photooxidized tar balls

1101   compared to the fresh tar ball particles: a) and c) extinction ratios at 375 and 405 nm, b) and d) absorption ratios

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1105   **Figure 11.** Calculated size-resolved simple radiative forcing (SRF, W g^{-1}) by tar ball aerosols, integrated over

1106   365~425 nm incident solar irradiation for fresh and NOx-dependent photooxidized tar balls: a) ground-based

1107   radiative forcing, b) snow-based radiative forcing.

1108   **Table 1**. Experimental conditions for tar ball particles photochemical oxidation

Experiment	O_3 (ppm)	N_2O mixing ratio	Endpoint NO_x (ppb)	RH (%)	water mixing ratio	Exposure	
						OH radical (molecules cm^{-3} s)	photon flux (photons cm^{-2})
P1	——	——	——	38.90	0.0126	——	7.47E+15
P2	——	——	——	39.70	0.0128	——	4.83E+16
P3	——	——	——	40.50	0.0130	——	1.00E+17
O_0.7	24.46	——	——	37.29	0.0120	8.68E+10	1.56E+15
O_1.7	24.76	——	——	37.66	0.0122	2.23E+11	7.47E+15
O_3.9	24.63	——	——	35.58	0.0115	5.11E+11	4.83E+16
O_6.7	25.31	——	——	35.67	0.0116	8.65E+11	5.17E+16
N_0.5	24.18	0.005	96.1	36.60	0.0118	5.37E+11	5.92E+16
N_2.0	28.21	0.020	528.3	35.90	0.0116	4.85E+11	1.00E+17

1109   Note: P1~P3 mean photolysis test, O_0.7~O_6.7 correspond to photochemical oxidation experiment from equivalent 0.7 day to 6.7 days

1110   ageing, and N_0.5 and N_2.0 indicate photochemical oxidation with N_2O addition at 0.5 vol.% and 2 vol.% mixing ratios (standard deviation

1111   for the parameters were not given in above table)

1112 **Table 2**. Compare of tar ball particle optical properties with reference values of BBOA (mean ± standard deviation)

BrC	Complex Refractive index			$Å_{abs}$	$Å_{abs\_UVVIS}$	$Å_{ext}$	Reference
	Average	375nm	405nm				
Nonpolar	(1.661±0.008)+(0.020±0.004)i	(1.671±0.003)+(0.025±0.003)i	(1.659±0.011)+(0.017±0.002)i	5.87 ± 0.37	5.74	3.81 ± 0.18	
Mixture (2:1 in vol.)	(1.670±0.010)+(0.017±0.004)i	(1.682±0.008)+(0.021±0.002)i	(1.668±0.007)+(0.013±0.001)i	6.79 ± 0.91	7.08	4.01 ± 0.09	
Mixture (1:1 in vol.)	(1.694±0.011)+(0.013±0.003)i	(1.703±0.015)+(0.017±0.001)i	(1.689±0.011)+(0.009±0.002)i	6.16 ± 0.54	7.38	3.73 ± 0.23	This work
Mixture (1:2 in vol.)	(1.672±0.010)+(0.011±0.004)i	(1.683±0.005)+(0.018±0.002)i	(1.667±0.003)+(0.006±0.003)i	6.66 ± 0.63	7.24	4.06 ± 0.11	
Polar	(1.635±0.009)+(0.003±0.003)i	(1.647±0.003)+(0.005±0.001)i	(1.635±0.004)+(0.004±0.003)i	6.72 ± 2.28 [a]	7.83	3.93 ± 0.06	
BBOA	1.590+0.029i@375nm, 1.570+0.010i@405nm (IPN)			6.4~7.4			Sumlin et al., 2017; 2018
BBOA	1.590+0.017i@405nm (IPN)						Flowers et al., 2010
BBOA	k: 0.009@404nm (CRDS-PAS)						Lack et al., 2012
Tar ball	1.78+0.015i, 1.83+0.0086i@405nm (IPN)			4.2~6.4			Chakrabarty et al., 2010
Tar ball	1.56+0.02i @405nm (CRDS-UVVIS)						Hand et al., 2005
BBOA	1.53+0.07i (WELAS,open fire), 1.54+0.04i (WELAS, smoldering)						Adler et al., 2011
BBOA	1.64+0.03i@405nm (BBCES-Neph)			4~6 [b]		2~3 [b]	Bluvshtein et al., 2017
BBOA_HULIS	1.653+0.002i, 1.685+0.002i@532nm(Nep-PAS)				6~7		Hoffer et al., 2006
BBOA_HULIS	1.616+0.023i@390nm(CRDS)						Dinar et al., 2008
BBOA	1.550+0.033i@365nm (BBCES)						Washenfelder et al., 2015
BBOA					6.9~11.4 [c]		Chen and Bond, 2010
BBOA					5.3~8.1 [c]		Xie et al., 2017
Ambient SOA					6.0~6.3 [c]		Huang et al., 2018
Ambient SOA	k: 0.046@365nm, 0.039@405nm, 0.036@420nm (LWCC)						Shamjad et al., 2018

1113 Note: $Å_{abs}$ and $Å_{ext}$ were calculated form tar ball particle with median diameter of 150 nm in this study

1114 [a] regressed over wavelength range of 365~400 nm, no absorption detected over 410 nm using BBCES system

1115 [b] regressed over wavelength range of 300~650 nm for bulk fire plume emissions

1116 [c] $Å_{abs\_UVVIS}$ of methanol extracts over whole range from 300/360~600 nm

1117 Instrument: IPN(integrated photoacoustic nephelometer), CRDS (cavity ring-down spectrometer), PAS (photoacoustic absorption spectrometer), WELAS (white light optical particle counter), LWCC (a liquid waveguide

1118 capillary cell)

4

Figure 1. Experimental setup for laboratory generation and aging of tar ball aerosol: including generation setup, OFR photochemical aging, gaseous-particulate chemical monitoring, particle size distribution and optical properties measurements.

1122

Figure 2. High-resolution AMS mass spectra of fresh polar and nonpolar tar ball particles. Four ion groups are grouped for

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1147

1148 **Figure 7.** Comparison of f44 and f43 values from ambient data sets (Ng. et al., 2010) and values from ambient biomass burning

1149 organic aerosol. The hollow circles present tar ball result in this work, and color legend indicate equivalent atmospheric

1150 oxidation days, black arrow more clearly shows the extent of NOx-free photochemical oxidation in this study.
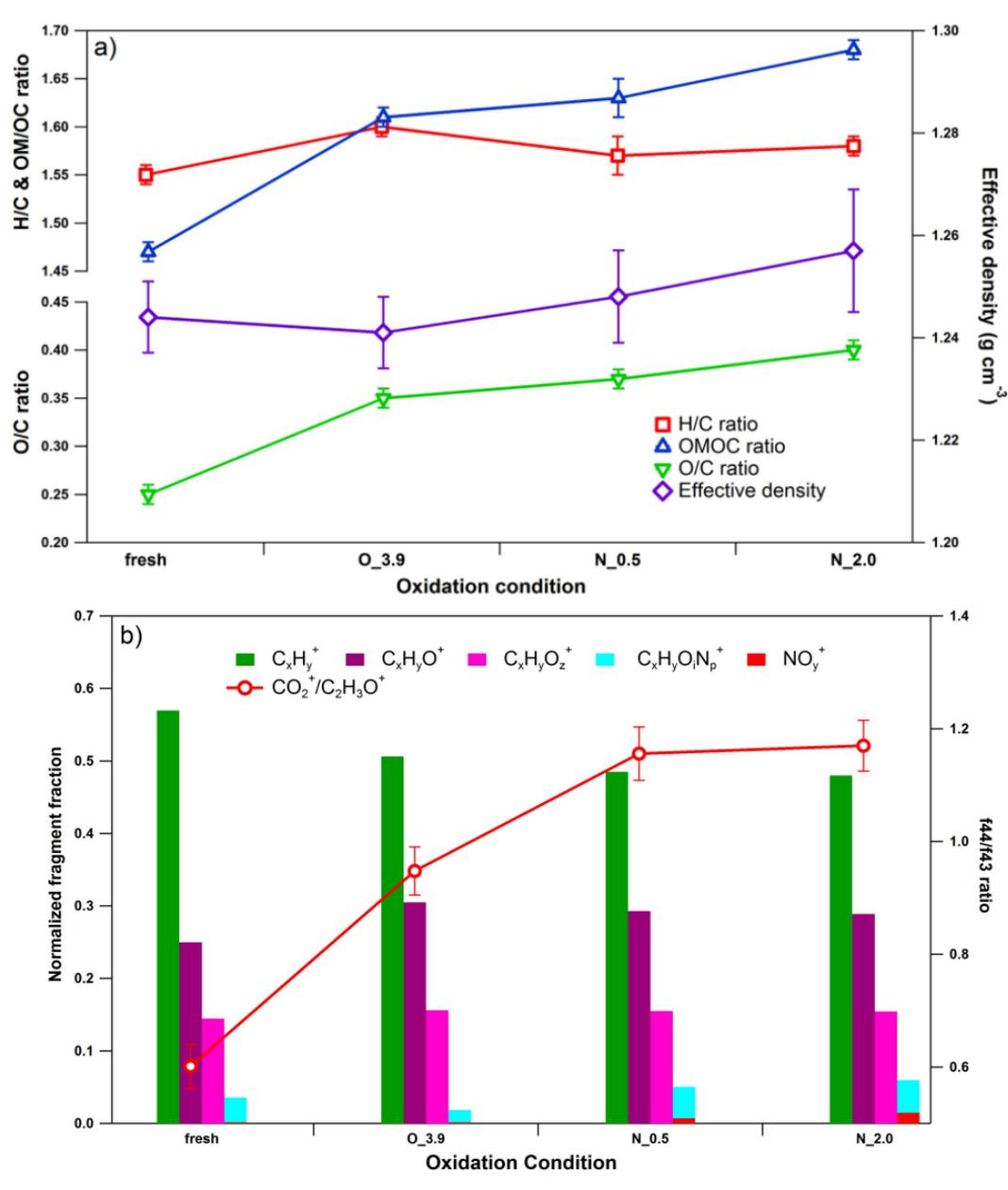
Figure 8. Dynamic changes for chemical characteristics of tar ball aerosols under NO_x-dependent OH photochemical oxidation: a) OM/OC, O:C, H:C, and particle density changes; b) mass spectra changes with different oxidation conditions in term of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, and $C_xH_yO_zN_p^+$ fragment groups. $C_xH_yO_zN_p^+$ include all nitrogen-containing fragments, (e.g., $C_xH_yON^+$, $C_xH_yO_zN_i^+$, $C_xH_yN^+$, etc.), NO_y^+ include NO^+ and NO_2^+. O_3.9 represents 3.9 days equivalent atmospheric photochemical aging in absence of NOx, N_0.5 and N_2.0 indicate photochemical oxidation with 0.5 and 2.0 vol.% N_2O addition at ~4.0 days atmospheric oxidation.
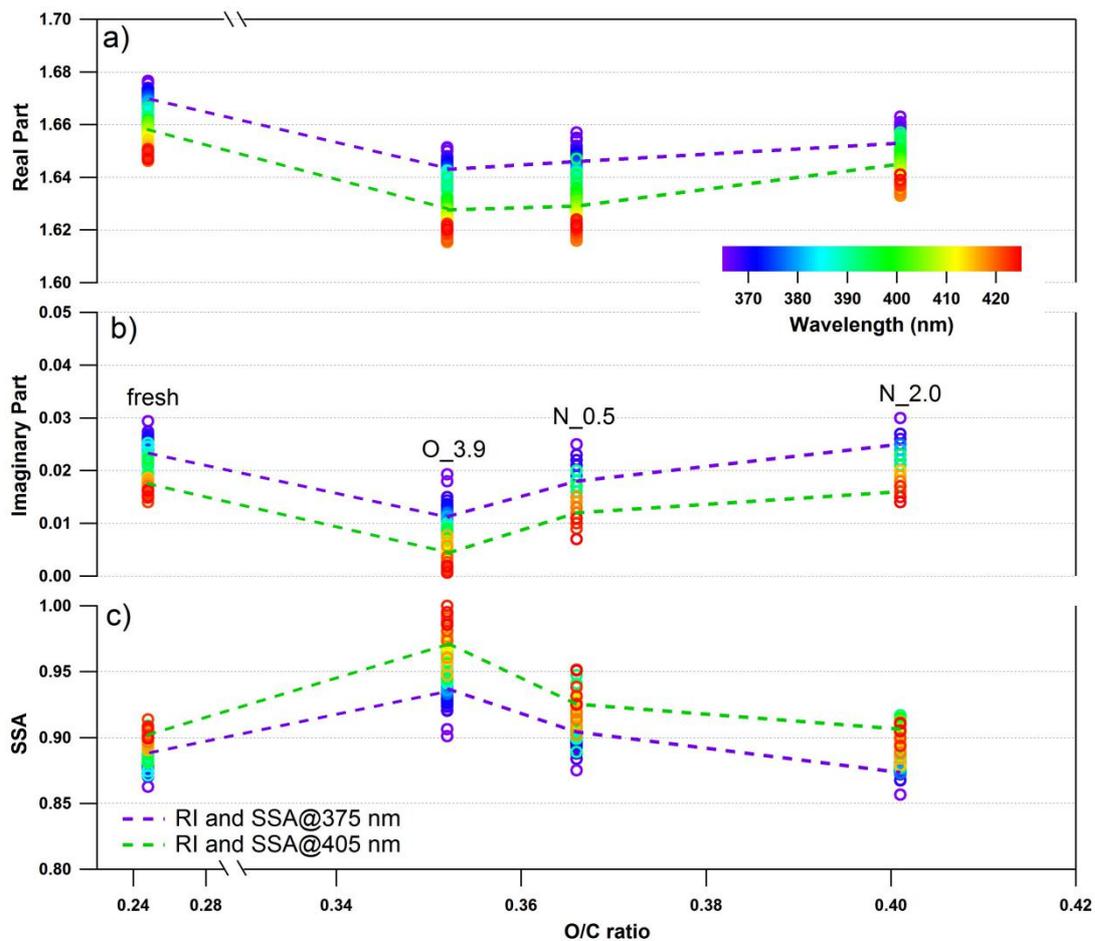
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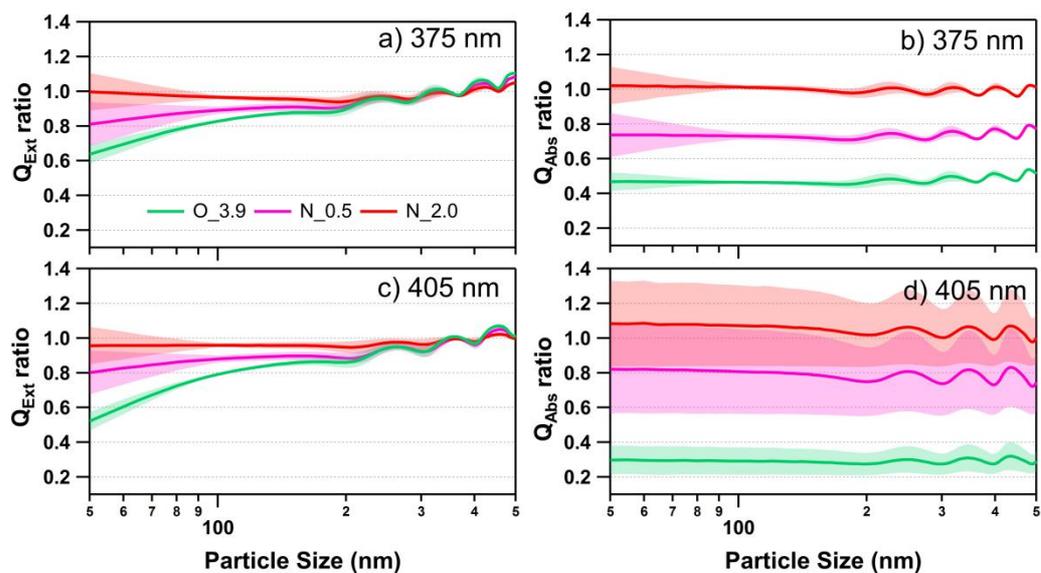
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1168

