Atmos. Chem. Phys. Discuss., 12, 14551–14589, 2012 www.atmos-chem-phys-discuss.net/12/14551/2012/ doi:10.5194/acpd-12-14551-2012 © Author(s) 2012. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Wavelength and NO_x dependent complex refractive index of SOAs generated from the photooxidation of toluene

T. Nakayama¹, K. Sato², Y. Matsumi¹, T. Imamura², A. Yamazaki³, and A. Uchiyama³

¹Solar-Terrestrial Environment Laboratory and Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan
 ²National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba 305-8506, Japan
 ³Meteorological Research Institute, Japan Meteorological Agency, 1-1, Nagamine, Tsukuba 305-0052, Japan

Received: 6 April 2012 - Accepted: 23 May 2012 - Published: 8 June 2012

Correspondence to: T. Nakayama (nakayama@stelab.nagoya-u.ac.jp)

Published by Copernicus Publications on behalf of the European Geosciences Union.

)iscussion Pa	ACPD 12, 14551–14589, 2012				
per	Complex refractive index of toluene-SOA				
Discus	T. Nakayama et al.				
ssion P	Title Page				
aper	Abstract	Introduction			
_	Conclusions	References			
Discu	Tables	Figures			
oissi	14	►I.			
n Pa	•	•			
per	Back	Close			
_	Full Screen / Esc				
Discussic	Printer-friendly Version				
n Paper					

Abstract

Recently, secondary organic aerosols (SOAs) generated from anthropogenic volatile organic compounds have been proposed as a possible source of lightabsorbing organic compounds "brown carbon" in the urban atmosphere. However, the atmospheric

- ⁵ importance of these SOAs remains unclear due to limited information about their optical properties. In this study, the complex refractive index (RI, m = n - ki) values at 405, 532, and 781 nm of the SOAs generated during the photooxidation of toluene (toluene-SOAs) under a variety of initial nitrogen oxide (NO_x = NO+NO₂) conditions were examined by photoacoustic spectroscopy (PAS) and cavity ring down spectroscopy (CRDS).
- ¹⁰ The complex RI values obtained in the present study and reported in the literature indicate that the *k* value, which represents the light absorption of the toluene-SOAs steeply increased to shorter wavelengths at < 405 nm, while the *n* value gradually increased to shorter wavelengths from 781 to 355 nm. The *k* values at 405 nm were found to increase from 1.8×10^{-3} to 7.2×10^{-3} with increasing initial NO_x concentra-
- ¹⁵ tion from 109 to 571 ppbv. The nitrate to organics ratio of the SOAs determined using a highresolution time-of-flight aerosol mass spectrometer (H-ToF-AMS) also increased with increasing initial NO_x concentration. The RI values of the SOAs generated during the photooxidation of 1,3,5-trimethylbenzene in the presence of NO_x (1,3,5-TMB-SOAs) were also determined to investigate the influence of the chemical structure of
- the precursor on the optical properties of the SOAs, and it was found that the light absorption of the 1,3,5-TMB-SOAs is negligible at all of the wavelengths investigated (405, 532, and 781 nm). These results can be reasonably explained by the hypothesis that nitro-aromatic compounds such as nitro-cresols are the major contributors to the light absorption of the toluene-SOAs. Using the obtained RI values, mass absorption
- $_{\rm 25}$ cross sections of the toluene-SOAs at 405 and 532 nm were estimated to be 0.08–0.48 and 0.002–0.081 m² g⁻¹, respectively, under typical conditions in an urban atmosphere during the daytime. These results indicate that light absorption by the SOAs potentially contributes to the radiation balance at ultraviolet wavelengths below ~ 400 nm,



specifically when the mass concentrations of the anthropogenic SOAs are significant compared with those of black carbon particles.

Introduction 1

25

- Atmospheric aerosol plays an important role in determining the visibility, health effects, heterogeneous chemistry, and radiation balance of the atmosphere on a local 5 and a global scale (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000). Recently, it has been suggested that the organic aerosols called "brown carbon" can absorb solar radiation, especially at ultraviolet (UV) and shorter visible wavelengths and contribute to the radiation balance and photochemical reactions in the atmosphere (Andreae and Gelencsér, 2006; Moosmüller et al., 2009; Alexander et al., 2008 and 10
- references therein). "Brown carbon" is operationally defined as a light absorbing carbonaceous material with a wavelength dependent imaginary part (k) of the complex refractive index (RI), m = n - ki.
- Sources of brown carbon have been reported to be the organic components generated during the combustion of biomass such as wood (Kirchsteller et al., 2004; Chen 15 and Bond, 2010) corn stem (Schnaiter et al., 2005), and rice straw (Faves et al., 2009), as well as fossil fuels such as propane (Schnaiter et al., 2006) coal (Bond, 2001) and the organic components included in diesel exhaust (Adler et al., 2010). Humic-like substances (HULIS) extracted from aerosols generated by biomass burning (Hoffer et al., 2006) and sampled in air pollution, rural forests, and fresh smoke conditions (Dinar 20 et al., 2008) was also reported to exhibit light absorption especially at UV and shorter visible wavelengths.

