

# Impact of nighttime aging on optical properties of toluene secondary organic aerosol

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Toluene is known as an important precursor of anthropogenic secondary organic aerosol (SOA) in the troposphere. In the atmosphere, toluene is mainly oxidized by OH radical to generate gaseous oxidation products in addition to SOA. Whereas OH aging of the toluene-SOA will be negligible under dark conditions after sunset, a part of these oxidation products in gas-phase and/or SOA can be further oxidized with NO<sub>3</sub> or O<sub>3</sub> even in the nighttime. The SOA generated during OH oxidation of toluene in the presence of NO<sub>x</sub> is known to have significant light absorption at the ultraviolet and shorter visible wavelengths (*i.e.*, known as brown carbon) [*e.g.*, Nakayama et al. 2013] and possibly contributes to the radiation balance and photochemical reactions in the atmosphere. In this work, the impact of NO<sub>3</sub> and O<sub>3</sub> aging on wavelength-dependent optical properties of the toluene SOA has been studied.

The SOA was generated during OH oxidation of toluene in the absence of NO<sub>x</sub> in a 6 m<sup>3</sup> stainless steel photochemical chamber with Teflon coating. As sources of OH, either of photolysis of H<sub>2</sub>O<sub>2</sub> or ozonolysis of tetramethylethylene was used. After enough amounts of SOA were generated, N<sub>2</sub>O<sub>5</sub> (precursor of NO<sub>3</sub>), O<sub>3</sub>, or NO<sub>2</sub> was injected to the chamber under dark conditions. The NO<sub>2</sub> injection experiment was conducted to confirm the possible effects of NO<sub>2</sub> reactions, because both of NO<sub>3</sub> and NO<sub>2</sub> were generated during thermal decomposition of N<sub>2</sub>O<sub>5</sub>. Temporal variations of the optical properties of the SOA were measured by two photoacoustic spectrometers (absorption and scattering at 375, 405, 532, 781 nm) and a cavity ring-down spectrometer (extinction at 532 nm). Chemical properties and size distributions of SOA were measured by an Aerodyne aerosol mass spectrometer and a scanning mobility particle sizer, respectively. Gaseous reactants and products were monitored by a Fourier transform-infrared spectrometer and a proton transfer reaction time-of-flight mass spectrometer.

Mass concentrations of toluene-SOA were significantly enhanced and nitrocresols and nitrosalicylic alcohols were generated after NO<sub>3</sub> aging, but no clear enhancement was observed after O<sub>3</sub> aging [Ramasamy et al. 2019]. The toluene-SOA did not show light absorption properties at all wavelengths studied before NO<sub>3</sub> or O<sub>3</sub> aging. Significant light absorption was observed after NO<sub>3</sub> aging at 375 and 405 nm, but neither O<sub>3</sub> nor NO<sub>2</sub> additions. Nitro-aromatic compounds such as nitrocresols and nitrosalicylic alcohols generated from cresols during NO<sub>3</sub> aging are considered to be responsible for the observed light absorption. In the presentation, the atmospheric implications of the results will also be discussed.

## References

Nakayama, T. et al., Wavelength and NO<sub>x</sub> dependent complex refractive index of SOAs generated from the photooxidation of toluene, *Atmos. Chem. Phys.*, 13, 531-545, doi:10.5194/acp-13-531-2013 (2013).  
Ramasamy, S. et al., Investigation of dark condition nitrate radical- and ozone-initiated aging of toluene secondary organic aerosol: Importance of nitrate radical reactions with phenolic products, *Atmos. Environ.*, 219, 117049, doi:10.1016/j.atmosenv.2019.117049 (2019).

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