Interactive comment on **"Dynamic changes of optical and chemical properties of tar ball aerosols by atmospheric photochemical aging"** ***by Li et al.***

Li et al.

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Anonymous Referee #1: Generally speaking, this is an interesting paper where 'tar ball aerosol particles' were produced and photochemically aged in an OFR. I am not sure whether tar balls in atmospheric aerosol particles are an important topic. As they are mentioned in the title, the reader expects tar balls to be central for this paper, but it seems to me, the real topic of the paper is BrC formed after wood combustion, and tar balls have been identified with that BrC. Maybe the authors can straighten this out with regard to the title and the focus of the introductory text part. The specific tar ball aerosol generation is interesting. However, this is a laboratory method to obtain as much as possible tar balls in the generated aerosols. How realistic is this aerosol for the environment? I wonder if some key parameters of the 'tar ball aerosol' generated in the lab should be given in the experimental, or, at the latest, early in the results section: Give the particle size distribution, give a rough chemical composition, OC/EC, WSOC, weight fraction of tar balls. Do these particles still contain inorganic constituents? How much?

When this is not done, the reader starts into the results section without knowledge about what has actually been generated and is now undergoing heterogeneous oxidation in the OFR. Much of this information is available, but scatter through the manuscript. I would strongly recommend to introduce a section 'Initial tar ball aerosol characteristics after generation'. Maybe the chemical information and the optical measurement results should be separated. Overall, the manuscript call for a better organization. The obtained results are interesting but their atmospheric relevance should be discussed in view of realistic fraction of tar balls over EC or over OC. Some statements in the conclusion section are very broad , line 676 ff.

Authors' reply: We appreciate the Reviewer's general comments. Tar balls are abundant carbonaceous particles produced by incomplete burning of biofuels. Tar balls contribute a significant number concentration and mass loading in fire emissions. These ubiquitous particles have strong absorption and present potential light absorption across the entire solar spectrum. Due to the strong absorption and high concentrations, they can alter local photochemistry and perturb the radiative balance in the atmosphere on regional and global scales (Pósfai et al., 2004; Hand et al., 2005; Alexander et al., 2008; Chen et al., 2017; Sedlacek III et al., 2018). In ambient 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).

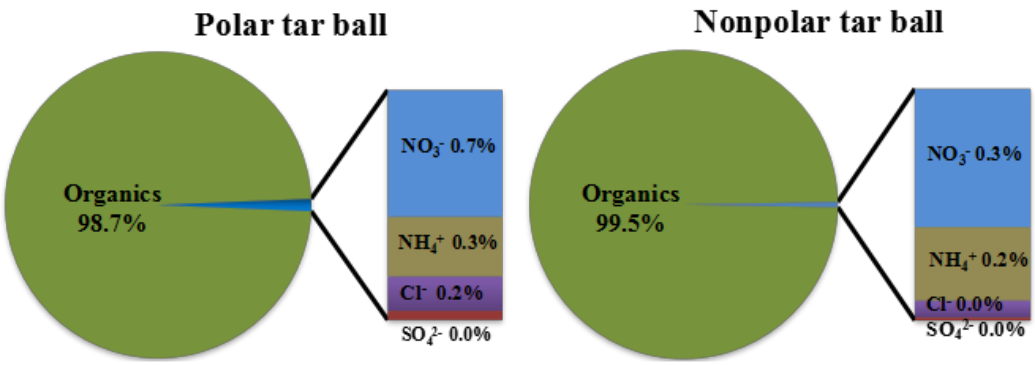


Figure R1. Chemical composition of polar and nonpolar tar ball aerosols obtained from AMS measurement