Secondary organic aerosols (SOAs) contain many different chemicals including high molecular weight products and thus may possibly act as "brown carbon" (Graber and Rudich, 2006; Hallquist et al., 2009). Jacobson (1999) suggested the possible influ-

ence of the near UV light absorption by nitrated and aromatic aerosol components on reductions in downward solar radiation in the Los Angeles region. Recently, SOAs



generated during the gasphase photooxidation of toluene in the presence of nitrogen oxides (NO_x = NO+NO₂) (Jaoui et al., 2008; Nakayama et al., 2010a; Zhong and Jang, 2011), the chemical aging of SOAs generated from the reaction of *d*-limonene with O₃ (Bones et al., 2010; Laskin et al., 2010) the irradiation of aqueous solutions containing H₂O₂ and phenolic compounds (Chang and Thompson, 2010), and aqueous phase re-

 $_{5}$ H₂O₂ and phenolic compounds (Chang and Thompson, 2010), and aqueous phase reactions involving glyoxal and methyglyoxal (Shapiro et al., 2009; Galloway et al., 2009; Sareen et al., 2010; Trainic et al., 2011) were reported to exhibit light absorption at UV and/or shorter visible wavelengths.

The photooxidation of aromatic hydrocarbons such as toluene, xylene, and trimethylbenzene (TMB) in the presence of NO_v is known as a major source of anthropogenic 10 SOAs (Kleindienst et al., 2004; Ng et al., 2007; Henze et al., 2008); therefore, quantitative characterization of the optical properties of these SOAs is required to estimate the effect of anthropogenic SOAs on the atmospheric radiation balance. However, only a few experimental studies to determine the RI values of light absorbing SOAs have been reported. Kim et al. (2010) reported the real part of the RI at 670 nm for the 15 SOAs generated during the photooxidation of toluene in the presence of NO_x (denoted by toluene-SOAs) under a variety of initial hydrocarbon ([HC]_{ini} = 1.71-3.75 ppmv) and NO_x ([NO_x]_{ini} = 820–3100 ppbv) conditions in the absence of seed particles and reported *n* values ranging from 1.4 to 1.6 using a polar nephelometer. Our group (Nakayama et al., 2010a) retrieved the real and imaginary parts of the RI values at 20 355 and 532 nm for the toluene-SOAs generated in the presence of $[HC]_{ini} = 4.0 \text{ ppmv}$ and $[NO_x]_{ini} = 540 \text{ ppbv}$ and absence of seed particles by measuring the extinction

and scattering coefficients using a cavity ring-down spectrometer (CRDS) and a nephelometer, respectively. The RI values of $m = (1.632^{+0.038}_{-0.035}) - (0.047^{+0.041}_{-0.036})i$ at 355 nm and $m = (1.483^{+0.032}_{-0.036}) - (0.007^{+0.030}_{-0.007})i$ at 532 nm were reported. A non-negligible *k* value was obtained at 355 nm, while no evidence of light absorption was found at 532 nm due to the difficulty of quantifying the small difference between the extinction and scattering coefficients. Therefore, direct measurements of the absorption coefficients are desired for the accurate determinations of small *k* values. Zhong and Jang (2011) measured



the absorption spectrum of toluene-SOAs that were generated with and without seed particles using a UV-visible spectrometer with an integrating sphere after collection on a filter. Based on the absorption spectrum, they reported the imaginary part of the RI value at 350 nm for the toluene-SOAs generated in the presence of [HC]_{ini} = 0.207 s and 0.202 ppmv and $[NO_x]_{ini}$ = 62 and 70 ppbv and absence of seed particles to be k = 0.0214 and 0.0215. They also reported that the SOAs generated in the presence of $(NH_4)_2SO_4$ or $NH_4HSO_4 + H_2SO_4$ (1 : 1 mixture molar mixture) seed particles have k values that are 2-3 times larger at 350 nm than those generated in the absence of seed particles. Nitrated aromatics compounds such as nitro-cresols were considered as plausible sources of the light absorption observed by Nakayama et al. (2010a) and Zhong and Jang (2011). The production quantum yield of nitrated aromatic compounds may depend on $[NO_x]_{ini}$; however the k values were measured under limited [NO_x]_{ini} conditions: 540 ppbv (Nakayama et al., 2010a) and 62–70 ppbv (Zhong and Jang, 2011).

- In this study, the wavelength and NO_x dependence of the complex RI values of the 15 toluene-SOAs are investigated in detail. To determine the small k value accurately, a 3λ photoacoustic spectrometer (Droplet Measurement Technologies, PASS-3) was used to directly measure the light absorption of the SOAs suspended in air. In addition, the complex RI values of the SOAs generated during the photooxidation of the 1,3,5-TMB
- in the presence of NO_x (denoted by 1,3,5-TMB-SOAs) were also determined to inves-20 tigate the influence of chemical structure on the optical properties of the SOAs from aromatic hydrocarbons. Using the obtained RI values, possible atmospheric implications of the light absorption of the anthropogenic SOAs are also discussed.