Figure 11. Calculated size-resolved simple radiative forcing (SRF, W g^{-1}) by tar ball aerosols, integrated over 365~425 nm incident solar irradiation for fresh and NOx-dependent photooxidized tar balls: a) ground-based radiative forcing, b) snow-based radiative forcing.

Supporting Information for

Dynamic changes of optical and chemical properties of tar ball aerosols by atmospheric photochemical aging

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Contents

1. Tar ball aerosol size distribution at downstream of the OFR

Tar ball particles were generated via TSI atomizer, and concentration of tar ball particles was mediated in the OFR before these aerosols being photochemically oxidized. Polar, nonpolar, and mixture tar ball particles present similar size distributions.
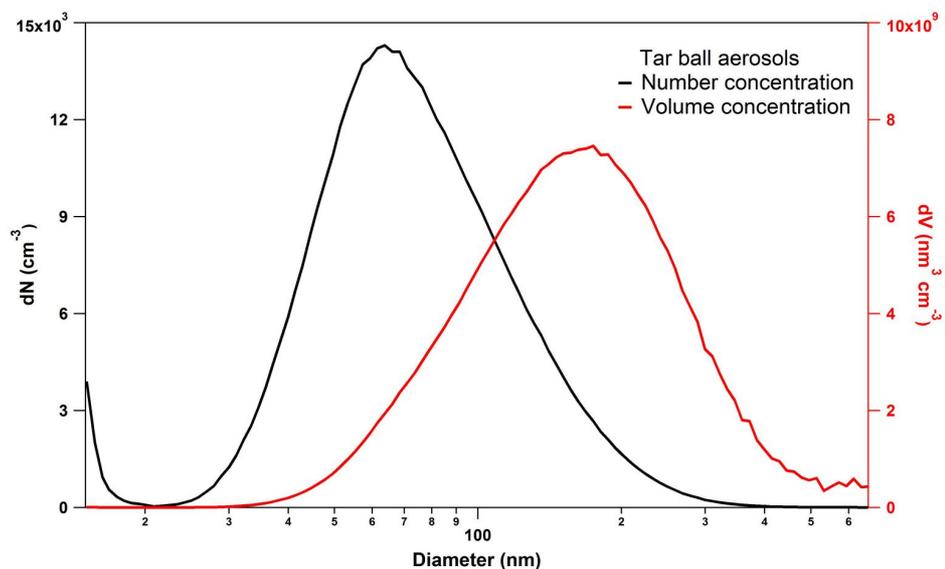
Figure S1. Size distribution of laboratory generated tar ball aerosols at downstream of the OFR. The distribution presents a norrow range with a single peak at ~70 nm diameter, similar to the size distribution of practical tar balls obtained from the wildfires and domestic biofuel burning (Pósfai et al., 2004; Chakrabarty et al., 2010).

3

2. OC-EC content of fresh polar and nonpolar tar ball aerosols

Non-refractory organic carbon (OC) and refractory elemental carbon (EC) in fresh tar ball aerosols were analyzed using a DRI Model 2015 multi-wavelength thermal/optical carbon analyzer (Desert Research Institute, Nevada, USA) with the IMPROVE_A protocol (Chow et al., 2011; Li et al., 2018). In details, fresh nonpolar and polar tar balls were collected onto pretreated quartz filters (Whatman, Mainstone, UK, baked over 450 ºC for 6 hr to eliminate any contamination), a circular punch (0.8 cm in diameter) of each loaded filter including operational blank filter was taken and analyzed. Four OC fractions (OC1, OC2, OC3, and OC4 correspond to gradient cutting temperature at 140, 280, 480, and 580 ºC, respectively, in a helium atmosphere), three EC fractions (EC1, EC2, EC3 with cutting temperature of 590, 780, and 840 ºC, respectively, in a 2% oxygen/98% helium atmosphere), and one PC fraction (pyrolyzed carbon content determined when transmitted laser returned to its original intensity after the sample was exposed to oxygen) were determined for each sample, and OC=OC1+OC2+OC3+OC4+PC, EC=EC1+EC2+EC3-PC, total carbon (TC) equals the sum of OC and EC. The blank-corrected and normalized carbon fractions for fresh tar ball aerosols were given below:

Tar ball	OC1	OC2	OC3	OC4	PC	EC1	EC2	EC3	OC	EC
Polar	38.8%	32.2%	18.4%	0.0%	10.6%	10.6%	0.0%	0.0%	100.0%	0.0%
Nonpolar	28.7%	25.8%	16.0%	7.7%	21.1%	21.7%	0.0%	0.0%	99.3%	0.7%

It is clear EC content was almost below detection limit for both polar- and nonpolar-tar balls, the slight EC fraction in nonpolar tar ball is less than 0.7% of TC content and resides in EC1, which can be termed as non-refractory char-EC, empirically defined as EC1−PC. Char-EC is stripped from some OC under oxygen-free heating during OC/EC measurement, which has much weak absorption, and thus can be distinguished as brown carbon rather than black carbon (Andreae and Gelencsér, 2006; Arora et al., 2015; Kim et al., 2011; Han et al., 2008, 2009). Many other studies on biomass burning emissions from wildfires and domestic burning have also reported negligible EC content in tar ball aerosols (Chakrabarty et al., 2010; Tivanski et al., 2007; Hand et al., 2005; China et al., 2013).

3. Fresh tar ball composition from HR-Tof-AMS measurement
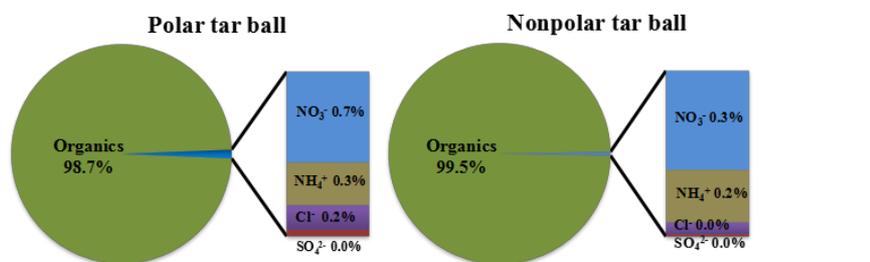
Figure S2. Fresh polar and nonpolar tar balls composition from HR-Tof-AMS measurement. Color mapping: organics-green, nitrates-blue, ammonium-yellow, chloride-purple, sulfates-red.

4. Organic elemental ratios for fresh tar ball aerosols were derived from AMS measurement at W mode, and effective densities of tar ball aerosols were calculated from aerodynamic diameter divided by mobility diameter assuming tar ball with sphericity of 1.0

Table S1. Summary of fresh tar ball particles chemical elemental ratios and effective densities

BBOA	Mass spectra			Density (g cm^{-3})	Reference
	O:C	H:C	M/z>100 fraction		
Nonpolar	0.25±0.01	1.55±0.01	0.32	1.24±0.01	
Mixture (2:1 in vol.)	0.30±0.01	1.59±0.02	0.29	1.27±0.02	
Mixture (1:1 in vol.)	0.36±0.01	1.62±0.04	0.27	1.29±0.02	this work
Mixture (1:2 in vol.)	0.39±0.01	1.61±0.03	0.24	1.30±0.01	
Polar	0.44±0.02	1.64±0.03	0.15	1.33±0.02	
BBOA	0.3~0.4				Aiken et al., 2008
BBOA	0.29~0.33	1.51~1.58			Li et al., 2012
BBOA	0.18~0.26	1.4~1.5			He et al., 2010
BBOA	0.15~0.7	1.5~1.6	0.11~0.20	1.4	Zhou et al., 2017
BBOA				1.5	Sedlacek III et al., 2018
BBOA	0.33	1.90		1.18~1.19	Sumlin et al., 2017; 2018

6

5. Aerodynamic size distribution for tar ball particles measured by SP-LD-REMPI-ToF-MS
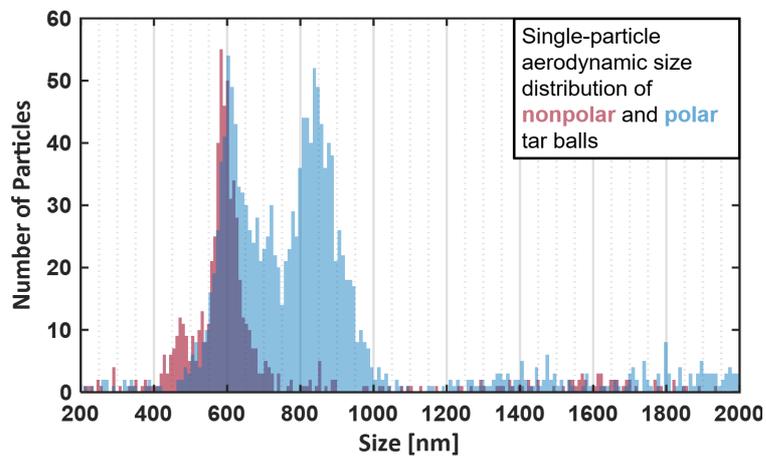
Figure S3. Particle aerodynamic size distributions for fresh nonpolar (red) and polar (blue) tar ball aerosols measured via laser velocimetry by the SP-LD-REMPI-ToF-MS instrument. The major mode peaks at about 550 nm for both particle classes while a second mode of larger particles occurs for polar tar balls and a second mode of smaller particles appears for nonpolar tar balls. Note that the detection efficiency drops rapidly below 250 nm due to the descending Mie scattering efficiency for particles much smaller than the wavelength (532 nm).

