Supporting information:

**Laboratory insights into the diel cycle of optical and chemical transformations of biomass burning brown carbon aerosol**

Chunlin Li, a Quanfu He, a Zheng Fang, a Steven S. Brown, b, e Alexander Laskin, d Sidney R. Cohen, e

Yinon Rudich a, ⁎

a Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 76100, Israel
b NOAA Chemical Sciences Laboratory, Boulder, Colorado 80305, United States
c Department of Chemistry, University of Colorado, Boulder, Colorado 80309-0215, United States
d Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States
e Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

Correspondence to: Yinon Rudich (yinon.rudich@weizmann.ac.il)
Contents

1. Experimental setup and parameters:
   Figure S1 & Table S1

2. Box-model simulations of heterogeneous reactions for O$_3$ and NO$_3$• in the AFR:
   Figure S2-S3 & Table S2-S3

3. Determination of equivalent ambient photolysis time in the PAM-OFR:
   Figure S4 & Table S4-S5

4. Detailed size distribution and AMS results for fresh and processed wood tar aerosols:
   Figure S5-S6 & Table S6

5. Particulate organic nitrate and absorption lifetime estimation for NO$_3$•-aged wood tar aerosol:
   Figure S7

Rest:

Figure S8-S14 & Table S7

Total 5 Sections, 14 Figures, 7 Tables.
1. Experimental setup and parameters

Figure S1. Experimental setup for aging experiments with laboratory-generated wood tar aerosol used as proxy for biomass BrC. The schematic setup shows the aerosol generation, O$_3$/NO$_3$• oxidation in an aerosol flow tube reactor (AFR), OH• photochemical oxidation in a potential aerosol mass oxidation flow reactor (PAM-OFR), instruments for chemical and optical characterization of the unprocessed and aged BrC particles.
Table S1. Experimental parameters in the AFR and the PAM-OFR study of wood tar aerosol

| Experiment | AFR | PAM-OFR |
|------------|-----|---------|
|            | NO (ppmv) | O₃ (ppmv) | RT (s) | O₃ (ppmv) | RH (%) | RT (s) | Photon flux exposure (photon cm⁻²) | OHexp (molec cm⁻³ s⁻¹) |
| 1          | --- | --- | 300 | --- | --- | 190 | --- | --- |
| 2          | --- | 5.16±0.10 | 300 | --- | --- | 190 | --- | --- |
| 3          | 3.0 | 5.16±0.10 | 300 | --- | --- | 190 | --- | --- |
| 4          | 3.0 | 5.16±0.10 | 300 | 33.1±0.4 | 35.2±0.4 | 190 | 8.5×10¹⁵ | (1.3±0.5)×10¹¹ |
| 5          | 3.0 | 5.16±0.10 | 300 | 33.1±0.4 | 35.2±0.4 | 190 | 4.2×10¹⁶ | (5.7±0.8)×10¹¹ |
| 6          | 3.0 | 5.16±0.10 | 300 | 33.1±0.4 | 35.2±0.4 | 190 | 9.3×10¹⁶ | (9.3±0.5)×10¹¹ |
| 7          | 3.0 | 5.16±0.10 | 300 | --- | 35.2±0.4 | 190 | 8.5×10¹⁵ | --- |
| 8          | 3.0 | 5.16±0.10 | 300 | --- | 35.2±0.4 | 190 | 9.3×10¹⁶ | --- |

Note: Experiment 1 characterized fresh particles. Experiment 2-3 investigated nighttime aging of wood tar particles with respect to O₃ and NO₃ radical reactions, respectively. Experiment 4-6 explored OH radical dominated photochemical aging of nighttime aged particles, corresponding to EAD-1.0 to EAD-7.2. Experiment 7-8 studied the UV-light induced photolysis of the nighttime aged particles for Weak and Strong photolysis, respectively.
2. Box-model simulations of heterogeneous reactions for O$_3$ and NO$_3$ radical in the AFR

Detailed information on the chemical box model development and simulation can be found in our previous publication.$^1$ In this experiment, the NO$_3$• was generated online via reaction between O$_3$ and NO rather than by thermo-decomposition of gaseous N$_2$O$_5$. O$_3$ and NO were premixed in the long Teflon tube Reactor (Length: 650 cm, I.D.: 1.4 cm) before entering the connected AFR (Length: 165 cm, I.D.: 10.5 cm) where the wood tar aerosol was introduced. The reactions to generate NO$_3$• in the Teflon tube reactor mainly include:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \quad \text{R1}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad k = 3.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \quad \text{R2}$$

$$NO_2 + NO_3 \leftrightarrow N_2O_5 \quad k_{eq}(T) = 2.7 \times 10^{-27} \times e^{11000/7} \quad \text{R3}$$

In the AFR, wood tar aerosol reacted simultaneously with O$_3$, NO$_3$•, and N$_2$O$_5$ in the presence of O$_2$ and NO$_2$. The overall sink of these oxidants in the experiment can be described by the pseudo-first-order loss to the particle surface and to the wall of the AFR via Equation 1 to 3:

$$\frac{d[G]}{dt} = -(k_p[G] + k_w[G]) \quad \text{Eq.1}$$

$$k_p = \frac{\gamma_{eff} \times \omega \times S}{4} = \frac{1}{4} \omega \times S \times \left( \frac{1}{\gamma_p} + \frac{1}{\Gamma_{diff-p}} \right)^{-1} \quad \text{Eq.2}$$

$$k_w = \frac{\gamma_{eff} \times \omega \times S_{AFR}}{4 \times V_{AFR}} = \frac{\omega}{D_{in}} \times \left( \frac{1}{\gamma_w} + \frac{1}{\Gamma_{diff-w}} \right)^{-1} \quad \text{Eq.3}$$