Experimental 2

10

The experimental setup used in this study, which is shown in Fig. 1, is similar to that 25 used in our previous study (Nakayama et al., 2010a). The SOAs were generated in a 6 m³ Teflon-coated stainless steel photochemical smog chamber (Akimoto et al.,



1979; Sato et al., 2007). The toluene (or 1,3,5-TMB), NO, methyl nitrate, and purified air were mixed in the chamber and continuously irradiated by light from a xenon arc lamp (19 kW) through Pyrex filters. Methyl nitrite (~0.01 ppmv) was used as the OH source. Toluene (Wako Chemicals, 99%), 1,3,5-TMB (Tokyo Chemical Industry, > 97%), and nitrogen oxide (Takachiho Chemical Industrial Co., 99.9%) were used without further 5 purification. No seed particles were added in the present study. The total pressure in the chamber was maintained at 1000-1030 hPa by adding a purified air during the measurements. All experiments were conducted under room temperature $(298 \pm 3 \text{ K})$ and dry ($[H_2O] < 1$ ppmv) conditions. Four experiments (runs A1-A4) were conducted for the toluene-SOAs with different [NOx]ini conditions (109-571 ppbv) to examine the 10 NO, dependence of the RI values as shown in Table 1. In addition, one experiment (run B1) was conducted for the 1,3,5-TMB-SOAs with a high $[NO_{x}]_{ini}$ condition (571 ppbv). The concentrations of toluene, 1,3,5-TMB, NO, NO₂, and O₃ were monitored using a Fourier transform infrared spectrometer (FT-IR; Nicolet, Nexus 670) combined with

¹⁵ a mirror system with a 221.5 m optical path. The particle size distribution was measured every 6 min using a scanning mobility particle sizer (SMPS; TSI, 3934). Typical temporal profiles of the toluene, NO, NO₂, O₃, mass concentrations and the surface mean diameters of the toluene-SOAs during "run A4" are shown in Fig. 2. When the mass concentration of the SOAs began to increase, the SOAs were introduced into the PASS-3 and a custom-built cavity ring down spectrometer (CRDS).

The PASS-3 instrument was used to measure the absorption $(b_{abs}(\lambda))$ and scattering $(b_{sca}(\lambda))$ coefficients at 405, 532, and 781 nm. The $b_{sca}(\lambda)$ data were calibrated using monodisperse polystyrene latex (PSL) particles. The $b_{abs}(405, 781 \text{ nm})$ data were calibrated using polydisperse propane soot particles, while the $b_{abs}(532 \text{ nm})$ data were calibrated using polydisperse propane soot particles, while the $b_{abs}(532 \text{ nm})$ data were

²⁵ calibrated with monodisperse nigrosin particles and gaseous NO₂. These calibration procedures are described in the Supplement. The $b_{sca}(532 \text{ nm})$ data obtained by the PASS-3 were not used in this study because a strong particle size dependence of the calibration factors was found. Uncertainties associated with the calibration were estimated to be 8, 10, 8, 6, and 6% for $b_{abs}(405 \text{ nm})$, $b_{abs}(532 \text{ nm})$, $b_{abs}(781 \text{ nm})$,



 $b_{\rm sca}(405 \,\rm nm)$, and $b_{\rm sca}(781 \,\rm nm)$, respectively. For background interpolation, measurements of filtered air were conducted using a particulate filter (Balston) typically for 4 min every 12 min. The typical detection limits for the 12 min averaged data of $b_{\rm abs}(405 \,\rm nm)$, $b_{\rm abs}(532 \,\rm nm)$, $b_{\rm abs}(781 \,\rm nm)$, $b_{\rm sca}(405 \,\rm nm)$, and $b_{\rm sca}(781 \,\rm nm)$ were estimated to be 1.0, 0.9, 0.4, 0.2, and 0.2 Mm⁻¹, respectively, by taking the two standard deviations (2σ) of

- $_{5}$ 0.9, 0.4, 0.2, and 0.2 Mm⁻¹, respectively, by taking the two standard deviations (2σ) of each signal during the filtered air measurements. It should be noted that these detection limits varied depending on the magnitude of the drift in each signal. Corrections of b_{abs} for the gas phase absorption of NO₂ were conducted using the mixing ratio measured by FT-IR, absorption cross section, and the transmission of NO₂ through the
- ¹⁰ particulate filter. Overall uncertainties for the PASS-3 data were estimated by taking into account the uncertainties in the calibration factors, in the background interpolations (estimated from the drift between neighboring filtered air measurements), and in the corrections of the gas phase absorption as well as detection limit values. The typical sampling flow rate of the PASS-3 was 1.0 lpm.
- ¹⁵ The CRDS instrument was used to measure the extinction coefficients at 532 nm $(b_{ext}(532 \text{ nm}))$. A detailed description of the CRDS instrument used in the present study is included in our previous papers (Nakayama et al., 2010a, b). Measurement of the ring-down time for the filtered air was conducted using a particulate filter (Pall), typically for 4 min every 12 min. A typical detection limit for the 12 min averaged data for $b_{ext}(532 \text{ nm})$ during the experiments was estimated to be 0.6 Mm^{-1} by taking the 2σ of each signal during the filtered air measurements. The accuracy and precision of the CRDS instrument were checked using monodisperse PSL particles and the uncertainties in the determination of $b_{ext}(532 \text{ nm})$ was estimated to be < 3% (Nakayama et al.,
- ties in the determination of $b_{ext}(532 \text{ nm})$ was estimated to be < 3% (Nakayama et al., 2010a, b). The typical sampling flow rate of the CRDS was 0.6 lpm. The chemical properties of the aerosols were also measured every 6 min using
- In the chemical properties of the aerosols were also measured every 6 min using an Aerodyne aerosol mass spectrometer (Aerodyne Research, H-ToF-AMS) in theVmode (Drewnick et al., 2005). The particles collected through an aerodynamic lens were heated at 873 K to evaporate the particulate compounds, and the vaporized compounds were then ionized by electron ionization and analyzed by a ToF-MS instrument