6. Exemplary <u>Proper</u> Polyaromatic Compounds indicated by the REMPI PAH Spectra in this study (Table S2)

Table S2.Exemplary <u>proper</u> (poly)aromatic compounds indicated by the REMPI PAH Spectra in Figure 3

m/z	Name	Formula	Polar tar ball	Nonpolar tar ball	BBOA Reference
110	Catechol	$C_6H_6O_2$	√		Veres et al., 2010; Yee et al., 2013
115	PAHs fragments		√	√	Adler et al., 2011; Bruns et al., 2015
124	Guaiacol	$C_7H_8O_2$	√		Li et al., 2017; Yee et al., 2013; Hoffmann et al., 2007
128	Naphthalene	$C_{10}H_8$	√	√	Samburova et al., 2016; Passig et al., 2017; Bruns et al., 2015
138	4-Methylguajacol	$C_8H_{10}O_2$	√	√	Adler et al., 2011; Yee et al., 2013
152	Vanillin 4-Ethylguajacol	$C_8H_8O_3$ $C_9H_{12}O_2$	√	√	Li et al., 2014; Passig et al., 2017;Yee et al., 2013; Hoffmann et al., 2007
158	Methoxynaphthalene 1,4-Naphthalenedione Methylnaphthol	$C_{11}H_{10}O$ $C_{10}H_6O_2$ $C_{11}H_{10}O$	√		Santos et al., 2016; Yee et al., 2013; Hoffmann et al., 2007
165	PAHs fragments		√	√	Adler et al., 2011; Bruns et al., 2015
168	4-Methylsyringol Vanillic acid	$C_9H_{12}O_3$ $C_8H_8O_4$	√		Santos et al., 2016; Hoffmann et al., 2007; Bruns et al., 2015
178	Phenanthrene Conifery aldehyde	$C_{14}H_{10}$ $C_{10}H_{10}O_3$	√	√	Samburova et al., 2016; Bente et al., 2008, 2009; Passig et al., 2017
182	Syringaldehyde 4-Ethylsyringol	$C_9H_{10}O_4$ $C_{10}H_{14}O_3$	√		Santos et al., 2016; Yee et al., 2013; Hoffmann et al., 2007
189, 190, 191	Retene fragments		√	√	Bente et al., 2008, 2009; Mandalakis et al., 2005
192	Methylphenanthrene	$C_{15}H_{12}$	√	√	Samburova et al., 2016; Bente et al., 2008, 2009; Passig et al., 2017
202	Pyrene Fluoranthene	$C_{16}H_{10}$	√	√	Adler et al., 2011; Bente et al., 2008, 2009; Passig et al., 2017
203, 204, 205	Retene fragments		√	√	Passig et al., 2017; Mandalakis et al., 2005
206	Ethylphenanthrene	$C_{16}H_{14}$		√	Samburova et al., 2016
219, 220	Retene fragments		√	√	Bente et al., 2008, 2009; Passig et al., 2017
234	Retene	$C_{18}H_{18}$	√	√	Samburova et al., 2016; Bente et al., 2008, 2009; Passig et al., 2017

| 248 | Methyl. Retene | $C_{19}H_{20}$ | | √ | Passig et al., 2017; Mandalakis et al., 2005 |
| 250 | Ox. Retene | $C_{18}H_{18}O$ | √ | √ | Samburova et al., 2016 |

Note: only some major and most proper aromatic compounds were listed in the table

7. Morphology of tar ball aerosols
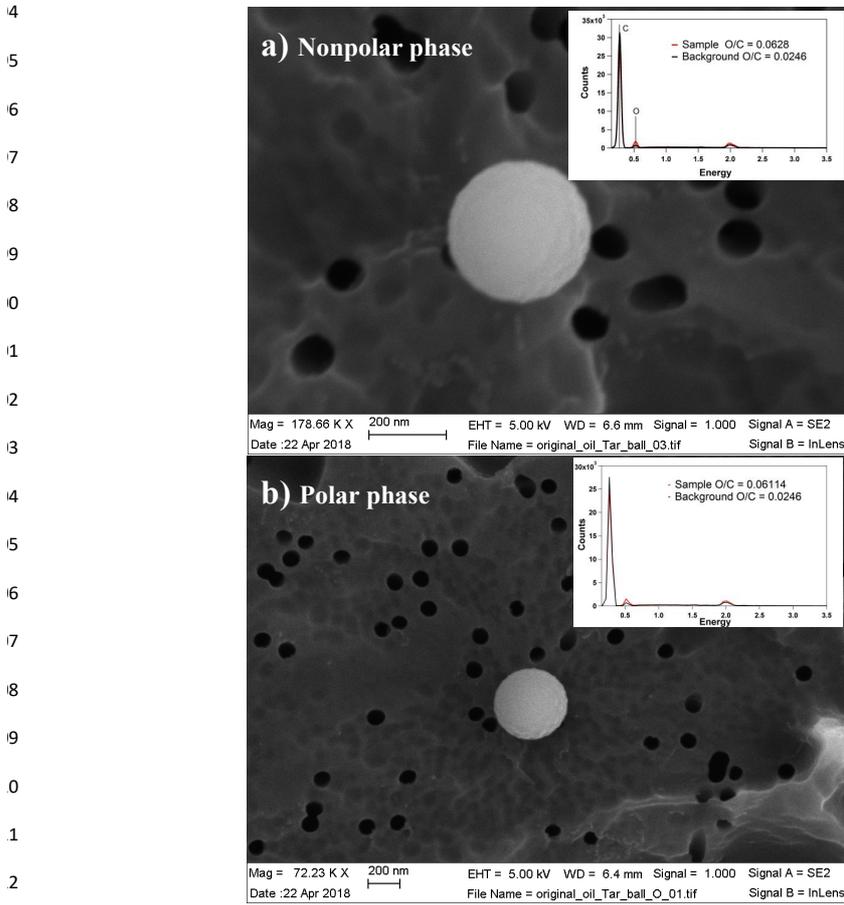
Figure S4. Morphology of fresh tar ball particles generated from polar and nonpolar phase tarry solutions. The particles are perfect spherical and amorphous in internal composition.

8. Refractive index for tar ball at mixture of 2:1 and 1:2 in volume of polar and nonpolar materials
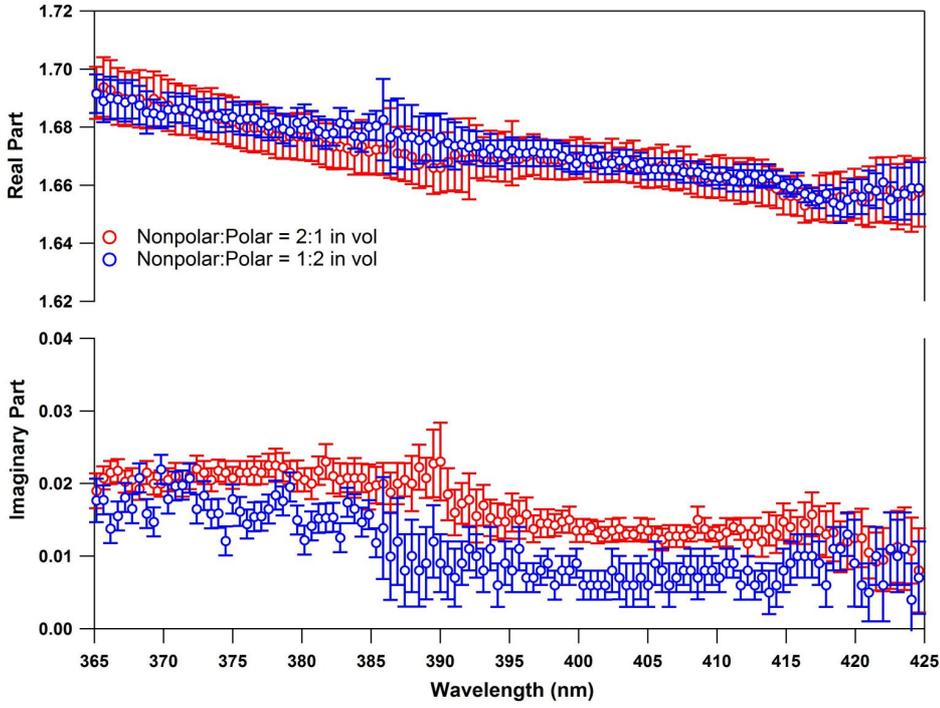
Figure S5. Wavelength-dependent refractive index (RI) for tar ball particles generated from polar and nonpolar phase solution mixtures

9. Example of absorption coefficients for some of the most absorbing PAHs identified in BBOA
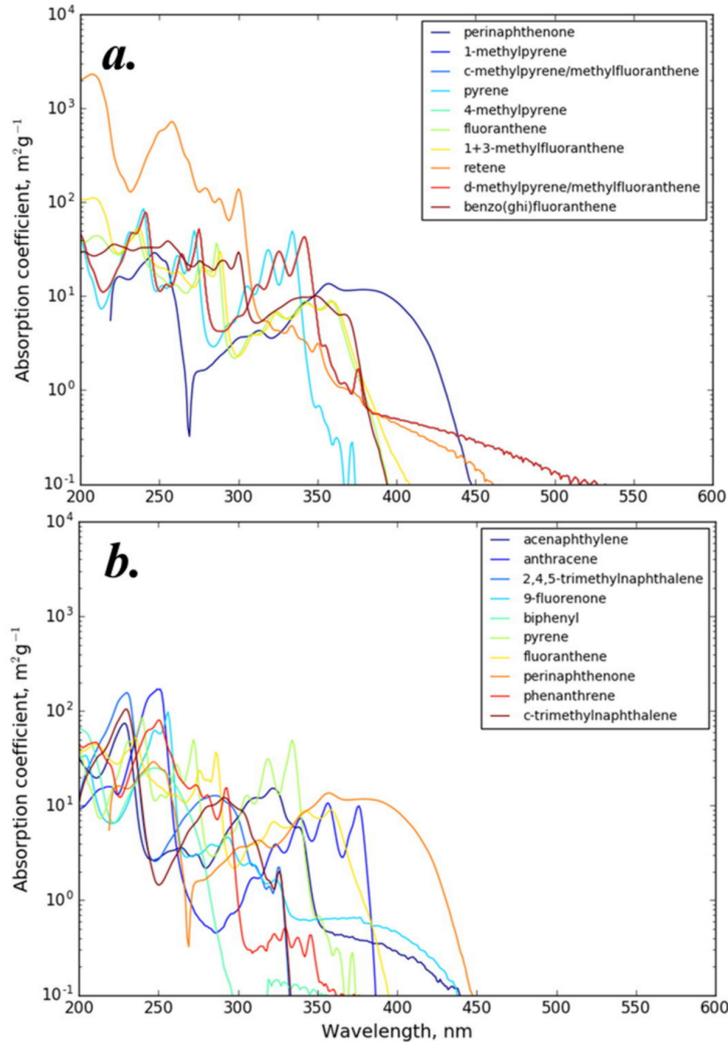
Figure S6. Absorption coefficients for some of the most absorbing PAHs identified in biomass burning emissions (Samburova et al., 2016).