Where $k_p$ and $k_w$ are pseudo-first order loss rates to the particles’ surface and to the reactor inner wall, respectively. $\gamma_{eff}$ is effective uptake coefficient (unitless) for gas G, such as O$_3$, NO$_3$•, NO$_2$, and N$_2$O$_5$. $\omega$ (m s$^{-1}$) is molecular speed of gas G. $S$ is the total particle surface area exposed to reactant (nm$^2$ cm$^{-3}$). $S_{AFR}$ and $V_{AFR}$ are inner surface area and volume of the reactor. $D_{in}$ is the inner diameter of the cylindrical flow reactor we used, that equals to 105 mm. $\gamma_p$ and $\gamma_w$ are uptake coefficient (unitless) to the particulate surface and to the AFR inner wall, respectively. $\Gamma_{diff}$ describes the gas phase diffusion limitation (unitless) in the surface uptake by particles and reactor inner wall. For the uptake onto monodisperse spherical particles, several methods have been suggested to calculate $\Gamma_{diff-p}$. The regular method is described as the Fuchs-Sutugin Equation:

$$\Gamma_{diff-p} = \frac{0.75 + 0.286 \times Kn}{Kn \times (Kn + 1)} \quad \text{Eq.4}$$

Where $Kn$ is Knudsen number, given by Equation 5:

$$Kn = \frac{6D}{\omega \times D_p} \quad \text{Eq.5}$$

The Knudsen number, $Kn$, is a function of particle diameter ($D_p$, nm), gas-phase diffusion coefficient ($D$, torr cm$^2$ s$^{-1}$) for gas G, and molecular speed $\omega$. For fast uptake process (lower $\Gamma_{diff}$ and higher $\gamma$) and large particles, gas phase diffusion can limit the overall uptake rate of G onto the particle surface. For heterogeneous reactions with the polydisperse particles, the
above first-order reaction kinetic \( k_p \) in Equation 2 should be modified as Equation 6, taking the first-order wall loss of the particles into account, that is the integrated result for each size of particle:

\[
k_p = \frac{1}{4} \omega \times \sum \left[ N_i \times \pi \times D_i^2 \times (1 - k_{\text{wall},i} \cdot t) \times \left( \frac{1}{\gamma_p} + \frac{1}{\Gamma_{\text{diff},p}} \right)^{-1} \right]
\]

\[\text{Eq. 6}\]

Where \( N_i \) is number concentration (\( \text{cm}^{-3} \)) for particle of size \( D_i \) (nm), \( k_{\text{wall},p} \) is first-order wall loss rate (s\(^{-1} \)) for the particles.

In our experiments, the wall loss rate for wood tar particles through the AFR can be neglected according to the CPC and SMPS measurements, thus, Equation 6 can be simplified:

\[
k_p = \frac{1}{4} \omega \times \sum \left[ N_i \times \pi \times D_i^2 \times (1 - k_{\text{wall},i} \cdot t) \times \left( \frac{1}{\gamma_p} + \frac{1}{\Gamma_{\text{diff},p}} \right)^{-1} \right]
\]

\[\text{Eq. 7}\]

\( \Gamma_{\text{diff},w} \) describes wall loss of \( \text{O}_3 \), \( \text{NO}_3 \), \( \text{NO}_2 \), and \( \text{N}_2\text{O}_5 \) to the AFR, as suggested in Equation 8:

\[
\frac{1}{\Gamma_{\text{diff},w}} = \frac{\omega \times D_{\text{int}}}{4 \times 3.66 \times D}
\]

\[\text{Eq. 8}\]

For the case where the loss rates of the gases to the reactor wall is not determined by surface reactivity, but by the diffusion through the gas phase (\( \gamma_p > \Gamma_{\text{wall}} \approx 7 \times 10^{-6} \)), the following expression holds:

\[
k_w = \frac{\omega \times D_{\text{int}}}{\gamma_w} \times \left( \frac{1}{\Gamma_{\text{diff},w}} + \frac{1}{\gamma_p} \right)^{-1} \approx \frac{\omega \times D_{\text{int}}}{\Gamma_{\text{diff},w}} \times \frac{4 \times 3.66 \times D}{D_{\text{int}}^2}
\]

\[\text{Eq. 9}\]

Equation 9 is valid for Peclet numbers in excess of \( \sim 20 \). Diffusion coefficients were cited as 92±46, 65±33, 106±37 Torr cm\(^2\) s\(^{-1} \) for \( \text{NO}_3 \), \( \text{N}_2\text{O}_5 \) and \( \text{NO}_2 \) in air/N\(_2\) environment (1 atm and 296.6 K), respectively.\(^7\) \( \text{O}_3 \) diffusivity in the air was estimated to be one fourth of that in He, and it was about 102±6 Torr cm\(^2\) s\(^{-1} \).\(^7\) This study results in Peclet numbers of about 48, 67, and 41 for \( \text{NO}_3 \), \( \text{N}_2\text{O}_5 \), and \( \text{NO}_2 \), respectively. Based on Equation 9, the pseudo-first-order wall loss rates were estimated as \( (1.64\pm0.82)\times10^{-2} \), \( (1.16\pm0.58)\times10^{-2} \), and \( (1.89\pm0.66)\times10^{-2} \) s\(^{-1} \) for \( \text{NO}_3 \), \( \text{N}_2\text{O}_5 \), and \( \text{NO}_2 \), respectively. \( \text{O}_3 \) loss to the AFR wall can be measured directly using the \( \text{O}_3 \) analyzer (2B Technology, Model 650L), we did not observe significant wall loss of \( \text{O}_3 \) within detection resolution of the \( \text{O}_3 \) analyzer. Thereby, the wall loss rate of \( \text{O}_3 \) in our AFR is less than \( 10^{-4} \) s\(^{-1} \).