with a mass resolution of \sim 2700. Data obtained by H-ToF-AMS were numerically analyzed using the ToF-AMS Analysis Toolkit program Version 1.48 combined with the ToF-AMS HR Analysis Program Version 1.07.

3 Results

⁵ The complex RI of the SOAs was determined using the same procedure that was used in our previous study (Nakayama et al., 2010a). Assuming homogeneous spherical particles, the effective absorption, scattering, and extinction efficiencies of polydisperse SOA particles with a surface mean diameter \bar{D}_s at wavelength λ (= 405, 532, or 781 nm), $Q_{abs}^{*}(\bar{D}_s, \lambda)$, $Q_{sca}^{*}(\bar{D}_s, \lambda)$, and $Q_{ext}^{*}(\bar{D}_s, \lambda)$ were calculated as follows:

¹⁰
$$Q_{\text{abs,sca,ext}}^*(\bar{D}_s,\lambda) = b_{\text{abs,sca,ext}}(\lambda) / \int N(D_p) \frac{\pi}{4} D_p^2 dD_p$$
 (1)

where D_p is the geometrical particle diameter and N is the number concentration of particles in the size bin dD_p with a mean diameter D_p per unit volume.

A 12-min average of the b_{abs} (405, 532, 781 nm), b_{sca} (405, 781 nm) and b_{ext} (532 nm) obtained by the PASS-3 and CRDS, and size distributions obtained by the SMPS were used for the analysis. The range of b_{abs} , b_{sca} , and b_{ext} values used for the determination of the RI values are listed in Table 2. Figures 3 and 4 show the Q_{abs}^* at 405, 532, and 781 nm, the Q_{sca}^* at 405 and 781 nm, and the Q_{ext} at 532 nm for "run A4" (toluene–SOAs, high [NO_x]_{ini} condition) and "run B1" (1,3,5-TMB–SOA, high [NO_x]_{ini} condition), respectively, as a function of \overline{D}_s . Significant light absorption was found at 405 and 532 nm in "run A4" (Fig. 3b). In contrast, no significant light absorption was detected at all wavelengths (405, 532, and 781 nm) in "run B1" within the uncertainties (Fig. 4b).



The effective absorption, scattering, and extinction efficiencies can also be calculated using the Mie theory as follows:

$$Q_{\text{abs,sca,ext}}^{*}(\bar{D}_{s},\lambda) = \int f(D_{p})Q_{\text{abs,sca,ext}}(D_{p},\lambda)dD_{p}$$

- ⁵ where $f(D_p)$ is the normalized surface area weighted size distribution function. $Q_{abs,sca,ext}(D_p,\lambda)$ represent the absorption, scattering, and extinction efficiencies, and are calculated based on the Mie theory using the BHMIE algorithm (Bohren and Huffman, 1983).
- In this study, the optimized RI values were determined using combinations of the data: (1) Q_{sca}^* and Q_{abs}^* at 405 and 781 nm and (2) Q_{ext}^* and Q_{abs}^* at 532 nm. To minimize the sum of the squared residual between the Q^* values obtained using Eq. (1) and those obtained using Eq. (2), the optimized RI value was determined. The *n* value was fixed between 1.2 and 1.7 and a positive value of *k* was chosen during the fitting procedure. The complex RI value was determined for each experimental run by assuming a constant RI value during the measurement. The results for Q_{abs}^* , Q_{sca}^* , and Q_{ext}^* calculated using Eq. (2) with the optimized RI values for "run A4" and "run B1" are shown as solid lines in Figs. 3 and 4, respectively. The obtained RI values and their uncertainties, which were estimated from the 2σ for the differences between the $Q^*(\bar{D}_s, \lambda)$ values obtained using Eqs. (1) and (2) and uncertainties in the measurements of the optical properties and size distributions of the SOAs are summarized in Table 2
- ²⁰ optical properties and size distributions of the SOAs, are summarized in Table 2.

