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

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

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

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

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

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

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

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

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

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

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

Authors' reply: In this study, light absorbing properties of polar and nonpolar chemical matrix from wood pyrolysis were characterized. We found that the refractive index for the mixture of polar and nonpolar organic fractions fit both volume and molar mixing rules (see supporting information of prediction of mixture tar ball optical properties based on different mixing rules). However, the actual fractions of the polar and nonpolar compounds contributing to the mass/absorption of ambient tar ball or BBOA are still under study, as they vary with biofuel, burning conditions, atmospheric processes, and also the method/efficiency used to classify the polar and nonpolar materials from the sample (Sengupta., et al., 2018; Lin et al., 2017; Chen and Bond, et al., 2010; Sumlin et al., 2017) (Page 6, Line 133-137). According to most previous studies, the nonpolar or less polar fractions have higher absorption properties compared with the polar fraction from BBOA. Sengupta et al. (2018) reported that the fuel mass normalized nonpolar fraction is 2-3 times more absorbing than the polar fraction, and complex fuel-dependence and atmospheric aging dependence were observed for absorption changes of both fractions. Lin et al. (2017) and Bluvshtein et al. (2017) tracked the absorption changes of BBOA with respect to different solvent extraction during a whole fire episode, and found distinct different absorbing features for the water-extracted fraction compared to the organic solvent extracts, while acetonitrile and orgmix (acetonitrile: dichloromethane: hexane = 2:2:1, *v/v*) extracts exhibited similar absorption. According to Lin et al. (2017), from the beginning to the end of the fire event, organic extracts showed higher light absorption at shorter wavelength (λ<380 nm). In contrast, higher light absorption with an absorption feature around 450 nm (attributed to nitro-phenols) hump was observed for water extracts.

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

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

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

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

Page 17, Line 451-456: "As mentioned above, the real fractions of polar and nonpolar BrC contributing to the mass/absorption of BBOA are undefined, some investigations report that the polar BrC dominate the tar balls' mass (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 the climatic impacts of biomass burning related BrC aerosol, when their chemical composition is classified."

Reference

Asa-Awuku, A., Sullivan, A., Hennigan, C., Weber, R., and Nenes, A.: Investigation of molar volume and surfactant characteristics of water-soluble organic compounds in biomass burning aerosol, Atmos. Chem. Phys., 8, 799-812, doi:10.5194/acp-8-799-2008, 2008.

Bluvshtein, N.; Lin, P.; Flores, J. M.; Segev, L.; Mazar, Y.; Tas, E.; Snider, G.; Weagle, C.; Brown, S. S.; Laskin, A., Broadband optical properties of biomass‐burning aerosol and identification of brown carbon chromophores. J. Geophys. Res. Atmos., 122, 5441-5456, doi:10.1002/2016JD026230, 2017.

Chen, Y., and Bond, T.: Light absorption by organic carbon from wood combustion, Atmos. Chem. Phys., 10, 1773-1787, doi:10.5194/acp-10-1773-2010, 2010.

Lin, P., Bluvshtein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event, Environ. Sci. Technol., 51, 11561-11570, doi:10.1021/acs.est.7b02276, 2017.

Lin, P.; Fleming, L. T.; Nizkorodov, S. A.; Laskin, J.; Laskin, A., Comprehensive Molecular Characterization of Atmospheric Brown Carbon by High Resolution Mass Spectrometry with Electrospray and Atmospheric Pressure Photoionization. Anal. Chem., 90, 12439-12502, doi:10.1021/acs.analchem.8b02177, 2018.

Rajput, P., and Sarin, M.: Polar and non-polar organic aerosols from large-scale agricultural-waste burning emissions in Northern India: implications to organic mass-to-organic carbon ratio, Chemosphere, 103, 74-79, doi:10.1016/j.chemosphere.2013.11.028, 2014.

Sengupta, D., Samburova, V., Bhattarai, C., Kirillova, E., Mazzoleni, L., Iaukea-Lum, M., Watts, A., Moosmüller, H., and Khlystov, A.: Light absorption by polar and non-polar aerosol compounds from laboratory biomass combustion, Atmos. Chem. Phys., 18, 10849-10867, doi:10.5194/acp-18-10849-2018, 2018.

Sumlin, B. J., Pandey, A., Walker, M. J., Pattison, R. S., Williams, B. J., and Chakrabarty, R. K.: Atmospheric Photooxidation Diminishes Light Absorption by Primary Brown Carbon Aerosol from Biomass Burning, Environ. Sci. Technol. Lett., 4, 540-545, doi:10.1021/acs.estlett.7b00393, 2017.