The reactive uptake coefficient (\( \gamma \)) depends on the type of surface, the gaseous reactant, and many environmental parameters.\(^2,3\) To biomass burning related aerosols, \( \text{NO}_3 \) uptake by the particle-phase surface can be \( \sim 3 \) orders of magnitude higher than those of \( \text{NO}_2 \) and \( \text{N}_2\text{O}_5 \).\(^8,9\) We collected the reactive uptake coefficients and applied the average values of \( (9.87\pm7.53)\times10^{-6} \), \( (1.1\pm0.2)\times10^{-2} \), \( (6.1\pm1.82)\times10^{-5} \), and \( (6.73\pm2.36)\times10^{-7} \) for \( \text{O}_3 \), \( \text{NO}_3 \), \( \text{N}_2\text{O}_5 \), and \( \text{NO}_2 \) onto wood tar aerosols, respectively.\(^10,11\)

The size distribution and concentration of fresh, \( \text{O}_3 \) and \( \text{NO}_3 \) aged wood tar aerosols were measured and are displayed in Figure S2. We did not observe significant size distribution change for wood tar aerosol due to \( \text{O}_3 \) oxidation, while the surface and volume concentration for the wood tar aerosols increased by 24% and 31%, respectively, after \( \text{NO}_3 \) aging. The results demonstrate secondary aerosol formation from \( \text{NO}_3 \) reactions, as a result, the equation 2 and 7 need to be modified regarding to the varied particle distributions. To make the model simple, we assumed that the particle surface area concentration increased linearly with reaction time through the AFR for \( \text{NO}_3 \)-aged wood tar aerosols, in short, the particle surface area can be described by Equation 10:

\[
S_t = S_0 + \kappa_s \times S_0 \times t
\]

\[\text{Eq. 10}\]
Where $S_0$ indicates the initial particle surface area concentration (unit: nm$^2$ cm$^{-3}$), $k_s$ (unit: s$^{-1}$) simply describes the growth rate of particle surface area. Given that the surface area concentration increased by 24.4% in residence time of 298.2 s, $k_s$ was estimated to be $4.17 \times 10^{-3}$ s$^{-1}$. The growth of particle surface area implies changes in the reactive surface uptake rates ($k_p$ in Equation 7) in the AFR. To make the model feasible, a particle surface area concentration weighted surface uptake rate was proposed, the first-order kinetic of surface uptake in Equation 7 was then modified as pseud-second-order kinetic ($\kappa_p$) in following Equation 11:

$$\kappa_p = \frac{1}{t} \times \omega \times \sum [N_i \times \pi \times D_i^2 \times \left(\frac{1}{f_p} + \frac{1}{f_{diff-p}}\right)^{-1}] \times \frac{1}{\sum (N_i \times \pi \times D_i^2)}$$

We found that $\kappa_p$ was not sensitive to the minor size changes of the wood tar particles in reactions, suggesting that we can keep $\kappa_p$ constant in all reactions.

The gas loss to the particles and the reactor wall can be described by Equation 12:

$$\frac{d[G]}{dt} = - (\kappa_p \times [G] \times S_t + \kappa_\omega \times [G])$$

Eq.12

According to the above equations and parameters summarized from the literature, the first-order wall loss rate of the gaseous species and second-order surface uptake rates of these gaseous oxidants are presented in Table S2.

**Table S2.** Summarized kinetics for gaseous oxidants loss to particle surface and reactor wall

| Gas     | Pseudo-second-order uptake rate (cm$^3$ nm$^{-2}$ s$^{-1}$) | Wall loss rate (s$^{-1}$) |
|---------|-----------------------------------------------------------|---------------------------|
| O$_3$   | $(8.93 \pm 6.81) \times 10^{-16}$                         | $\leq 1 \times 10^{-4}$   |
| NO$_3^•$| $(8.71 \pm 1.61) \times 10^{-13}$                         | $(1.61 \pm 0.80) \times 10^{-2}$ |
| N$_2$O$_5$ | $(3.68 \pm 1.10) \times 10^{-15}$                        | $(1.14 \pm 0.57) \times 10^{-2}$ |
| NO$_2$  | $(6.22 \pm 2.18) \times 10^{-17}$                         | $(1.85 \pm 0.65) \times 10^{-2}$ |
Acetonitrile was used as a solvent to dissolve the wood tar in the atomizer. Although sufficient charcoal denuders were applied downstream of the aerosolization to remove the outgas, residual acetonitrile in that gas phase may still be involved in competitive reactions with NO$_3^•$ in the AFR. We assumed that each denuder has filtration efficiency of 80%, the residual gaseous acetonitrile in the AFR can get to $\sim$5.26×10$^{13}$ molec cm$^-3$ (296 K and 1 atm).$^{12,13}$ Applying the above simplified kinetic parameters, a chemical box model including gaseous NO$_3^•$ formation and gaseous oxidants uptake by wood tar particles and reactor wall was initialized using the COPASI software (complex pathway simulator, http://copasi.org/), and the result is displayed in Figure S3.

![Figure S3](image)

Figure S3. Chemical box model simulation of NO$_3^•$ and N$_2$O$_5$ productions in O$_3$-NO reactions and their heterogeneous reactions with wood tar particles through the AFR, only quasi first-order surface uptakes by particle and reactor inner wall were considered to simplify the sensitivity tests. Dashed lines indicate the variation and production of gaseous pollutants, the solid lines tell the particle uptaked oxidants as a function of reaction time in the AFR.

Based on chemical box model simulation, it was found that NO$_3^•$ uptake by wood tar particle was about one magnitude order higher than that of N$_2$O$_5$ and O$_3$, demonstrating that the NO$_3^•$ reaction is the dominate reaction pathway to oxidize wood tar aerosol. To prove the practical significance of the result, wood tar aerosol aging due to NO$_3^•$ in the laboratory was compared with outdoor nighttime aging of smoke aerosol by NO$_3^•$ in field plume, and the aging content was quantified to equivalent aging time at night (EAN, unit: hour) for ambient biomass burning aerosols. The detailed quantification method can be found in our previous study.$^1$ The surface uptake of NO$_3^•$ and N$_2$O$_5$ was first normalized to the wood tar particle surface area concentration:
Where $[NO_3]_{up}$ and $[N_2O_5]_{up}$ are NO$_3^*$ and N$_2$O$_5$ incorporated into the wood tar particles, respectively. $S$ is average wood tar particle surface area concentration.