4 Discussion

4.1 Wavelength dependence of the RI values for toluene-SOAs

Figure 5 shows the wavelength dependence of the *n* and *k* values for the toluene-SOAs obtained in the present study (*n* and *k*, runs A1–A4, filled circles) and reported in the literature. Nekayama et al. (2010a) (*n* and *k* area circles). Kim et al. (2010b) (*n* area *k* area circles).

literature, Nakayama et al. (2010a) (*n* and *k*, open circles), Kim et al. (2010) (*n*, open inverted triangle), and Zhong and Jang (2011) (*k*, open triangle).



(2)

The *n* values at 405, 532, and 781 nm obtained in the present study range between 1.4 and 1.6 and show a gradual increase to shorter wavelengths. The *n* value of $1.498^{+0.015}_{-0.014}$ at 532 nm under high $[NO_x]_{ini}$ condition $([NO_x]_{ini} = 571 \text{ ppbv}, \text{ run A4})$ is in good agreement with that obtained in our previous study $(1.483^{+0.032}_{-0.036})$ (Nakayama et al., 2010a) under high $[NO_x]_{ini}$ condition $([NO_x]_{ini} = 540 \text{ ppbv})$. Interpolation of all of our results at 532 and 781 nm gives an *n* value of ~ 1.43 at 670 nm, which lies in the lower part of the range between 1.4 and 1.6, reported by Kim et al. (2010) under a variety of $[HC]_{ini}$ and $[NO_x]_{ini}$ conditions $([HC]_{ini} = 1.71-3.75 \text{ ppmv}, [NO_x]_{ini} = 820-$ 3100 ppbv). The results may be explained by their use of higher $[NO_x]_{ini}$ conditions than those of the present study.

Significant *k* values at 405 nm, which range from $(1.8^{+1.3}_{-1.3}) \times 10^{-3}$ to $(7.2^{+1.0}_{-1.0}) \times 10^{-3}$ are obtained for the toluene-SOAs in the present study. The *k* value depends on the $[NO_x]_{ini}$ as discussed in detail in the next section. At 532 nm, a non-negligible *k* value $(1.0^{+0.7}_{-0.8} \times 10^{-3})$ is also obtained under high $[NO_x]_{ini}$ conditions (run A4), while the values for the other runs (A1, A2, and A3) are negligibly small within the experimental uncertainties. At 781 nm, the *k* values are found to be negligible for all runs. In our previous study (Nakayama et al., 2010a), the RI values were determined from the measurements of the extinction and scattering coefficients. Therefore, precise determination of a small *k* value was difficult because of the large uncertainties (typically ~ 4 × 10⁻²) as

²⁰ shown by the larger error bars in Fig. 5b. In the present study, by directly measuring the absorption coefficients using the PASS-3, the *k* values could be determined with a higher precision (typical uncertainties of $\sim 1 \times 10^{-3}$).

In contrast to the n values, which gradually increased to shorter wavelengths from 781 to 355 nm, the k values obtained in the present study and reported in the litera-

²⁵ ture (Nakayama et al., 2010a; Zhong and Jang, 2011) indicate that the light absorption of the toluene-SOAs steeply increases to shorter wavelengths at < 405 nm. The observed features of the wavelength dependence of the *n* and *k* values are qualitatively consistent with the theoretically predicted features, if the absorption peak (resonant wavelength) is assumed to be shorter than 350 nm (e.g. Moosmüller et al., 2011).



4.2 NO_x dependence of the RI values for toluene-SOAs

Figure 6a, b shows the $[NO_x]_{ini}$ dependence of the *n* and *k* values at 405 nm (filled circles) and 532 nm (open circles) for the toluene-SOAs obtained in the present study. The *n* values at 405 and 532 nm slightly increased from 1.45 to 1.57 and 1.43 to

- ⁵ 1.50, respectively, with increasing [NO_x]_{ini} from 109 to 571 ppbv as shown in Fig. 6a. The difference in the *n* values at 405 and 532 nm also increased from ~ 0.02 to ~ 0.07 with increasing [NO_x]_{ini}. These results are again consistent with the theoretically predicted features when the light absorption of a shorter resonant wavelength is taken into account (e.g. Moosmüller et al., 2011), because the stronger light absorption under high [NO_x]_{ini} conditions would cause a larger increase in the *n* values on the long-wavelength side. It should be noted that a change in chemical properties, such as the O/C ratio, may also contribute to the observed [NO_x]_{ini} dependence of the *n* values:
- a positive correlation has been reported for squalane and azelaic acid by Cappa et al. (2011).
- ¹⁵ The *k* values at 405 nm increase from 1.8×10^{-3} to 7.2×10^{-3} with increasing $[NO_x]_{ini}$ from 107 to 571 ppbv as shown in Fig. 6b. Under the high $[NO_x]_{ini}$ condition (571 ppbv), the non-negligible *k* value (1.0×10^{-3}) was also observed at 532 nm. As a plausible source of light-absorption for the toluene-SOAs, nitro-aromatic compounds, particularly nitro-cresols, have been proposed (Nakayama et al., 2010a; Zhong and Jang, 2011) because nitro-cresols such as 4-nitro-*o*-cresol 4-nitro-*m*-cresol, 2-nitro-*p*-cresol, and
- 4,6-dinitro-*o*-cresol, which were identified as products of toluene-SOAs (Jang and Kamens, 2001; Sato et al., 2007), exhibit strong light absorption at > 350 nm (Jacobson, 1999; Chen et al., 2011).