10. Methanol extractable BrC mass absorption cross sections (MAC) for fresh tar ball aerosols from 360 to 450 nm
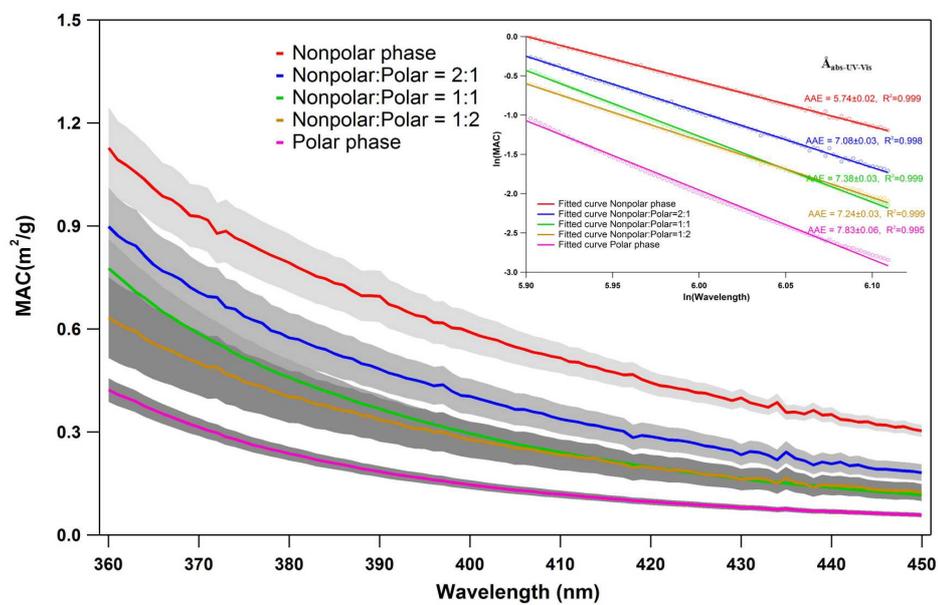
Figure S7. BrC mass absorption cross section (MAC) for methanol extracted fresh tar ball particles. Inset chart presents example of $Å_{abs\_UV-Vis}$ calculated from natural logarithm regression of MAC and wavelength.

11. Prediction of mixture tar ball optical properties based on different mixing rules

There are many mixing rules currently in use to predict optical properties of aerosol from matrix of various substances: 1) molar refraction and absorption (Jacobson, 2002; Tang, 1997); 2) a volume-weighted linear average of the refractive indices (d'Almeida et al., 1991); 3) the Maxwell-Garnet rule (Chýlek et al., 1984); and 4) the dynamic effective medium approximation (Jacobson, 2006). Due to the complexity of undefined chemical composition of tar ball particles, the Maxwell-Garnet and dynamic effective medium approximation are not feasible in this study, therefore, the simple molar fraction and volume-weighted mixing rules were discussed to fit the optical results.

The "linear mixing rule" simplifies mixing state and interaction between matrix, assumes that total real and imaginary refractive indices of the mixture are result of the indices of the components weighted by their their volume fractions:

$$n_{tot} = \sum_n f_i n_i$$
$$k_{tot} = \sum_n f_i k_i$$
[1]

Where f_i, n_i, and k_i are the volume fraction, real part, and imaginary part of each component

The molar fraction mixing rule assumes that the total molar refraction of a mixture is given by the linear average of the molar refraction of each component weighted by their molar volumes, i.e.,

$$\frac{\overline{M}}{\rho} \frac{n^2-1}{n^2+2} = \sum_n \chi_i \frac{M_i}{\rho_i} \frac{n_i^2-1}{n_i^2+2}$$
$$\frac{\overline{M}}{\rho} k = \sum_n \chi_i \frac{M_i}{\rho_i} k_i$$
$$\sum_n \chi_i = 1$$
[2]

Where x_i, M_i, and ρ_i are the molar fraction, molecular weight, and material density.

Refractive indices for tar ball generated from polar and nonpolar fraction mixture at solution mixing ratios of 1:2,1:1, and 2:1 will be calculated from RI of polar and nonpolar optical results based on above two rules. The exact volume and molar fraction for bulk polar and nonpolar part in particles can be estimated from particle density and chemical elemental ratios:

$$\rho_{tot} = f_1\rho_1 + f_2\rho_2$$
$$f_1 + f_2 = 1$$
[3]

$$R_{\overline{O/C}} = \chi_1 R_{\overline{O/C_1}} + \chi_2 R_{\overline{O/C_2}}$$
$$\chi_1 + \chi_2 = 1$$
[4]

Where $R_{O/C}$ is oxygen to carbon ratio from AMS measurement of tar ball particles, and calculated particulate volume and molar fraction are given below:

1

Table S3. Particulate molar and volume fractions of bulk polar and nonpolar tar

Polar:Nonpolar prepared solution ratio	O/C molar ratio	O/C retrieved molar mixing ratio	Density (g cm^{-3})	density retrieved volume mixing ratio
1:0	0.44	1:0	1.329±0.021	1:0
2:1	0.39	2.8:1	1.298±0.022	1.8:1
1:1	0.36	1.4:1	1.285±0.019	0.98:1
1:2	0.3	1:2.8	1.274±0.013	1:1.72
0:1	0.25	0:1	1.242±0.005	0:1

Molecular weight for polar and nonpolar fractions were simplified as $M_{bulk\text{-}polar}$ and $M_{bulk\text{-}nonpolar}$, and mixture tar ball particles follow the function below:

$$\frac{\overline{M}}{\overline{\rho}} = \frac{x_1 M_{bulk-polar}}{\rho_1} + \frac{x_2 M_{bulk-nonpolar}}{\rho_2}$$

$$\overline{M} = x_1 M_{bulk-polar} + x_2 M_{bulk-nonpolar}$$

[5]

And it was calculated as $M_{bulk\text{-}nonpolar} \approx 1.3 M_{bulk\text{-}polar}$

For convenience and clarity, wavelength-dependent RI for tar ball were exponential or power-law fitted, the results were showed in Figure S8 and corresponded parameters were summarized in Table S4:

1
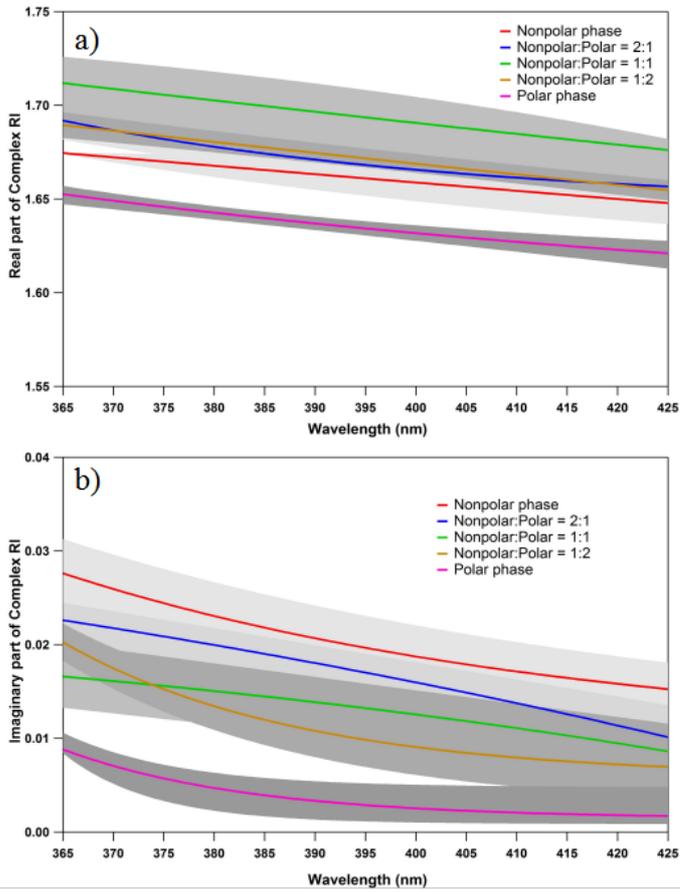
Figure S8. Regressed RI for tar ball particles of various mixing ratios: a) real part, and b) imaginary part

Table S4. Parameterization of the Wavelength-Dependent (365 to 425 nm) Effective Complex RI of tar ball particles

Tar ball		Real			Imaginary		
		Co	C1	C2	Co	C1	C2
Nonpolar phase	min	1.604	7.148	-1.27E-02	0.164	-8.89E-02	1.27E-03
	average	1.033	0.831	-7.08E-04	0.010	2.37E+01	-1.97E-02
	max	1.677	-1.95E-09	3.80E-02	0.010	8.75E+00	-1.65E-02
Nonpolar:polar 2:1	min	1.627	22.067	-1.65E-02	0.028	-1.05E-05	1.80E-02
	average	1.646	321.800	-2.43E-02	0.046	-1.81E-03	7.06E-03
	max	1.658	2819.637	-3.04E-02	0.330	-2.47E-01	5.86E-04
Nonpolar:polar 1:1	min	1.657	55.140	-1.98E-02	-0.291	3.52E-01	-4.01E-04
	average	1.324	0.697	-1.61E-03	0.023	-5.69E-16	5.10E+00
	max	1.754	-5.09E-18	6.145	-0.220	3.00E-01	-6.09E-04
Nonpolar:polar 1:2	min	1.832	-0.044	3.35E-03	0.002	6.88E+04	-4.19E-02
	average	1.306	0.683	-1.58E-03	0.006	8.43E+04	-4.27E-02
	max	1.550	0.826	-4.75E-03	0.009	1.56E+40	-1.64E+01
Polar phase	min	1.921	-0.133	1.97E-03	0.016	-5.83E-19	6.33E+00
	average	1.585	3.174	-1.06E-02	0.001	3.02E+06	-5.43E-02
	max	1.615	53.051	-1.95E-02	0.005	5.43E+11	-8.81E-02

Note: Non-shaded cells were fitted with an exponent; $n\&k(\lambda)=C_0+C_1\times e^{(C_2\times\lambda)}$. Shaded cells were fitted with a power law; $n\&k(\lambda)=C_0+C_1{}^{\lambda\times C_2}$

The calculated RI following "volume linear mixing rules" for tar ball were presented in Figure S9 and compared with experimental data in Figure S10.
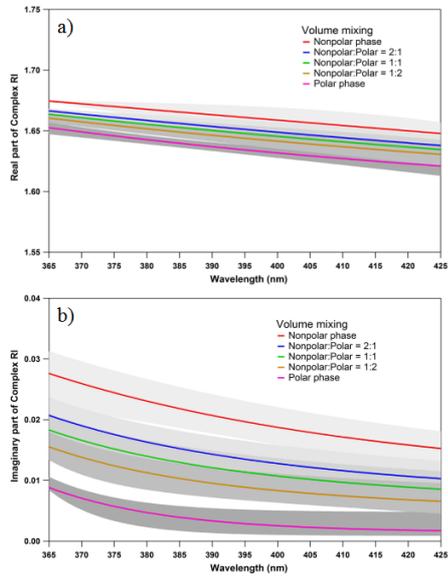
1

Figure S9. Estimated RI for tar ball particles of various mixing ratios based on volume linear mixing rule: a) real part, and b) imaginary part
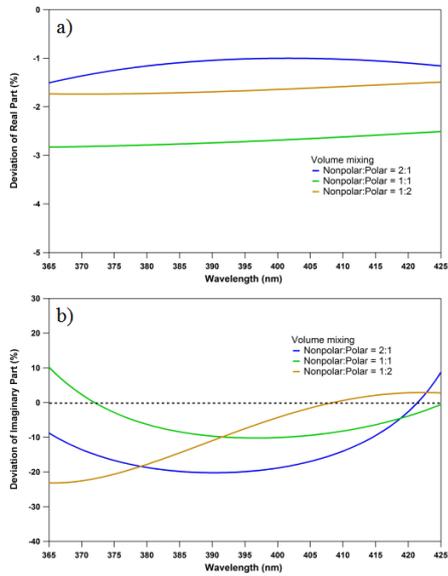
Figure S10. Deviation between experimental RI and predicted RI from volume linear mixing rule: a) real part, and b) imaginary part