In ambient biomass burning plume, we assume an equilibrium of NO$_3^*$ with NO$_2$-O$_3$ reaction as source and sink of VOCs dominated gaseous reactions and primary smoke aerosol uptake. The dynamic NO$_3^*$ concentration can be described as follow equation:

$$K_{NO_2-O_3} \times [NO_2] \times [O_3] = \sum_i K_{NO_3-VOCi} \times [NO_3] \times [VOC_i] + K_{NO_3} \times [NO_3]$$

$$K_{NO_3} = K_{eq} \times [NO_2] \times K_{aerosol-NO_2} + K_{aerosol-NO_3}$$

Equation 14 depicts NO$_3^*$ fate in smoke emissions, left part is NO$_3^*$ generation and right part consists of homogeneous reactions with VOCs and heterogeneous uptake by particles. We attributed surface uptake of N$_2$O$_5$ to NO$_3^*$ heterogeneous sink in Equation 15. According to Decker et al. and Brown et al.,$^{14,15}$ gas phase reactions with VOCs are the dominant sink of NO$_3^*$ compared to particle phase uptake, and sink of NO$_3^*$ due to homogeneous reactions can be a factor of 100-1000 greater than that by particle surface uptake. But, considering the rapid aging and dilution of VOCs and also smoke particle growth due to condensation and coagulation during biomass burning emissions transport, the NO$_3^*$ reactivity due to surface uptake should weigh more in the total reactivity with fire plume transporting. Here, we followed the same method proposed in our previous study (SI, Text S6.2)$^1$ and assumed a median and constant ratio of 500 for total NO$_3^*$ reactivity to smoke particle uptake. That is:

$$\sum_i K_{NO_3-VOCi} \times [NO_3] \times [VOC_i] + K_{NO_3} \times [NO_3] \approx 500 \times K_{aerosol} \times [NO_3]$$

$$K_{NO_2-O_3} \times [NO_2] \times [O_3] = 500 \times K_{aerosol} \times [NO_3]$$

Based on Equation 17, the NO$_3^*$ sink rate to the particles can be estimated, and it was then normalized to the surface area concentration as below:

$$R_{NO_3} = \frac{K_{aerosol} \times [NO_3]}{S_{aerosol}} = \frac{K_{NO_2-O_3} \times [NO_2] \times [O_3]}{500 \times S_{aerosol}}$$

Where $S_{aerosol}$ is field smoke particle surface area concentration in biomass burning plume. Combining Equation 13 and Equation 18, the equivalent ambient nighttime aging time ($EAN$) due to NO$_3^*$ can be assessed for laboratory aged wood tar aerosol in Equation 19:

$$EAN = \frac{P_{NO_3}}{R_{NO_3}} = \frac{P_{NO_3} \times 500 \times S_{aerosol}}{K_{NO_2-O_3} \times [NO_2] \times [O_3]}$$

In this study, the typical ambient NO$_2$, O$_3$, and smoke particle surface density were taken as 25 ppbv, 35 ppbv, and 2×10$^8$ nm$^2$ cm$^{-3}$, respectively, referring to reference and also our previous work.$^{1,14,16}$ The estimated $EAN$ under such condition were estimated to be 20.7±5.8 h for wood tar particles in the AFR experiment. In addition to the above quantification method, NO$_3^*$ exposure ($[NO_3]_{exp}$, molec cm$^{-3}$ s) can also be used to assess aging degree of wood tar aerosol:

$$[NO_3]_{exp} = \int_0^{RT} [NO_3] dt$$
From the results of chemical box model simulation in Figure S2, NO$_3^\bullet$ exposure was estimated as $(2.74\pm0.62)\times10^{15}$ molec cm$^{-3}$ s$^{-1}$. In the field, NO$_3^\bullet$ concentration has large variation from several to hundreds pptv level, and its concentration depends on the air pollution and environment conditions. In field fire plume, although the NO$_3^\bullet$ can be ultralow, it has a rapid formation rate up to ppbv h$^{-1}$ level. Referring to a previous study on ambient nitrate radical chemistry as summarized in Table S3, the typical mixing ratio of NO$_3^\bullet$ was taken as 20 pptv at night (1 atm and 296 K). Then the equivalent ambient nighttime aging due to NO$_3^\bullet$ reaction can be estimated via Equation 21:

$$EAN = \frac{[NO_3]^\text{exp}}{[NO_3]} \quad \text{Eq. 21}$$

**Table S3.** Summarized ambient NO$_3^\bullet$ concentration in outdoor environment.

| NO$_3$ radical concentration (pptv) | Technique and detection limit (pptv) | Research Environment | Reference$^{14, 15, 19-24}$ |
|-----------------------------------|--------------------------------------|----------------------|-----------------------------|
| 10-30                             | CRDS (0.5)                           | field                | Gaffney et al., 2002        |
| 3-400                             | CRDS (0.5)                           | field campaign       | Decker et al., 2019         |
| 0-200                             | LP-DOAS                              | PARADE campaign (mountains) | Sobanski et al., 2017 |
| 27.3-70                           | LP-DOAS (8.5)                        | field, Jerusalem, Palestine | Asaf et al., 2010          |
| 0-400                             | CRDS (0.5)                           | TexAQS campaign      | Brown et al., 2011b         |
| 20-40                             | CRDS (1.0)                           | Taunus Observatory, Germany | Crowley et al., 2010a |
| 21.8 ± 1.8                        | DOAS (3.6)                           | Guangzhou, China     | Li et al., 2012             |
| 0-149                             | DOAS (3)                             | Houston, US          | Stutz et al., 2010          |

Note: LP-DOAS is long path differential optical absorption spectroscopy, IBBCEAS is incoherent broadband cavity-enhanced absorption spectroscopy. CRDS is cavity-ring down spectroscopy.

Based on the simulated NO$_3^\bullet$ exposure in the AFR and ambient typical NO$_3^\bullet$ concentration of 20 pptv, the $EAN$ was calculated to be $15.6\pm3.5$ h, which is on the low end of the $EAN$ (20.7±5.8 h) quantified based on particle surface uptake method. In short, the wood tar aerosol aging via NO$_3^\bullet$ in the AFR should be comparable with the field smoke aerosol aging in biomass burning plume at night, demonstrating the environmental significance of the study.
3. Equivalent ambient photolysis time in the PAM-OFR

The low-pressure mercury lamp (254nm characteristic irradiation) in the PAM-OFR does not replicate the ambient solar spectrum, but is intended rather as an efficient OH source via O₃ photolysis and further reaction with water vapor. Here, we use the photolysis effect in the PAM-OFR to estimate equivalent ambient solar irradiation by normalizing the integrated photolysis rates for some nitroaromatic proxies that have been measured with high abundance in the nitrated wood tar aerosols and ambient BB-BrC, including 2-nitrophenol (2-NP), 4-nitrocatechol (4-NC), 2,4-dinitrophenol (2,4-DNP), 4-nitroguaiacol (4-NG), and 2-nitrobenzaldehyde (2-NBA).¹²⁵,²⁶ The photolysis rate constant of specific compound was calculated using the following equation:

\[ J = \sum \sigma(\lambda) \cdot \phi(\lambda) \cdot F(\lambda) \cdot d\lambda \]