Figure 7 shows one of the significant reaction schemes for the formation of nitrocresols during the photooxidation of toluene in the presence of NO_x . There are two steps in the reaction of toluene with OH: abstraction of a H from toluene (~ 10%) and formation of a toluene-OH adduct (~ 90%). The toluene-OH adduct reacts with O_2 or NO_2 , and subsequent reactions of the corresponding products lead to SOA formation.



Under our experimental conditions, most of the toluene-OH adduct reacts with O₂, while only a few percent of the adduct reacts with NO₂ (Koch et al., 2007 and references therein). Although cresols (*o*-, *m*-, *p*-cresol) can be generated from both of the reactions, the cresols are considered to be mainly generated from the reaction of the toluene-OH adduct with O₂, because the yields of *o*-, *m*-, and *p*-cresol are reported to be ~ 0.12, ~ 0.03, and ~ 0.03, respectively, and do not strongly depend on the initial NO_x conditions (Smith et al., 1998; Klotz et al., 1998). The H atom abstraction from cresols by OH leads to the formation of methyl phenoxy radicals. Nitro-cresols are considered to be mainly generated from the reactions of methyl phenoxy radicals with NO₂, as shown in Fig. 7 (Forstner et al., 1997; Sato et al., 2007).

The reaction of the cresol-OH adducts with NO₂ possibly contributes to the formation of nitro-cresols. However, the contribution should be small because most of the cresol-OH adducts react with O₂ rather than NO₂ (Koch et al., 2007). The fact that the yields of nitro-cresols in the OH-induced oxidation of cresols are similar to the calculated fraction

- of the reaction proceeding via H atom abstraction from the OH group indicates that the nitro-cresols are mainly generated through methyl phenoxy radicals (Atkinson et al., 1992; Olariu et al., 2002; Coeur-Tourneur et al., 2006). It should also be noted that nitrotoluenes, such as 3-nitrotoluene, are generated through the reaction of toluene-OH adducts with NO₂, particularly at high [NO_x]_{ini} conditions (typically, > 1 ppm) (Forstner et al., 1997; Smith et al., 1998; Sato et al., 2007). The contributions of nitrotoluenes to the light absorption of the toluene-SOAs should be minimal, however, because both the
- yield and absorption cross section of nitrotoluenes have been estimated to be smaller than those of nitro-cresols under our experimental conditions (Forstner et al., 1997; Smith et al., 1998; Sato et al., 2007; Shama, 1991; Chen et al., 2011).
- ²⁵ The observed [NO_x]_{ini} dependence of the *k* values may be explained by competition reactions of the methyl phenoxy radicals with NO₂ and other oxidants, as shown in Fig. 7. Although the rate constants for the reactions of the methyl phenoxy radials with NO₂ and other oxidants are not available, those for the reactions of phenoxy radical (C₆H₅O) with NO₂, NO, and O₃ were reported to be $k_{NO_2} = 2.1 \times 10^{-12}$ (Platz et al.,



1998), $k_{NO} = 1.88 \times 10^{-12}$ (Platz et al., 1998), and $k_{O_3} = 2.86 \times 10^{-13}$ (Tao and Li, 1999), cm³ molecule⁻¹ s⁻¹ at room temperature (296–298 K), respectively. The reaction of the phenoxy radical with O₂ was reported to be negligible (Platz et al., 1998). Although possible contributions of the reactions of the phenoxy radical with HO₂ and alkylperoxy (RO₂) radical cannot be ruled out, the rate constants for these reactions are not available. Assuming that the rate constants for methyl phenoxy radicals are similar to those for the phenoxy radical and that the reactions with HO₂ and RO₂ are negligible, the effective yield of the reaction of methyl phenoxy radicals with NO₂ (Y_{NO_2}) is estimated by the following equation

10
$$Y_{NO_2} = \frac{k_{NO_2}[NO_2]_{eff}}{k_{NO_2}[NO_2]_{eff} + k_{NO}[NO]_{eff} + k_{O_3}[O_3]_{eff}}$$

where $[NO_2]_{eff}$, $[NO]_{eff}$, and $[O_3]_{eff}$ are the effective concentrations of NO_2 , NO, and O_3 , respectively, during the formation of the SOAs. The $[NO_2]_{eff}$, $[NO]_{eff}$, and $[O_3]_{eff}$ are calculated by the following equation,