1

The calculated RI following "molar fraction mixing rules" for tar ball were presented in Figure S11 and compared with experimental data in Figure S12.
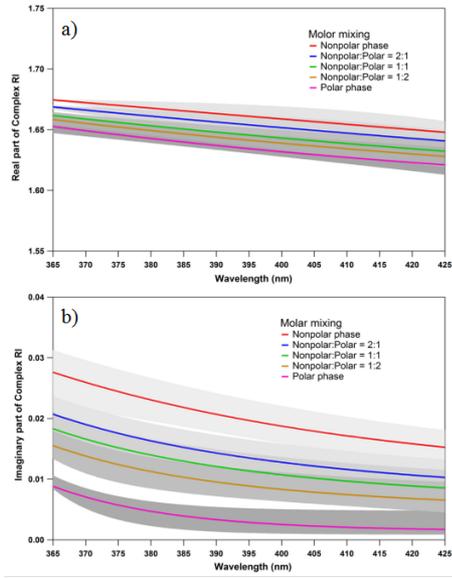
Figure S11. Estimated RI for tar ball particles of various mixing ratios based on molar fraction mixing rule: a) real part, and b) imaginary part
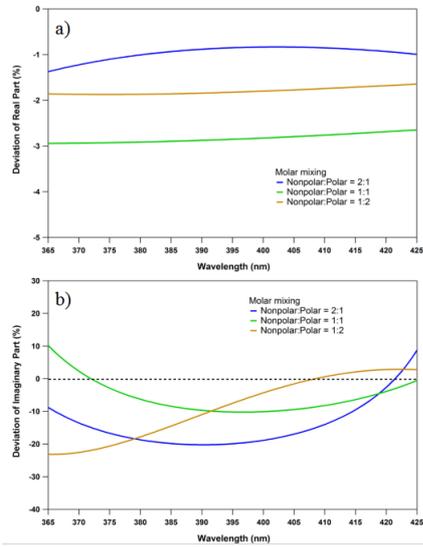
Figure S12. Deviation between experimental RI and predicted RI from molar fraction mixing rule: a) real part, and b) imaginary part

12. Summary of optical parameters for tar ball aerosol upon NOx-dependent photochemical aging

Table S5. Summary of RI and Ångström exponent changes for tar ball particles upon photochemical oxidation (mean ± standard deviation)

| Tar ball | Complex Refractive index | | | SSA (average) | $Å_{abs}$ | $Å_{abs\_UVVIS}$ | $Å$ |
	Average	375nm	405nm				
Fresh	(1.661±0.008)+(0.020±0.004)i	(1.671±0.003)+(0.025±0.003)i	(1.659±0.011)+(0.017±0.002)i	0.89 ± 0.01	5.87 ± 0.37	6.74	3.81
O_0.7	(1.641±0.010)+(0.014±0.006)i	(1.652±0.001)+(0.021±0.001)i	(1.635±0.001)+(0.010±0.002)i	0.92 ± 0.02	9.33 ± 3.38	6.11	4.21
O_1.7	(1.639±0.011)+(0.008±0.005)i	(1.651±0.002)+(0.015±0.004)i	(1.631±0.002)+(0.005±0.003)i	0.96 ± 0.03	10.96 ± 3.23	6.46	4.33
O_3.9	(1.632±0.010)+(0.007±0.004)i	(1.643±0.001)+(0.011±0.002)i	(1.628±0.002)+(0.004±0.001)i	0.96 ± 0.02	10.63 ± 3.17	6.31	4.11
O_6.7	(1.624±0.007)+(0.007±0.003)i	(1.630±0.003)+(0.009±0.003)i	(1.623±0.002)+(0.004±0.003)i	0.96 ± 0.02	9.89 ± 2.59	6.02	3.74
N_0.5	(1.635±0.011)+(0.015±0.004)i	(1.646±0.001)+(0.018±0.001)i	(1.629±0.001)+(0.012±0.002)i	0.91 ± 0.01	6.92 ± 1.35	6.41	4.01
N_2.0	(1.648±0.008)+(0.019±0.004)i	(1.653±0.002)+(0.025±0.003)i	(1.645±0.002)+(0.016±0.001)i	0.89 ± 0.01	5.60 ± 0.69	6.35	3.76

2

13. Methanol extractable BrC mass absorption cross sections (MAC) for NOx-free photochemical aged tar ball aerosols from 360 to 450 nm
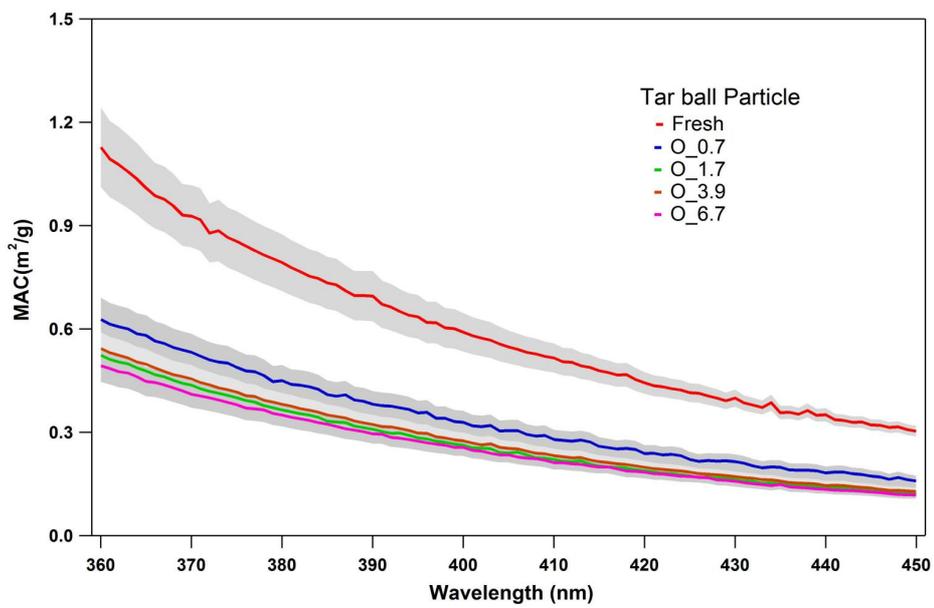
Figure S13. Diminishing in tar ball BrC mass absorption cross section (MAC) upon daytime NOx-free photochemical oxidation

14. Optical and chemical changes for tar ball aerosols due to photolysis from UV light irradiation in the OFR

Studies have reported that BrC formation and SOA decomposition due to directly UV/near UV-short visible light irradiation of various precursors in both liquid and air (Bateman et al., 2011; Malecha and Nizkorodov, 2016; Wong et al., 2017). During photochemical aging through the OFR at residence time of 144s, tar ball particles were also exposed to high photon flux at 254 nm. We performed several experiments to estimate the influence of UV illumination on tar ball evolution. Irradiation tests of P1 and P2 repeated the same aging process of O_1.7 and O_3.9 without external O_3, and P3 was conducted at a full power of the UV lamps in the OFR. We observed slight chemical composition changes in the tar ball aerosols due to photolysis, as the O/C ratio continuously increased while H/C decreased with extension of irradiation (Table S6 and Figure S14). The O/C ratio increased by 0.04 for maximal irradiation exposure, which was much smaller than that from photochemical oxidation. This indicates that OH-initiated oxidation rather than photolysis reactions play a more dominate role in tar ball aging.

The decrease of the H/C ratio due to photolysis exhibited a distinct different chemical pathway than by OH photooxidation. According to the mass spectra analysis, particularly for the P3 experiment shown in Figure S14, the fractions of signals attributed to $C_xH_y^+$ and $C_xH_yO_z^+$ fragments decreased, and as a consequence, the contribution of the $C_xH_yO^+$ fractions increased in photolyzed tar ball aerosols. Comparing to the fresh tar ball mass spectra, alkyl/alkenyl chains, carboxylic acids/peroxides (CO_2^+, CHO_2^+), and carbonyl/aldehyde groups (CO^+, CHO^+, $C_2H_3O^+$) fragments depleted due to irradiation by UV light. Furthermore, increase of the $f44/f43$ ratio with photolysis shown in Figure S14, indicates decay of CO_2^+ to a less extent compared to the loss of $C_2H_3O^+$. Photolysis occurs in the condensed phase as particles containing photolabile compounds that efficiently absorb light at actinc wavelengths. Oxygenated species such as carbonyls, carboxylic acids, and peroxides are more vulnerable to photolysis, especially in the UV. With cleavage of the oxygenated functional groups, molecules become more volatile and may desorb to the gas phase (Henry and Donahue, 2012). Considerable amount of VOCs productions, including small molecular acids, ketones, aldehydes (e.g., acetic acid, formic acid, acetaldehyde, acetone, etc.), and hydrocarbon species (e.g., methane, ethene, propane, etc.), were detected from photo-degradation of various SOA (Malecha and Nizkorodov, 2016; Mang et al., 2008), and photocleavage of carbonyls has been emphasized in photolysis of SOA. Bateman et al. (2011) reported that exposure to UV irradiation increased the O/C ratio of dissolved ambient SOA, and they attributed the chemical changes to photodissociation of molecules containing carbonyl groups and net production of carboxylic acids that overweigh their decomposition in pH modified solution. Detailed mechanisms were proposed such as n-π* Norrish type-I and -II splitting of carbonyls and n-σ* photolysis of peroxides to form production of carboxylic acids in the presence of dissolved oxygen (Norrish, 1934; Pitts et al., 1964).

In the current experiments, photolysis occurred in particle phase which can be different from photolysis in liquid phase. First, the photolysis of particles should be less efficient as quenching is more likely and fragment caging can prevent rapid recombination. Second, photolysis products (volatile molecules and radicals) can more easily transfer to the gas phase rather than accumulate in the solution and be involved in further reactions. Epstein et al. (2014) isolated photolysis influence on α-pinene SOA. They reported suppression of SOA mass loading and marked decomposition of particle-bound organic peroxides from UV light illumination. The fraction of $C_xH_y^+$ fragments slightly decreased while the oxygenated fragments increased upon irradiation. Wong et al. (2014) highlighted RH-dependent photolysis as a sink for SOA in the atmosphere, in particular, photolysis results in more oxidized SOA due to kinetic preference for degradation of less oxidized components, and they attributed the slower decay of $f44$ (CO_2^+) to photodissociation of peroxides and the formation of carboxylic acids in SOA upon UV irradiation.

The optical properties of SOA can change upon photolysis of photolabile carbonyl/carboxylic organics, peroxides, and other chromophores. Liu et al. (2016) investigated the influences of various environmental factors on light absorption of aromatic SOA from ozonolysis in the presence of NO_x. They suggested that photolysis, rather than hydrolysis, bleached SOA absorption due to degradation of nitrogen-containing chromophores. This conclusion was also confirmed by similar studies by Lee et al. (2014) and Aiona et al. (2018). In our study, the changes in the optical properties as a function of O/C ratio for tar balls upon photolysis are

shown in Figure S16. The relevant parameters are summarized in Table S7, MAC changes for tar ball upon photolysis are presented in Figure S17. RI of both real and imaginary parts weakly diminished during irradiation, and the average RI at 375 nm decreased by 0.012+0.006i for maximum photolyzed tar ball, corresponded MAC at 375 nm decreased by ~31.3%.