Eq.22

Where \( F(\lambda) \) denotes the light flux (photon cm\(^{-2}\) s\(^{-1}\)), such as the ambient solar actinic flux and the photon flux in the PAM-OFR. The \( F(\lambda) \) for solar actinic flux also depends on zenith angle and altitude. \( \sigma(\lambda) \) and \( \phi(\lambda) \) represent absorption cross sections (cm\(^2\) molecule\(^{-1}\)) and photolysis quantum yield (molecule photon\(^{-1}\)) of target species, respectively. Based on the photolysis rates, the equivalent ambient photolysis time, \( t_{atm} \), can be estimated as:

\[ t_{atm} = \frac{J_{OFR}}{J_{atm}} \times RT \]

Eq.23

Where \( J_{OFR} \) and \( J_{atm} \) are photolysis rates for the PAM-OFR and ambient conditions, and RT (187 s) is the residence time for target species passing through the PAM-OFR. The integrated 254 nm photon flux exposures in the PAM-OFR during experiments were estimated based on OHexp traced by SO₂ decay and OHexp photochemical modeling.²⁷-²⁹ Light spectra in the PAM-OFR was recorded by a spectrometer (Ocean Optics, Model USB650), which was used to calculate the photon flux at other wavelengths. The 24 h averaged solar actinic flux was acquired using the Tropospheric Ultraviolet and Visible (TUV) model from the National Center for Atmospheric Research (NCAR, http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/), the summertime (June 30\(^{th}\), 2019) solar actinic flux was for 0-80° zenith angles at cloudless condition and at ground level with an albedo of 0.19.³⁰

The molecular absorption cross sections for nitroaromatic compounds depend on their phase states and particle surface environment and liquid acidity, and the reported absorption cross sections for 2-NP have large variance between different studies.³¹-³³ In this estimation, we applied the absorption cross sections for both gaseous and particle-bound, specifically azelaic acid particle-adsorbed, 2-nitrophenol from Hinrichs et al.³² There is a lack of comprehensive gaseous or particle-bound absorption cross sections for 2,4-DNP, 4-NC and 4-NG, therefore, we have to cite their absorbing results in aqueous phase. Only absorption cross sections for pronated nitrophenols were considered,³² because these nitrophenols should stay in molecular state in the organic aerosol. 2-NBA is commonly used as chemical actinometer to determine photon flux in laboratory photochemical study.³⁴,³⁵ The continuous-wavelength resolved gaseous and methanol-dissolved absorption cross sections for 2-NBA were considered in the model.³⁶,³⁷ The absorption cross sections for the selected nitroaromatic proxies and photon flux for the PAM-OFR lamp and ambient solar irradiation as a function of the zenith angle were displayed in Figure S4.

Both HONO and OH radical productions have been detected in the near UV photolysis of 2-NP in the liquid and gas phases.³³,³⁸-⁴¹ But the HONO and OH quantum yields from the photodissociation of 2-nitrophenol and the variation of the quantum yields with excitation wavelength are rarely updated, the limited product quantum yields present larger variance. Chen et al. recalculated the overall HONO quantum yield in photodissociation of gaseous 2-nitrophenol to be 1.15×10⁻³.
upon irradiation by 320-450 nm light ($\lambda_{\text{max}}=370\text{nm}$). Sangwan and Zhu measured the OH quantum yield to be 0.69 at 308 nm and 0.70 at 351 nm, while the HONO quantum yields from laser-induced 2-nitrophenil photolysis to be 0.34 at 308 nm and 0.39 at 351 nm. The HCO radical formation and NO$_2$ formation represents two vital channels occur in photolysis of 2-NBA, and 0.5 was recommended as the photolysis quantum yield in photodissociation of 2-NBA in gas, aqueous, and solid states by the near-UV irradiation. Albinet et al. measured an ultralow photolysis rate for 2,4-DNP in solution that was irradiated by 300-500 nm Xenon lamp, the calculated quantum yield was influenced by the acidity of the solution, and it was in the range of $(3.4-8.1)\times10^{-5}$. The photolysis quantum yield for 4-NC and 4-NG is not available, we applied the quantum yield of 2-NP for these analogous nitrophenols. Moreover, we assumed these nitroaromatic proxies have high quantum yield around 250 nm, thereby, unity of photolysis quantum yield was assigned for the 250-280/290nm range. The quantum yields for these proxies and applied in this modeling were summarized in Table S4.

The final equivalent ambient photolysis times corresponding to the high UV exposure ($9.30\times10^{16}\text{photon cm}^{-2}$) in the PAM-OFR were calculated and summarized in Table S5, it is clear the photolysis time varies with different nitroaromatic compounds and with the ambient solar irradiation, or the Solar Zenith Angle (SZA). The average equivalent ambient photolysis time over the proxies and the SZA is estimated as $2.49\pm1.55\text{h}$ (1σ) corresponding to the high UV exposure in the PAM-OFR for the nitrated wood tar aerosol, while the equivalent ambient photolysis time was $0.34\pm0.29\text{h}$ for low UV exposure in the PAM-OFR.