15
$$[X]_{eff} = \frac{\int_{t_0}^{t_{max}} [X]_t \Delta M_t dt}{\int_{t_0}^{t_{max}} \Delta M_t dt}$$
 (X=NO₂, NO, O₃), (4)

where *t* and t_{max} are the time when the irradiation began and when the volume (mass) concentration of the SOAs, which was measured by the SMPS, reached a maximum, respectively; $[X]_t$ are the concentrations of X at time *t*; and ΔM_t is the change in mass concentration of the SOAs during the time d*t*. The $[X]_{eff}$ is identical to the average concentration of X weighted with the change in mass concentration of the SOAs during the period ($t_0 < t < t_{max}$). The estimated Y_{NO_2} value, as well as $[NO_2]_{eff}$ [NO]_{eff}, and $[O_3]_{eff}$, for each experimental run are listed in Table 3. As a result, Y_{NO_2} was found to increase with increasing $[NO_x]_{ini}$. The observed $[NO_x]_{ini}$ dependence of the *k* values is consistent with the hypothesis that nitro-cresols, which are generated through the

Jiscussion Pape

Jiscussion Pape

(3)

mechanism described above, are the main contributors to the light absorption of the SOAs.

The observed $[NO_x]_{ini}$ dependence of the RI values was compared with the chemical properties of the SOAs, which were simultaneously measured by the H-TOF-AMS. The

- ⁵ ratio averages ($\pm 1\sigma$) of the nitrate to the organics (HRNO₃/HROrg) and the oxygen atoms to the carbon atoms (O/C) calculated from the H-ToF-AMS data for the same period used for determinations of the RI values are listed in Table 3. The HRNO₃/HROrg ratio increases with an increase in the [NO_x]_{ini} from 0.023 to 0.037 as shown in Fig. 6c with the open triangles. Particulate nitro-aromatic compounds are known to be detected
- ¹⁰ as nitrate by AMS (Bahreni et al., 2005; Sato et al., 2010, 2012). It should be noted that the mass concentration of the SOAs may also contribute to the HRNO₃/HROrg ratio since the mass concentration increases with an increase in the $[NO_x]_{ini}$ under the present experimental conditions with a constant $[HC]_{ini}$, as shown in Table 1. However, Sato et al. (2012) reported that the HRNO₃/HROrg ratio for the SOAs generated from
- ¹⁵ photooxidation of toluene in the presence of NO_x (denoted by toluene-SOAs) was not dependent on the mass loading, but closely dependent on the [NO_x]_{ini}. Therefore, the AMS data reinforce the hypothesis that the nitro-aromatics including nitro-cresols contribute to the observed light absorption. The average of the O/C ratio was also found to increase with increasing [NO_x]_{ini} from 0.64 to 0.73 as shown in Fig. 6c with the filled triangles. This suggests that the oxidation processes of the precursors may also
- ²⁰ filled triangles. This suggests that the oxidation processes of the precursors may also contribute to the enhancement of the light absorption of the toluene-SOAs.

4.3 RI values of 1,3,5-TMB-SOAs

25

The RI values of 1,3,5-TMB-SOAs were also determined to investigate the influence of the chemical structure of the aromatic hydrocarbons on the optical properties of the SOAs. The RI values of the 1,3,5-TMB-SOAs at 405, 532, and 781 nm were determined to be $1.485^{+0.025}_{-0.024} - 0.2^{+0.4}_{-0.2}i$, $1.459^{+0.016}_{-0.017} - 0^{+1.0}_{-0}i$, and $1.423^{+0.015}_{-0.016} - 0.2^{+0.7}_{-0.2}i$, respectively, under high [NO_x]_{ini} condition ([NO_x]_{ini} = 571 ppbv). The *n* value slightly increased to shorter wavelengths similar to that observed for the toluene-SOAs. In



contrast to the toluene-SOAs, however, the *k* values for 1,3,5-TMB were found to be negligible at all the wavelengths studied (405, 532, and 781 nm). The average $(\pm 1\sigma)$ of the HRNO₃/HROrg and O/C ratios during the same period as that used for determination of the RI values were 0.019 ± 0.001 and 0.49 ± 0.01 , respectively (Table 3). These values are lower than those for the toluene-SOAs (0.023-0.037 (HRNO₃/HROrg) and 0.64-0.73 (O/C)) obtained under conditions where the [NO_x]_{ini} was between 107 and 571 ppbv.

In 1,3,5-TMB, the hydrogen atoms in two meta sites to the methyl group in toluene are substituted by other methyl groups. The difference in the light absorption properties between toluene-SOAs and 1,3,5-TMB-SOAs may be explained by the difference in the production of nitro-phenols. Sato et al. (2012) compared the chemical properties

10

- of the 1,3,5-TMB-SOAs with those of SOAs generated from the photooxidation of benzene in the presence of NO_x (denoted by benzene-SOAs) based on H-ToF-AMS and liquid chromatography/time of flight mass spectrometry (LC/TOF-MS) analyses. They
- ¹⁵ reported that nitrophenols were not detected in the 1,3,5-TMB-SOAs while they were detected in the benzene-SOAs and that the HRNO₃/HROrg ratio for 1,3,5-TMB was lower than that for the benzene-SOAs and not dependent on the $[NO_x]_{ini}$ These results were explained by the instability of the NO₂ adducts of the phenoxytype radicals produced from 2,4,6-trimethyphenol, which was formed from the reaction of the 1,3,5-TMB
- with OH (Sato et al., 2012). In the resonance structures of the phenoxytype radicals, the carbon atoms at the radical's center are bonded with methyl groups and therefore the NO₂ adducts of the phenoxytype radicals immediately dissociate to reactants again (Sato et al., 2012). The fact that no light absorption was revealed for the 1,3,5-TMB-SOAs in the present study is consistent with the hypothesis that nitro-aromatics such
- as nitro-cresols are the main sources of the light absorption for the toluene-SOAs. The non-zero HRNO₃/HROrg ratio observed in the present study may be due to the contributions of nitrate and nitrite compounds other than nitro-aromatics to the HRNO₃ signals.