Table S6. Summary of mass spectra characters and effective density changes for tar ball particles upon photolysis from UV light irradiation (mean ± standard deviation)

Tar ball	O:C	H:C	N:C	m/z>100 fraction	density
Fresh	0.25±0.01	1.55±0.01	0.012±0.002	0.32	1.24±0.01
P1	0.26±0.01	1.53±0.01	0.013±0.003	0.33	1.24±0.01
P2	0.27±0.01	1.51±0.01	0.011±0.001	0.32	1.24±0.01
P3	0.29±0.01	1.49±0.01	0.012±0.002	0.33	1.24±0.01
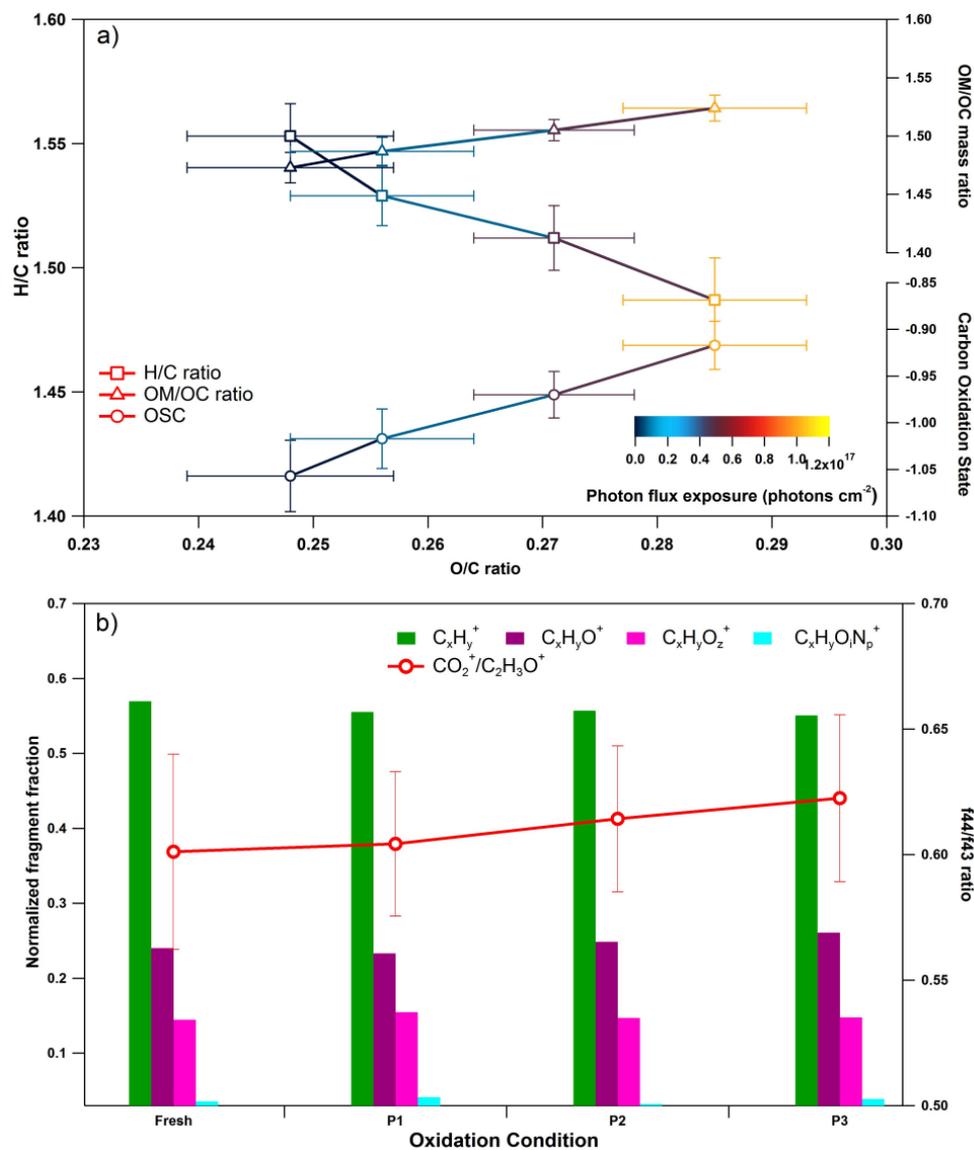
Figure S14. Dynamic changes for chemical characteristics of tar ball particle upon UV light irradiation: a) OM/OC, H/C ratio, and average carbon oxidation state ($\overline{OSc}$) changes as a function of O/C ratio; b) mass spectra evolution with photolysis extension in term of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, and $C_xH_yO_iN_p^+$ fragment groups
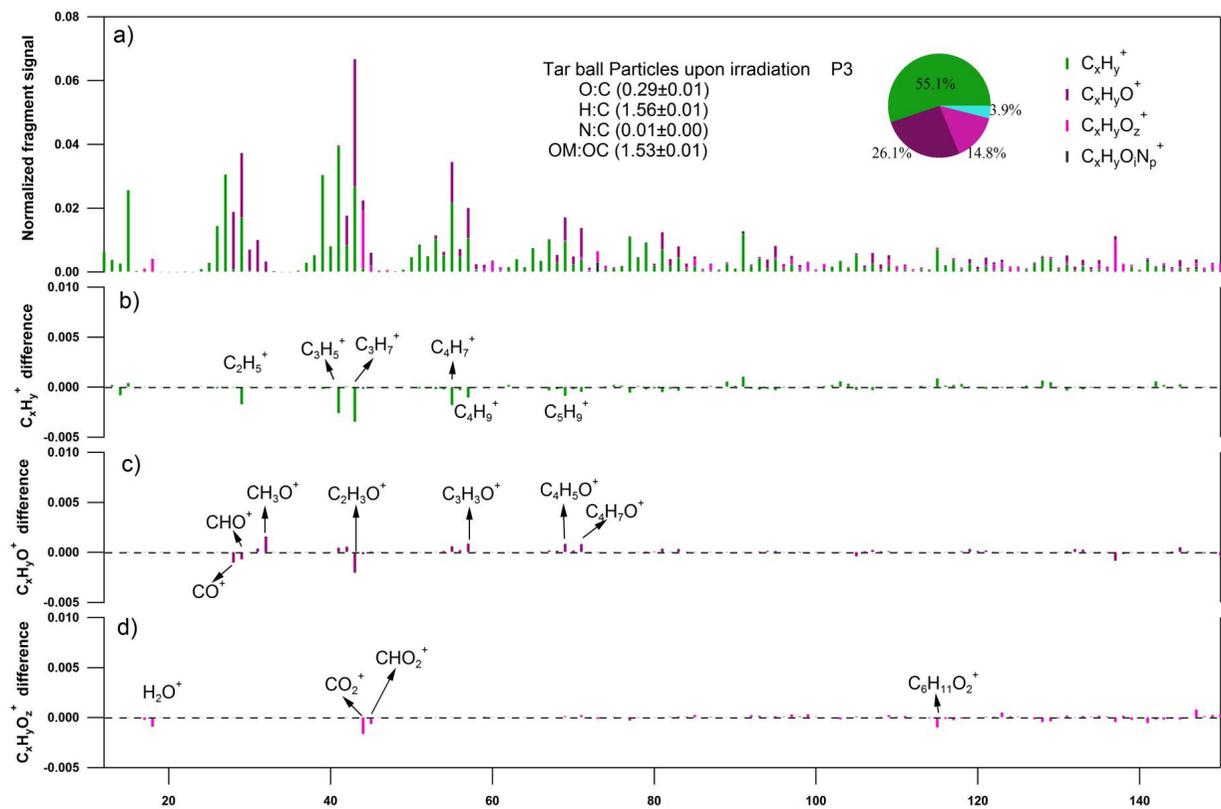
Figure S15. High-resolution mass spectra changes for nonpolar tar ball particles after maximum photolysis in P3 test, four ion groups were grouped for clarity as: $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$ ($z>1$), $C_xH_yO_iN_p^+$($i\geqq0,p\geqq1$). Ions O^+, OH^+, and H_2O^+ were included in the $C_xH_yO_z^+$ group. Mass fraction of the four fragment groups was pie-chart presented. a) normalized mass spectra of aged tar ball particles, b)~d) changes of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, and $C_xH_yO_iN_p^+$ comparing with fresh tar ball normalized mass spectra

2

Table S7. Summary of RI and Ångström exponent changes for tar ball particles upon photolysis (mean ± standard deviation)

Tar ball	Complex Refractive index			SSA (average)	$Å_{abs}$	$Å_{abs\_UVVIS}$	$Å_{ext}$
	Average	375nm	405nm				
Fresh	(1.661±0.008)+(0.020±0.004)i	(1.671±0.003)+(0.025±0.003)i	(1.659±0.011)+(0.017±0.002)i	0.89 ± 0.01	5.87 ± 0.37	6.74	3.81 ± 0.18
P1	(1.658±0.010)+(0.022±0.006)i	(1.668±0.001)+(0.027±0.001)i	(1.653±0.002)+(0.018±0.001)i	0.88 ± 0.02	6.92 ± 0.60	6.59	3.94 ± 0.03
P2	(1.649±0.008)+(0.018±0.004)i	(1.656±0.002)+(0.023±0.002)i	(1.647±0.002)+(0.014±0.003)i	0.90 ± 0.02	6.99 ± 1.22	6.50	3.79 ± 0.05
P3	(1.649±0.010)+(0.015±0.004)i	(1.659±0.005)+(0.019±0.004)i	(1.644±0.004)+(0.013±0.003)i	0.92 ± 0.01	7.42 ± 0.53	6.56	4.01 ± 0.01
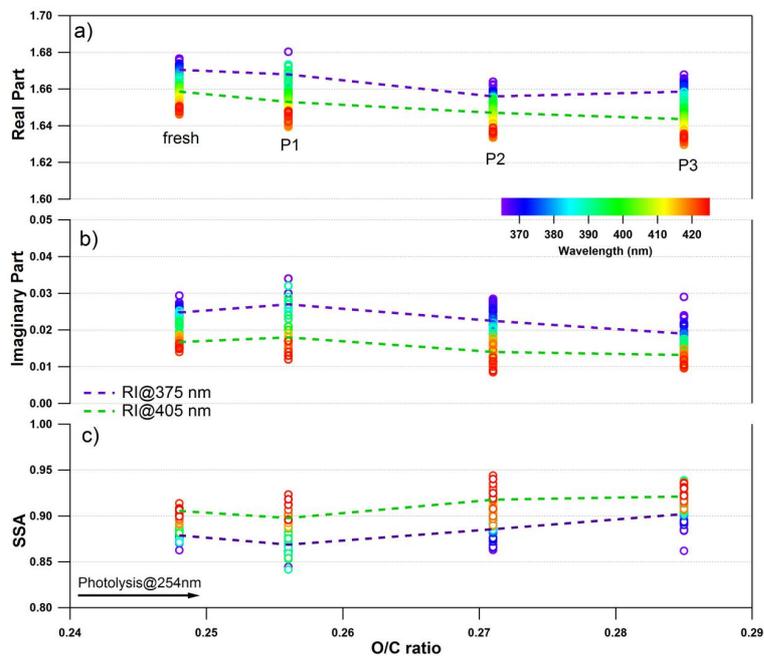
Figure S16. Changes in the retrieved spectral-dependent complex RI and SSA as a function of O/C ratio for tar ball particles upon 254 nm illumination: a) real part, b) imaginary part, and c) SSA calculated for 150 nm particles. The color scale shows the span in the RI for the wavelengths measured from 365 to 425 nm. For clarity, error bars for O/C ratio (±0.01), RI (±0.008 for real part, and ±0.003 for imaginary part on average) and SSA (±0.006) are not shown. The two dashed lines trace RI and SSA at 375nm (purple) and 405nm (green). P1~P3 represent photolysis studies with low to maximal photon flux exposures.
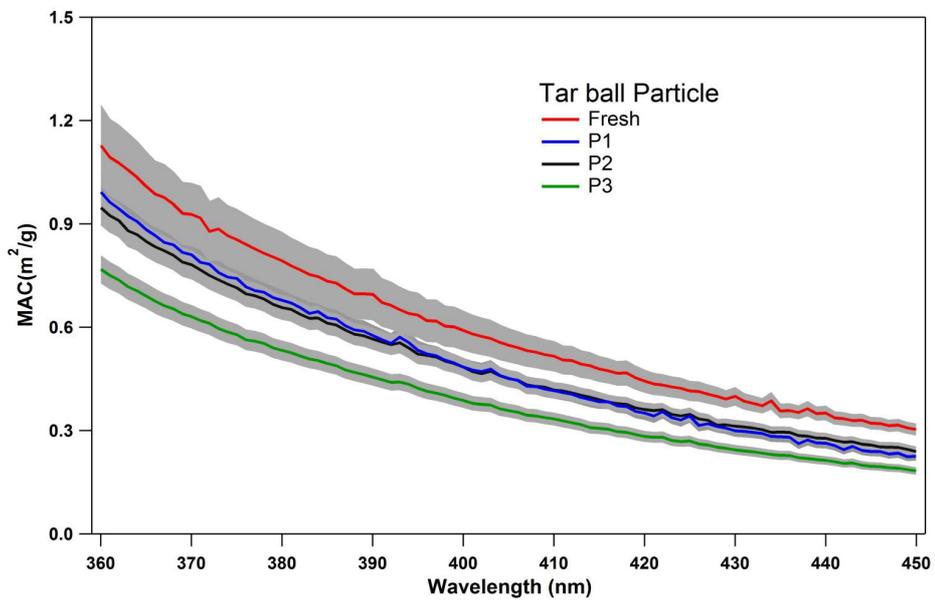
Figure S17. Changes of tar ball BrC mass absorption cross section (MAC) as a function of wavelength upon UV photolysis