**Figure S4.** Determination of equivalent ambient photolysis time in the PAM-OFR. (A) the PAM-OFR photon flux (strong UV exposure condition) vs. the solar actinic flux as a function of the zenith angle. (B) absorption cross sections as a function of wavelength for 2-nitrophenol (2-NP) in both gas and particle phases. (C) absorption cross sections for protonated and deprotonated 2,4-dinitrophenol (2,4-DNP), 4-nitrocatechol (4-NC), and 4-nitroguaiacol (4-NG) in aqueous phase. (D) absorption cross sections for 2-nitrobenzaldehyde (2-NBA) in gas phase and dissolved in methanol.
Table S4. Photolysis quantum yield for nitroaromatic compounds and the values applied in the modeling

| Proxy                        | Quantum yield                                                                 | Reference                                   | Quantum yield applied in this model                             |
|------------------------------|-------------------------------------------------------------------------------|---------------------------------------------|-----------------------------------------------------------------|
| 2-Nitrophenol                | (G) $\Phi$(OH)=($0.69\pm0.07$) at 305nm and ($0.70\pm0.07$) at 351 nm $\Phi$(HONO)=($0.34\pm0.09$) at 305nm and ($0.39\pm0.07$) at 351 nm | Sangwan and Zhu, 2016                       | 1.0 for 250-310nm, 0.7 for 310-350nm, 0.00115 for 350-480nm, 0 for 480-500 nm |
|                              | (L) $\Phi$=$1.3\times10^{-3}$ at 254nm and $2.2\times10^{-6}$ at 365 nm       | Chen et al., 2011                          |                                                                  |
|                              |                                                                              | Alif et al., 1991                          |                                                                  |
| 2-Nitrobenzaldehyde          | (G) $\Phi$(HCO)$\leq0.022$ at 308nm $\Phi$(NO$_2$)$\leq0.064$ at 308nm $\Phi$(HONO)=$0.4-0.5$ for 280-405 nm | Xiang et al., 2009                         | 1.0 for 250-280nm, 0.5 for 280-405nm, 0 for 405-500 nm          |
|                              | (L&S) $\Phi$=($3.4-8.1$)$\times10^{-5}$ for 300-500nm                       | Galbavy et al., 2010                       |                                                                  |
| 2,4-Dinitrophenol            |                                                                              | Albinet et al., 2010                       | 1.0 for 250-290nm, 8.1$\times10^{-5}$ for 290-400nm, 0 for 400-500 nm |

Note: G, L, and S is short for gaseous, liquid, and ice state of each target compound. Quantum yields for 4-nitrocatechol and 4-nitroguaiacol were applied as the same values for 2-nitrophenol.

Table S5. Estimated equivalent ambient photolysis time for the high UV exposure in the PAM-OFR

| High exposure corresponded | $t_{sim}$ (h) | Solar Zenith Angle (degree) |       |       |       |       |
|---------------------------|---------------|----------------------------|-------|-------|-------|-------|
|                           | 0             | 30                         | 60    | 80    |       |       |
| 2-NP_Gaseous_2016         | 0.45          | 0.59                       | 1.60  | 8.99  |       |       |
| 2-NP_Gaseous_2011         | 0.06          | 0.08                       | 0.22  | 1.16  |       |       |
| 2-NP_Particle-NaCl        | 0.33          | 0.43                       | 1.20  | 6.78  |       |       |
| 2-NP_Particle-KCl         | 0.30          | 0.41                       | 1.13  | 6.50  |       |       |
| 2-NP_Particle-(NH$_4$)$_2$SO$_4$ | 0.40     | 0.53                       | 1.41  | 7.70  |       |       |
| 2-NP_Particle-azelaic acid | 0.38         | 0.51                       | 1.38  | 7.71  |       |       |
| 2-NBA_Gaseous_2009        | 0.11          | 0.14                       | 0.31  | 1.35  |       |       |
| 2-NBA_Gaseous_2017        | 0.93          | 1.21                       | 2.90  | 13.03 |       |       |
| 2-NBA_Aqueous_2008        | 0.84          | 1.33                       | 2.67  | 11.56 |       |       |
| 2,4-DNP_Protonated        | 0.34          | 0.43                       | 1.19  | 6.72  |       |       |
| 2,4-DNP_Depronated        | 0.33          | 0.42                       | 1.10  | 5.82  |       |       |
| 4-NC_Pronated             | 0.16          | 0.21                       | 0.59  | 3.36  |       |       |
| 4-NC_Depronated           | 0.47          | 0.55                       | 1.40  | 6.77  |       |       |
| 4-NG_Pronated             | 0.13          | 0.18                       | 0.49  | 2.78  |       |       |
| 4-NG_Depronated           | 0.16          | 0.21                       | 0.55  | 2.93  |       |       |
| **Average**               | **0.43±0.25** | **0.58±0.37**               | **1.46±0.74** | **7.51±3.02**   |       |       |

Note: 2-NP, 2-NBA, 2,4-DNP, 4-NC, and 4-NG is short for 2-nitrophenol, 2-nitrobenzaldehyde, 2,4-dinitrophenol, 4-nitrocatechol, and 4-nitroguaiacol, respectively. The shaded results were taken as reasonable photolysis times.
### Table S6. Summarized chemical characters for fresh and processed wood tar aerosols from HR-Tof-AMS results

| Wood tar aerosol | O/C          | H/C          | N/C          | NO$_2^+$/NO$^+$ | $f_{\text{HR-NO}_3}$ (wt.%) | $f_{m/z>100}$ (wt.%) | $\overline{OS}$ |
|------------------|--------------|--------------|--------------|-----------------|----------------------------|----------------------|------------------|
| Fresh            | 0.318 ± 0.005| 1.596 ± 0.009| 0.007 ± 0.003| 0.44            | 0.6 ± 0.2                  | 16.7                 | -0.99 ± 0.01     |
| O$_3$ oxidation  | 0.429 ± 0.008| 1.604 ± 0.009| 0.008 ± 0.003| 0.44            | 0.7 ± 0.2                  | 14.5                 | -0.79 ± 0.01     |
| NO$_2^*$ oxidation | 0.472 ± 0.003| 1.544 ± 0.004| 0.071 ± 0.002| 0.19            | 7.2 ± 0.2                  | 10.6                 | -0.96 ± 0.01     |
| EAD-1.0          | 0.492 ± 0.003| 1.574 ± 0.004| 0.045 ± 0.003| 0.24            | 5.2 ± 0.3                  | 8.9                  | -0.81 ± 0.02     |
| EAD-4.4          | 0.540 ± 0.011| 1.534 ± 0.005| 0.038 ± 0.007| 0.25            | 4.3 ± 0.6                  | 8.1                  | -0.65 ± 0.04     |
| EAD-7.2          | 0.636 ± 0.009| 1.518 ± 0.006| 0.029 ± 0.005| 0.26            | 3.2 ± 0.5                  | 7.7                  | -0.40 ± 0.02     |
| Weak photolysis  | 0.445 ± 0.002| 1.533 ± 0.003| 0.061 ± 0.003| 0.22            | 6.3 ± 0.2                  | 11.3                 | -0.95 ± 0.02     |
| Strong photolysis| 0.437 ± 0.002| 1.522 ± 0.003| 0.050 ± 0.003| 0.26            | 4.7 ± 0.1                  | 11.7                 | -0.90 ± 0.02     |