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

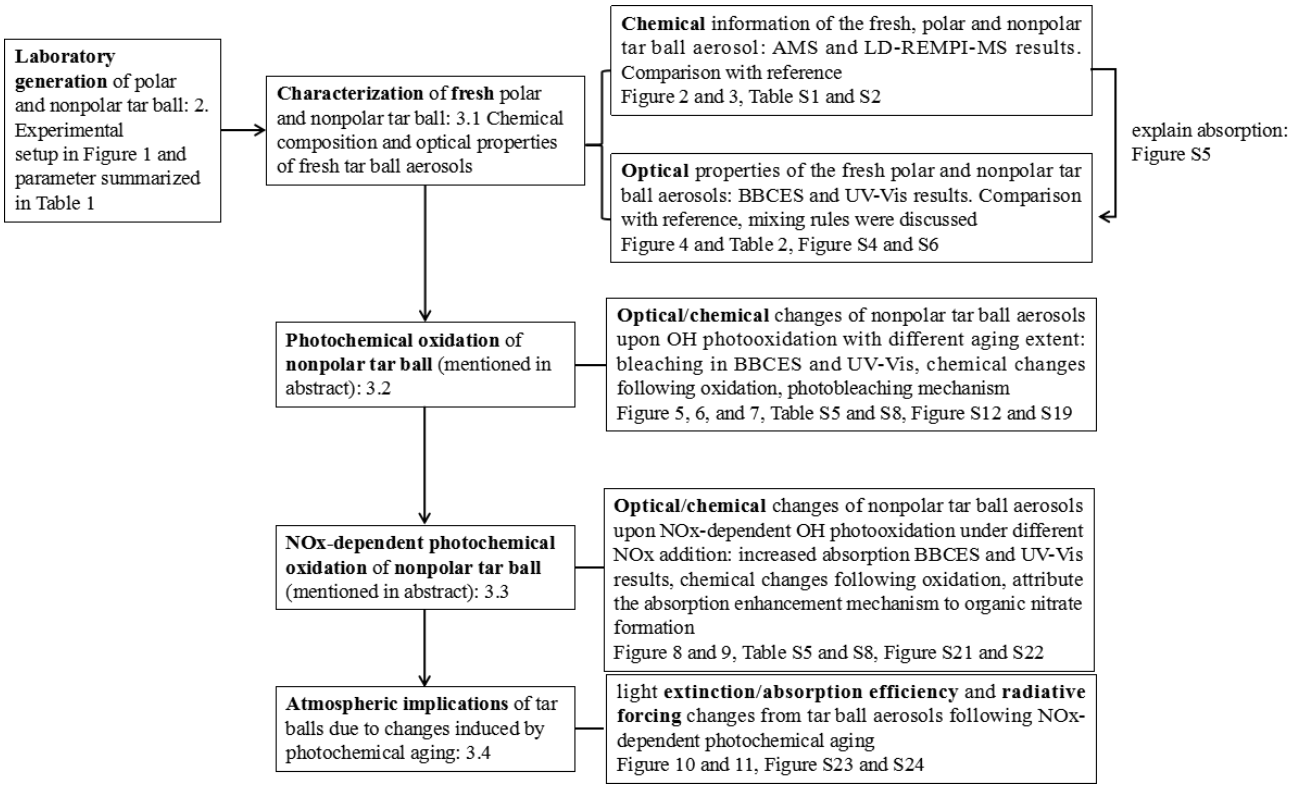
Tar ball Carbon (μg cm^{-2})	OC1	OC2	OC3	OC4	PC	EC1	EC2	EC3	OC	EC
Polar	7.3	6.1	3.5	0.0	2.0	2.0	0.0	0.0	18.9	0.0
Nonpolar	10.8	9.6	6.0	2.9	7.9	8.1	0.1	0.0	37.2	0.3

Note: OC1, OC2, OC3, OC4 are four organic fractions determined at 140, 280, 480, and 580 °C pyrolysis temperatures, respectively, in a helium (He) atmosphere. EC1, EC2, and EC3 are three EC fractions being oxidized at 580, 740, and 840 °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

values at some discrete wavelength and the spectral-dependence trends of the RI further justify the use of the laboratory-generated tar balls for studying the optical and chemical behavior of ambient tar ball and/or BBOA in atmospheric process. The RI of tar balls were retrieved based on Mie-Lorenz scattering theory from size- and wavelength-resolved extinction cross section measurements of 200~350 nm tar ball aerosols (see the method in manuscript and tar ball size distribution in Figure S1, SI).

This manuscript focuses on the changes in absorption by tar ball aerosols upon photochemical aging. It was found that OH oxidation bleached the tar balls by depleting of absorbing moieties, while addition of NOx during aging inhibited the bleaching and even restored the absorption of tar balls by forming nitrogen-containing functional groups. The changes in the broadband optical properties of the tar balls under different oxidation conditions are presented in the paper, and the chemical mechanisms attributing to the optical changes were discussed. The entire manuscript follows the following scheme:



To summarize: this study probed for the first time changes in the optical and chemical properties of proxies for tar ball aerosols due to OH radical aging with different oxidation extent from 0.7 to 6.7 atmospheric equivalent days in the presence/absence of NOx. We also assessed pristine photolysis under different photon fluxes and O_3 oxidation of tar balls in the OFR. Finally the atmospheric and climatic implications of tar balls were discussed using a simple radiative transfer model.

The particulate inorganic and OC-EC composition have been discussed and added in the manuscript and in the supporting information:

Page 11, Line 272 in manuscript: "as no other refractory elemental carbon (EC) content was detected in our samples with a thermal-optical analysis method (details see in SI)."

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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