15. Optical and chemical changes of tar ball aerosols due to O₃ oxidation

Prior to photochemical aging experiments, blank test of tar ball oxidation via O_3 under dark was conducted in the OFR. Initial environmental conditions (e.g., O_3 and tar balls concentrations, relative humidity, residence time, etc) were maintained the same with following daytime evolution simulations, while UV lamps were not turned on. Dynamic optical and chemical changes for tar balls were characterized and presented in Figure S18 and S19. We did not observe significant refractive index changes for tar balls after 28.6 ppm O_3 oxidation, taking ambient O_3 concentration of 50 ppb, equivalent atmospheric O_3 exposure for tar balls through the OFR was about one day. RIs of fresh tar ball are $(1.671\pm0.003)+(0.025\pm0.003)i$ and $(1.659\pm0.011)+(0.017\pm0.002)i$ at 375 and 405 nm, respectively. After O_3 oxidation, RIs became $(1.677\pm0.012)+(0.023\pm0.003)i$ and $(1.668\pm0.011)+(0.013\pm0.004)i$ at at 375 and 405 nm, respectively. In Figure S19, O_3 oxidation weakly increased O/C and OM/OC ratios of tar balls, O/C ratio increased by 0.02 from initial 0.25, and OM/OC increased from 1.47 to 1.50, while H/C ratio remained during O_3 oxidation of tar ball particles. It was found $C_xH_y^+$ fractions slight decreased in compensation of more $C_xH_yO^+$ and $C_xH_yO_z^+$ fragments formation, indicating oxygenated moieties produced.
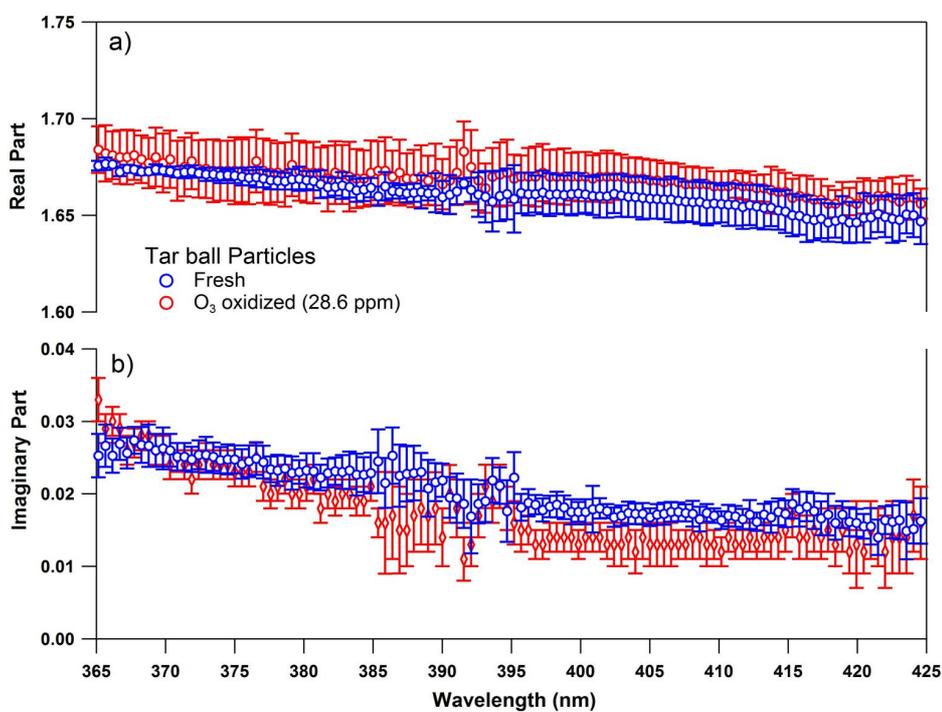
Figure S18. Refractive index as a function of wavelength for fresh and O3 oxidized tar balls, a) real part, b) imaginary part
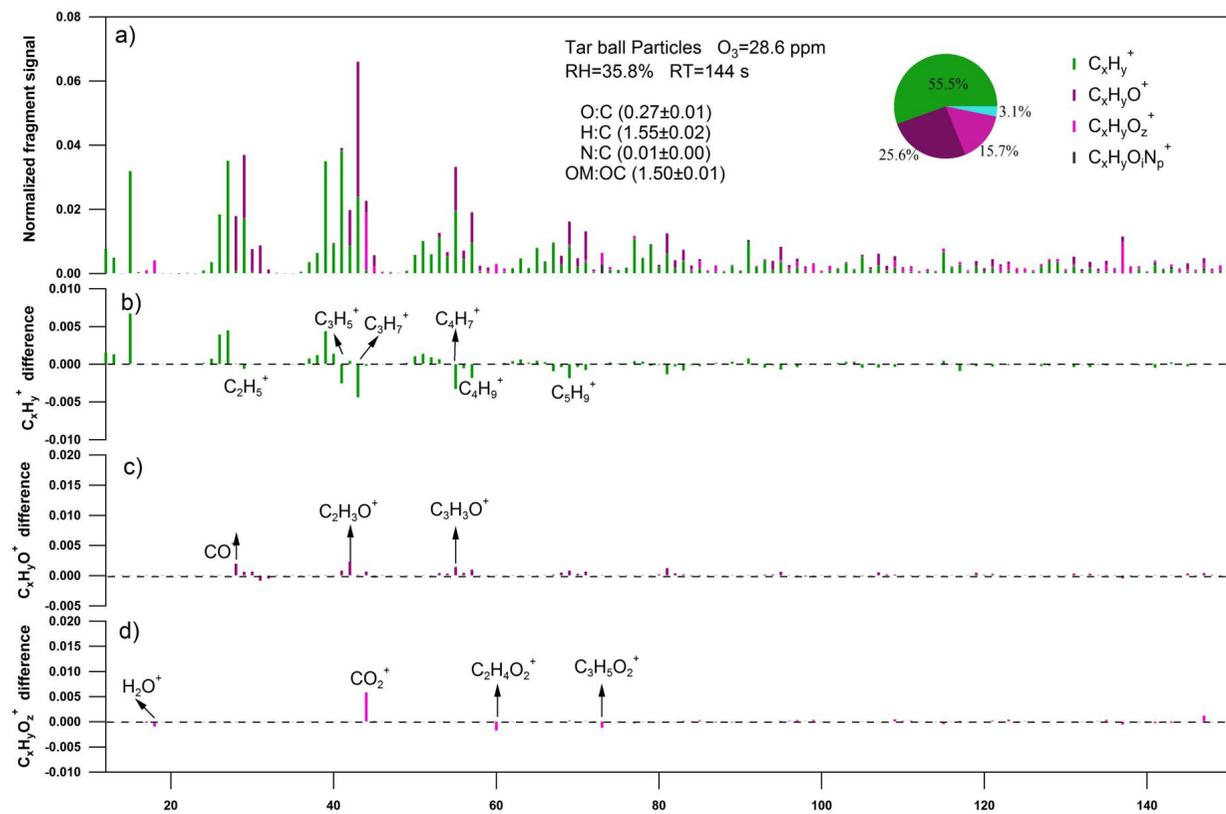
Figure S19. High-resolution mass spectral changes for nonpolar tar ball particles oxidized via O_3. Four ion groups were grouped for clarity: $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$ ($z>1$), $C_xH_yO_iN_p^+$($i\geqq0,p\geqq1$). Ions O^+, OH^+, and H_2O^+ were included in the $C_xH_yO_z^+$ group. Mass fraction of the four fragment groups was pie-chart presented. a) normalized mass spectra of O_3 oxidized tar ball particles, b)~d) changes of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, and $C_xH_yO_iN_p^+$ comparing with fresh tar ball normalized mass spectra

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16. Mass spectra characters and effective density changes for tar ball particles upon photochemical oxidation

Table S8. Summary of mass spectra characters and effective density changes for tar ball particles upon photochemical oxidation (mean ± standard deviation)

Tar ball	O:C	H:C	N:C	m/z>100 fraction	density
Fresh	0.25±0.01	1.55±0.01	0.012±0.002	0.32	1.24±0.01
O_0.7	0.32±0.01	1.59±0.01	0.012±0.000	0.28	1.24±0.01
O_1.7	0.35±0.01	1.60±0.01	0.009±0.002	0.24	1.24±0.01
O_3.9	0.35±0.01	1.59±0.01	0.010±0.003	0.24	1.24±0.01
O_6.7	0.38±0.01	1.62±0.03	0.011±0.001	0.21	1.24±0.01
N_0.5	0.37±0.01	1.57±0.02	0.012±0.001	0.25	1.25±0.01
N_2.0	0.41±0.01	1.58±0.01	0.015±0.004	0.25	1.26±0.01

17. Detailed mass spectra changes for tar ball upon 6.7 EAD photochemical aging
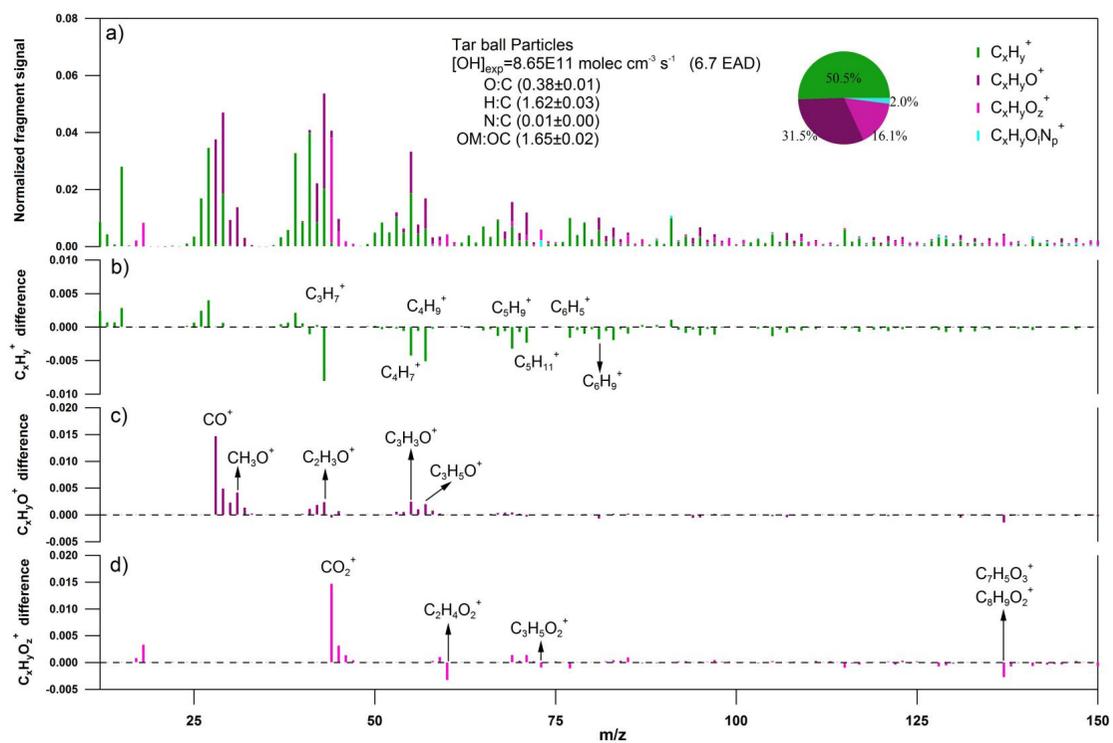
Figure S20. High-resolution mass spectral changes for nonpolar tar ball particles upon 6.7 EAD photochemical oxidation in absence of NOx. Four ion groups were grouped for clarity: $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$ ($z>1$), $C_xH_yO_iN_p^+$ ($i\geqq0,p\geqq1$). Ions O^+, OH^+, and H_2O^+ were included in the $C_xH_yO_z^+$ group. Mass fraction of the four fragment groups was pie-chart presented. a) normalized mass spectra of 6.7 EAD aged tar ball particles, b)~d) changes of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, and $C_xH_yO_iN_p^+$ comparing with fresh tar ball normalized mass spectra