Note: EAD-1.0 indicates equivalent 1.0 day of atmospheric OH$^*$ photochemical aging, by analogy for EAD-4.4 and EAD-7.2. Weak and Strong UV photolysis indicate UV exposures same with experiments of EAD-1.0 and EAD-7.2 in the PAM-OFR but in absence of O$_3$ and OH$^*$. UV light exposures for weak and strong photolysis equal to ambient 0.3 and 2.5 h of solar irradiation, respectively. The elemental ratios have been modified accounting for the organic nitrate compositions. $f_{\text{HR-NO}_3}$ means particle-phase nitrate fraction measured by HR-Tof-AMS. $f_{m/z>100}$ indicates mass fraction of fragments with molecular weight larger than 100 from HR-Tof-AMS result. $\overline{OS}$ is carbon oxidation state that equals to $(2 \times O/C - H/C - 5 \times N/C)$. 

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Figure S5. AMS mass spectra for wood tar aerosols in multiple atmospheric aging processes. (A) Fresh wood tar aerosol. (B) O₃ oxidized aerosol. (C) NO₃ oxidized aerosol. (D) Equivalent 7.2 days of atmospheric aging (EAD-7.2) occurred to NO₃-oxidized wood tar aerosol. (E) Strong photolysis result of NO₃-oxidized wood tar aerosol. The UV light exposure are the same for (D) and (E). Normalized mass fractions of the categorized ions are pie-chart presented. Some typical fragments were identified and marked. The acquired ions were classified into five categories based on their elemental characters, as CₓHᵧ⁺, CₓHᵧOᵢ⁺, CₓHᵧOᵢNᵢ⁺, and NOᵧ⁺, respectively, where x≥1, y≥1, i≥1, and p≥1.
Figure S6. Particle size distributions for NO$_3$-aged wood tar aerosols as a function of photochemical aging (error bar was not presented for clarity).
5. Particulate organic nitrate and absorption lifetime estimation for NO$_3$•-aged wood tar aerosol

We assumed a time-dependent exponential decay for particulate nitrate and particle absorption. Based on the fitted first-order kinetic (k, s$^{-1}$), the lifetime for particulate nitrate and absorption was estimated. See method below:

\[
\ln \left( \frac{C_t}{C_0} \right) = a + kt
\]  

Eq. 24

$C_t$ and $C_0$ indicate time-dependent and initial concentration of a parameter. In this study, $C_t$ is particle absorption coefficient ($C_{abs,t}$, Mm$^{-1}$) and particulate organic nitrate ($C_{ON,t}$, $\mu$g m$^{-3}$).

\[
C_{ON,t} = V_t \times \rho_t \times f_{ON,t}
\]  

Eq. 25

\[
C_{abs,t} = V_t \times \rho_t \times MAC_t
\]  

Eq. 26

Where $V_t$ (μm$^3$ cm$^{-3}$) and $\rho_t$ (g cm$^{-3}$) are wood tar aerosol volume concentration and particle effective density measured by the SMPS and AAC (results in Figure S6 and Table S7). $f_{ON,t}$ (w.t.%) and $MAC_t$ (m$^2$ g$^{-1}$) are the organic nitrate mass fraction from the AMS measurements and wavelength-weighted average mass absorption cross section (results in Table S6 and S7, method in $MAC_t$ calculation given in manuscript). The subscript $t$ indicates equivalent aging time due to net OH• reactions (1.0 and 7.2 days) and solely photolysis (0.3 and 2.5 h).

The lifetime ($\tau$) can be estimated via Equation 27:

\[
\tau = \frac{1}{k}
\]  

Eq. 27

The fitting results for decay of particulate nitrate and absorption are presented in Figure S7:
Figure S7. Exponential decay regression of particulate organic nitrate and aerosol absorption as a function of aging time. (A) Particulate organic nitrate concentration degradation with photolysis and OH• oxidation. (B)-(C) wood tar aerosol absorption decay regrading to UV (330-400 nm), Visible (400-550 nm), and overall (330-550 nm) average wavelength ranges due to photolysis and OH• oxidation.
Figure S8. Changes of the integrated nitrate (\(-\text{ONO}_2\) stretching at 1645, 1280, and 854 cm\(^{-1}\)) and nitro (\(-\text{NO}_2\) stretching at 1359, 1528, and 1554 cm\(^{-1}\)) absorption area percentage for nitrated wood tar aerosol in photochemistry. Only 1 and 7.2 days of atmospheric photochemical aging (EAD-1.0 and EAD-7.2) results are presented, the photodissociation result is from the Strong UV light exposure experiments same as with EAD-7.2 experiment in the PAM-OFR. The size of the markers correlates with the integrated area ratio of \(\nu(-\text{ONO}_2) / \nu(-\text{NO}_2)\), which can help determine the preference of organonitrates and nitro-aromatics in photochemical reactions. For initial nitrated wood tar aerosol, the value was 1.04, with \(\text{OH}\)\(^*\)-initiated photochemical oxidation, the value increased to 1.16 and to 1.22 after equivalent 1 and 7.2 days of photochemical aging, respectively. The only value for photo-dissociated aerosol increased to 1.21, indicating that the nitro-aromatics preferentially dissociate compared to organonitrates in photochemistry.
Figure S9. Proposed photochemical reaction pathways in nitrate degradation for some prominent nitroaromatics and organonitrates in NO$_3$• processed wood tar aerosols. Denitration due to both photolysis (A) and OH• photo-oxidation (B) are summarized based on the MCM mechanism (http://mcm.leeds.ac.uk/MCM) and some related work.$^{45-49}$ R’ could be alky or hydrogen.
Figure S10. AFM image of unprocessed wood tar particles

