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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Wavelength and NO_x dependent complex refractive index of SOAs generated from the photooxidation of toluene" *by* T. Nakayama et al.

Anonymous Referee #2

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Nakayama et al. investigate the optical properties of toluene SOA formed in the presence of high levels of NOx using photoacoustic spectrometry and cavity ring-down spectroscopy at 405, 532, and 781 nm. In particular, the authors retrieve the complex refractive index at these wavelengths and are therefore able to study the wavelength-dependence of the real and imaginary components of this property. The study contributes to understanding a finding from field observations in urban areas, namely that there is a marked increase in particle absorption at short wavelengths. The resulting attenuation of near-ultraviolet light by particles can significantly alter the local and regional radiative balance and photochemistry, e.g., through lower photolysis rates of O3 and NOx. As Jacobsen (1999) has pointed out, nitrated aromatic compounds in the

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particle phase are likely to be major contributors to this absorption. Consistent with this hypothesis, Nakayama et al. find that the absorption of toluene SOA becomes appreciable at 405 nm, and increasingly so with higher NOx concentrations. The NOx dependence is rationalised on basis of the concentration of nitro-cresols, which are known products of OH oxidation chemistry. In contrast, absorption at longer wavelengths is small or negligible and particles are almost purely scattering (SSA $\approx$ 1). Nakayama et al. also studied the optical properties of 1,3, 5-trimethylbenzene, whose photooxidation and SOA does not produce nitroaromatic compounds to any significant extent. In this case, no absorption was observed even in under high NOx conditions. These observations are evidence in support of the particular importance of nitroaromatic compounds in affecting the optical properties of anthropogenically-influenced SOA.

I have no major criticisms of the work, and the experimental results in the paper appear robust and with low enough uncertainty for the subsequent level of analysis. In this regard, it should be noted that measuring the particle absorption with sufficient accuracy remains an experimental challenge. Nevertheless, it is regrettable that the paper does not explore the near-UV optical properties directly. Although previous work (including that by the authors) has shown that toluene SOA absorption is much larger at 355 nm, measurements at even shorter wavelengths (e.g., below 330 nm) are desirable to evaluate the influence of particle absorption on O3 photolysis rates. Nakayama et al. estimate the mass absorption cross-sections (MAC) at shorter wavelengths based on angstrom exponents from field work. Although commonly done, it is not clear that this approach is sound for these particles: the extrapolation starts from 405 nm (which is in the tail-end of the absorption) and estimates an extinction near the maximum of the strong absorption band of the nitro-cresols. The authors should provide a stronger justification for this approach in the text, particularly with reference to the absorption spectra of these nitro-cresols.

The findings of this paper therefore highlight the need for further measurements in the near-UV, and for new experimental systems or methods to study the optical proper-

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ties of particles in this region. Doing so will contribute to a deeper understanding of particles on the influence on local photochemistry and radiative balance.

Technical corrections:

p.14552,3: “light absorbing”

p.14552, 16: “high-resolution”

p.14554, 1: “gas phase”

p.14557,26: should this be “V-mode”?

“phenoxy-type” on p.14565 lines 18,20, p.14566, 4, p.14571, 5

p.14570, 3: Define “AAE”

p. 14570, 6: “. . .combustion-OA may be several times. . .”

p.14571, 5: “2,4,6-trimethylphenol”

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 14551, 2012.