18. Standard AMS spectra for inorganic salt of NH₄NO₃
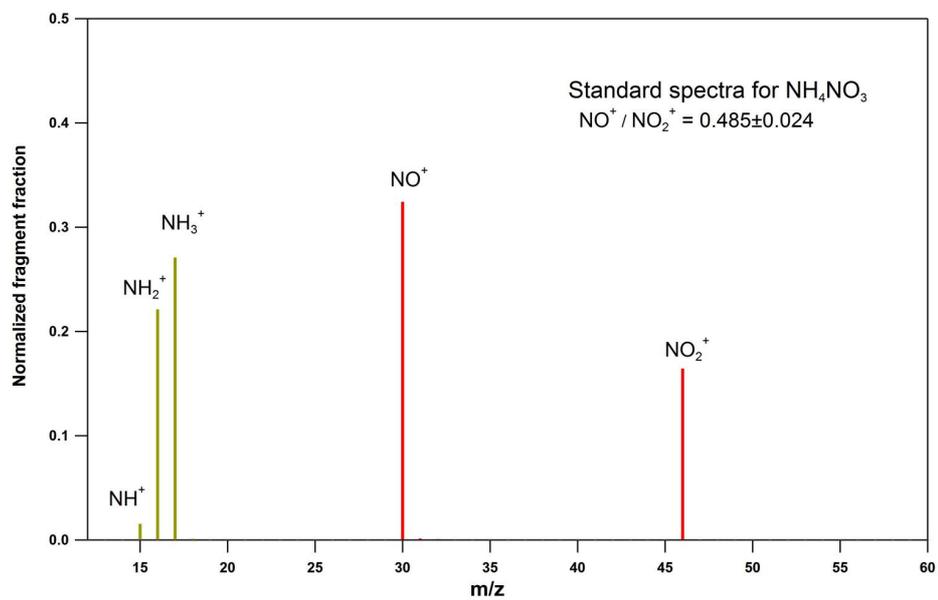
Figure S21. Standard mass spectra for NH_4NO_3 measured using HR-Tof-AMS system: NO^+ and NO_2^+ for nitrate, NH^+, NH_2^+, and NH_3^+ for ammonium

19. Detailed mass spectra changes for tar ball aerosols upon 4 EAD photochemical aging with 2.0 vol.% N₂O addition
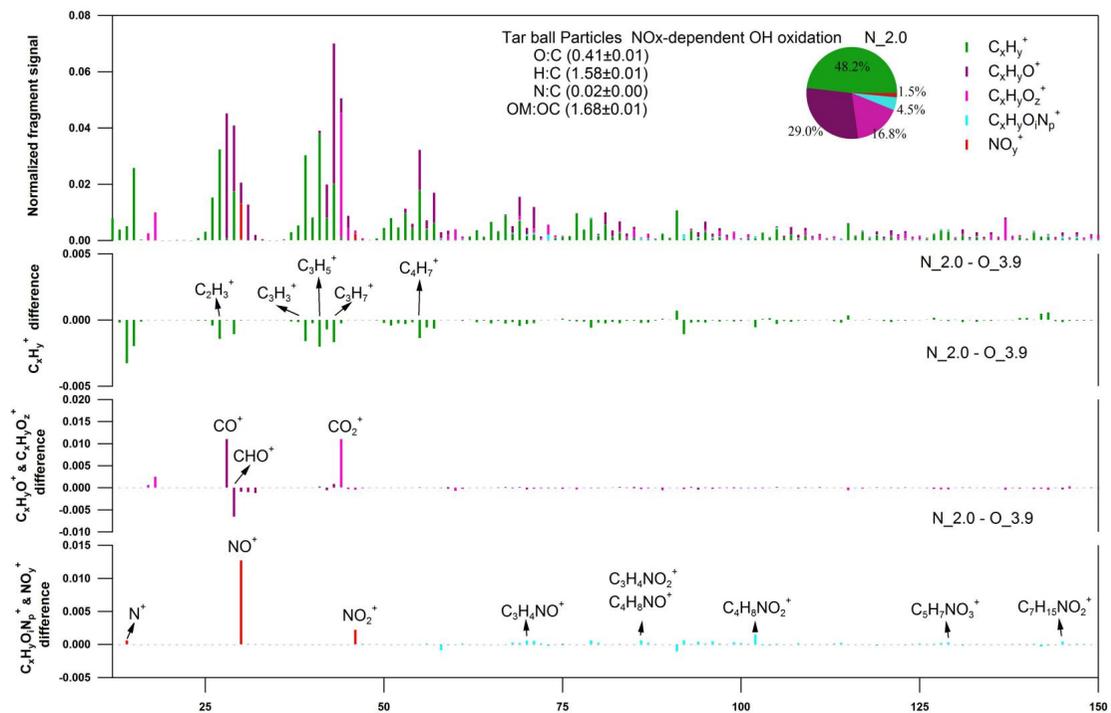
Figure S22. High-resolution mass spectra changes for nonpolar tar ball particles upon photochemical oxidation in presence of NOx, five ion groups were grouped for clarity as: $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$ (z>1), $C_xH_yO_iN_p^+$(i≧0,p≧1), and NO_y^+ (NO⁺ and NO_2^+). Ions O⁺, OH⁺, and H_2O^+ were included in the $C_xH_yO_z^+$ group. Mass fraction of the four fragment groups was pie-chart presented. a) normalized mass spectra of aged tar ball particles, b)~d) changes of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, $C_xH_yO_iN_p^+$, and NO_y^+ comparing with photochemical oxidized tar ball in absence of NOx

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20. Methanol extractable BrC mass absorption cross section (MAC) for tar ball aerosols upon various NOx-dependent photochemical aging processes
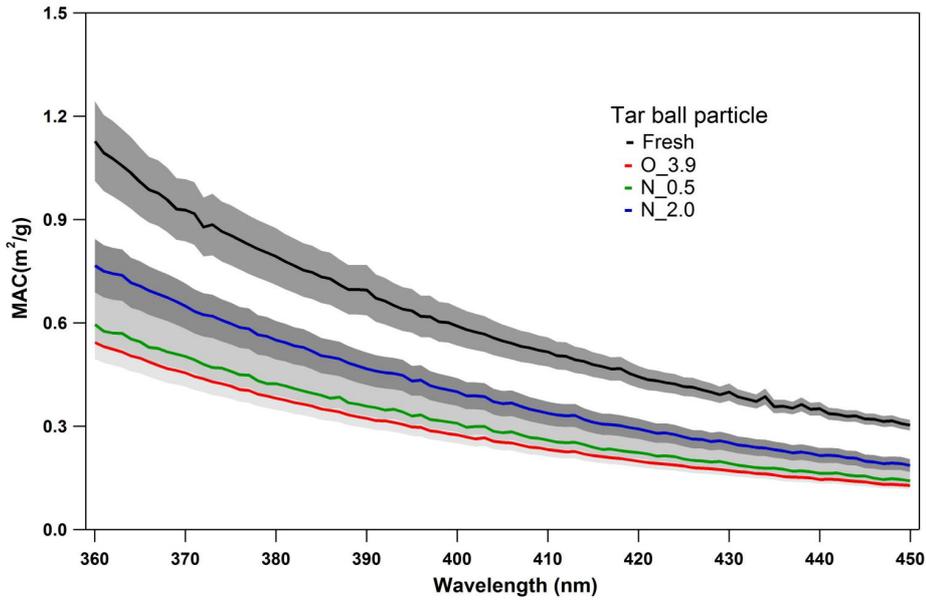
Figure S23. Methanol extractable BrC mass absorption cross section (MAC) for tar ball upon NOx-dependent photochemical oxidation as a function of wavelength

21. Particle size- and light wavelength-resolved radiative forcing for tar ball aerosols oxidized via various NOx-dependent oxidation processes
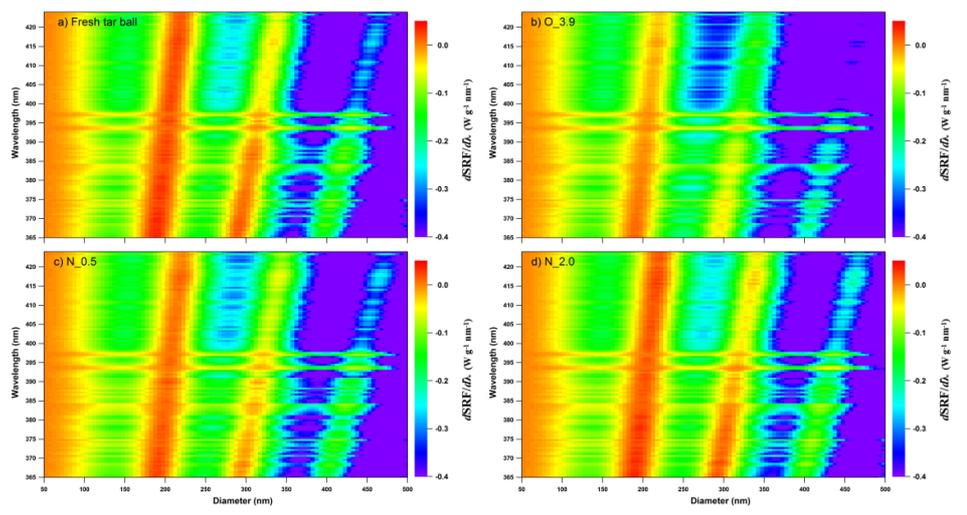
Figure S24. Ground based size-resolved radiative forcing spectra over solar irradiation of 365~425 nm for tar ball under various oxidation: a) fresh tar ball, b) 3.9 EAD daytime photochemical oxidized tar ball, c) photooxidized tar ball with 0.5 vol.% N_2O addition, d) photooxidized tar ball with 2.0 vol.% N_2O addition.
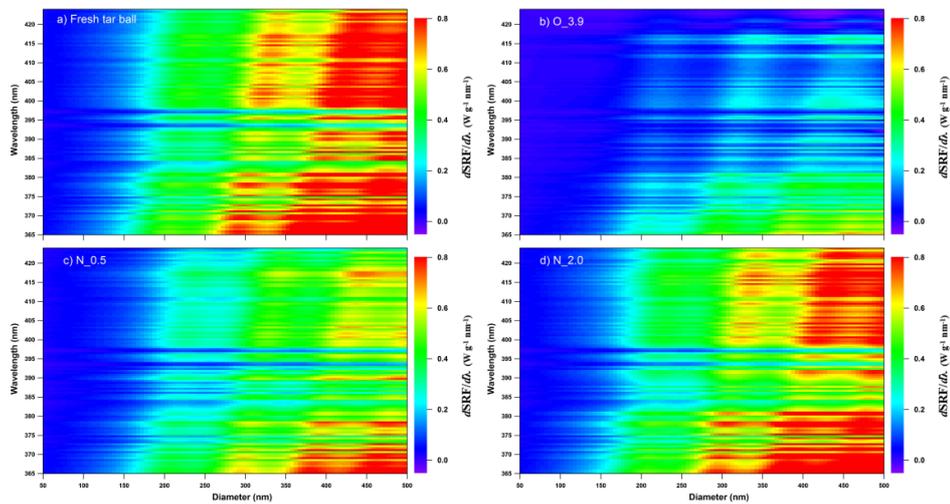
Figure S25. Snow based size-resolved radiative forcing spectra over solar irradiation of 365~425 nm for tar ball under various oxidation: a) fresh tar ball, b) 3.9 EAD OH initiated photochemical oxidized tar ball, c) photooxidized tar ball with 0.5 vol.% N_2O addition, d) photooxidized tar ball with 2.0 vol.% N_2O addition.

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