Figure S11. Chemical composition of wood tar aerosol as a function of particle size. (A) NO$_3^-$ reacted wood tar aerosol, (B) NO$_3^-$-aged aerosol after 7.2 days of atmospheric aging (EAD-7.2), (C) nitrated wood tar aerosol after strong UV exposure same with EAD-7.2 experiment in the PAM-OFR. The shaded area indicates the size range (175-350 nm) we selected in optical measurements.
Table S7. Summarized optical results for fresh and processed wood tar aerosol

| Wood tar aerosol       | Refractive index | SSA | Wavelength-weighted MAC absorption coefficient (MAC) | AAE | Particle density (g cm⁻³) |
|------------------------|------------------|-----|----------------------------------------------------|-----|--------------------------|
|                        | 365nm | 405nm | 535nm | 365nm | 405nm | 535nm | MAC_{UV} (m² g⁻¹) | MAC_{Vis} (m² g⁻¹) |                  |
| Fresh                  | 1.627 + 0.038i   | 1.621 + 0.017i | 1.609 + 0.000i | 0.854 | 0.918 | 1.000 | 1.27 ± 0.38 | 0.16 ± 0.03 | 8.9 ± 0.6 | 1.22 ± 0.02 |
| O₃ oxidation           | 1.648 + 0.036i   | 1.635 + 0.011i | 1.623 + 0.000i | 0.862 | 0.952 | 1.000 | 1.21 ± 0.44 | 0.12 ± 0.06 | 10.9 ± 0.5 | 1.21 ± 0.01 |
| NO₂• oxidation         | 1.603 + 0.091i   | 1.595 + 0.044i | 1.593 + 0.006i | 0.702 | 0.803 | 0.958 | 2.79 ± 0.30 | 0.48 ± 0.06 | 7.5 ± 0.5 | 1.18 ± 0.01 |
| EAD-1.0                | 1.588 + 0.068i   | 1.572 + 0.034i | 1.548 + 0.004i | 0.750 | 0.833 | 0.967 | 2.25 ± 0.31 | 0.32 ± 0.12 | 7.5 ± 0.2 | 1.23 ± 0.01 |
| EAD-4.4                | 1.546 + 0.060i   | 1.551 + 0.028i | 1.551 + 0.003i | 0.765 | 0.851 | 0.976 | 1.71 ± 0.42 | 0.26 ± 0.06 | 7.8 ± 0.6 | 1.25 ± 0.01 |
| EAD-7.2                | 1.550 + 0.056i   | 1.538 + 0.025i | 1.540 + 0.000i | 0.772 | 0.861 | 1.000 | 1.57 ± 0.42 | 0.20 ± 0.07 | 8.3 ± 0.7 | 1.22 ± 0.01 |
| Weak photolysis        | 1.611 + 0.084i   | 1.594 + 0.040i | 1.581 + 0.003i | 0.722 | 0.817 | 0.978 | 2.55 ± 0.49 | 0.41 ± 0.12 | 7.7 ± 0.9 | 1.21 ± 0.01 |
| Strong photolysis      | 1.598 + 0.064i   | 1.588 + 0.033i | 1.569 + 0.004i | 0.765 | 0.842 | 0.969 | 2.16 ± 0.29 | 0.33 ± 0.07 | 7.7 ± 0.5 | 1.21 ± 0.01 |

Note: EAD-1.0 indicates equivalent 1.0 day of atmospheric OH• photochemical aging, by analogy for EAD-4.4 and EAD-7.2. Weak and Strong UV photolysis indicate UV exposures the same with experiments of EAD-1.0 and EAD-7.2 in the PAM-OFR but in the absence of O₃ and OH•. UV light exposures for weak and strong photolysis equal to ambient 0.3 and 2.5 h of solar irradiation, respectively. Uncertainties for the RIs and SSA are not present (±0.007 for real part, ±0.005 for imaginary part, ±0.013 for SSA on average for 365, 405, and 535 nm). SSA was estimated based on RI values for 200 nm particles. Mass absorption coefficient (MAC, m² g⁻¹) was calculated from imaginary RIs and particle density. Here we presented wavelength-weighted MAC for convenience that were grouped as UV range (330-400nm) and visible range (400-550nm). AAE was fitted over the measured effective wavelength range of 330-550 nm.
Figure S12. Evolution of the optical properties of nitrated wood tar aerosols in a series of photochemical transformation configurations. The optical changes due to photolysis or/and OH• reactions were compared. (A) Changes of the real refractive index. (B) Changes of the imaginary refractive index and corresponding Absorption Ångström exponent (AAE). (C) Changes of the single scattering albedo (SSA) for 200 nm wood tar particle. (D) Changes of the wavelength-weighted mass absorption coefficients (MAC, m² g⁻¹) for wood tar aerosols in the UV region (330-400 nm) and in the visible range (400-550nm). Uncertainties for each RI and SSA distributions (±0.005 for real part, ±0.006 for imaginary part, ± 0.013 for SSA on average from 330-550 nm) are not presented for clarity.
**Figure S13.** Exemplary wavelength dependent refractive index (RI) distributions for wood tar aerosols. (A) Real part as a function of wavelength, (B) Imaginary part as a function of wavelength, (C) Bulk methanol-extractable solution absorption derived imaginary RIs for unprocessed and aged wood tar aerosols as a function of wavelength. Error bar for imaginary parts of fresh and O$_3$ oxidized wood tar aerosols are not presented in Panel B for clarity. Average imaginary errors were ±0.005 and ±0.007 for fresh and O$_3$ oxidized wood tar aerosols, respectively. Photolysis results are from the strong UV exposure experiments. The strong photolysis effect equals to 2.5 h of ambient solar irradiation.
Figure S14. Logarithmic regression of wood tar aerosol absorption decay due to OH• oxidation and photolysis. Data (fresh, 1.7 days, 3.9 days photochemical oxidation, P1 and P2 photolysis) was from our previous study on photochemical aging of tar ball aerosol (Li et al., 2019), calculation methods of absorption coefficient and equivalent photolysis time follow above. The mass absorption cross section (MAC) was averaged in wavelength range of 365-425nm. Based on the regressed kinetics, absorption lifetime due to photolysis can be estimated to be around 8.3 days, while the lifetime against net OH• reactions is about 4.3 days. It is clear fresh wood tar aerosol is more susceptible to OH• reactions rather than solar irradiation.
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