In the case of many other aromatic hydrocarbons such as benzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,4-TMB, and ethylbenzene, there are other meta sites for which the hydrogen atom is not substituted by an alkyl group. Therefore, the photooxidation products of these precursors include stable NO₂ adducts of phenoxytype radicals, and the SOAs generated from these precursors presumably contain nitro-phenols and ex-

the SOAs generated from these precursors presumably contain nitro-phenols hibit light absorption at UV and shorter visible wavelengths.

5 Atmospheric implications

10

15

To estimate the possible contribution of the light absorption by the toluene-SOAs, mass absorption cross sections (MACs) were calculated using the obtained RI values.

If the nitro-cresols generated from the methyl phenoxy radicals with NO₂ are the main sources of light absorption of the toluene-SOAs and the yield of the methyl phenoxy radicals is constant, as discussed in Sect. 4.2, then *k* can be considered to be proportional to Y_{NO_2}

$$k(\lambda) = A(\lambda) \times Y_{NO_2}$$

= $A(\lambda) \times \frac{k_{NO_2}[NO_2]_{eff}}{k_{NO_2}[NO_2]_{eff} + k_{NO}[NO]_{eff} + k_{O_3}[O_3]_{eff}}$ (5)

where $A(\lambda)$ is the wavelength dependent factor that is proportional to the effective absorption cross section of the light absorbing species (i.e. nitro-cresols). Because [NO]_{eff} is smaller than both [NO₂]_{eff} and [O₃]_{eff} under our experimental conditions, the ob-²⁰ served *k* values of the SOAs are substantially determined by the ratio of [NO₂]_{eff} to [O₃]_{eff} during SOA formation. Figure 8b shows the [NO₂]_{eff}/[O₃]_{eff} ratio dependence of the *k* values at 405 and 532 nm for the toluene-SOA. Minimizing the sum of the squared residual between the measured $k(\lambda)$ values and those calculated using Eq. (5), the $A(\lambda)$ values at 405 and 532 nm were determined to be $(8.3^{+1.8}_{-2.1}) \times 10^{-3}$ and $(1.5 \pm ^{+1.0}_{-1.2}) \times 10^{-3}$,



respectively. The quoted uncertainties include 2σ for the differences between the observed *k* values and those calculated using Eq. (5) and uncertainties in the experimentally determined *k* values.

The *n* values at 405 and 532 nm slightly depend on $[NO_2]_{eff}/[O_3]_{eff}$, as shown in ⁵ Fig. 8a, possibly due to their contributions to the light absorption as discussed in Sect. 4.2. Assuming that *n* (532 nm) value obtained under high $[NO_x]_{ini}$ conditions (run A1), $1.431^{+0.016}_{-0.017}$, is a typical *n* value for the toluene-SOAs without light absorption, the $[NO_2]_{eff}/[O_3]_{eff}$ dependence of the $n(\lambda)$ values can be estimated using the following equation

10
$$n(\lambda) = 1.431^{+0.016}_{-0.017} + B(\lambda) \times Y_{NO_2}$$

= $1.431^{+0.016}_{-0.017} + B(\lambda) \times \frac{k_{NO_2}[NO_2]_{eff}}{k_{NO_2}[NO_2]_{eff} + k_{NO}[NO]_{eff} + k_{O_3}[O_3]_{eff}}$

where $B(\lambda)$ is the wavelength dependent factor that is proportional to the contribution of the light absorbing species to *n*. Minimizing the sum of the squared residual between ¹⁵ the measured $n(\lambda)$ values and those calculated using Eq. (6), the $B(\lambda)$ values at 405 and 532 nm were determined to be $0.13^{+0.06}_{-0.07}$ and $0.06^{+0.04}_{-0.03}$, respectively. The quoted uncertainties include 2σ for the differences between the observed *n* values and those calculated using Eq. (6) and the uncertainties in the experimentally determined *n* values. The solid (dashed) lines in Fig. 8a, b show the best estimation (and upper or lower limit) values of the $n(\lambda)$ and $k(\lambda)$ calculated using Eqs. (5) and (6) with the optimized $A(\lambda)$ and $B(\lambda)$ values respectively, assuming a constant [NO]_{eff}/[NO₂]_{eff} value of 0.4 which is the average for the experimental runs (A1–A4).

Using the obtained $[NO_2]_{eff}/[O_3]_{eff}$ dependent $n(\lambda)$ and $k(\lambda)$ values, the MAC values of the toluene-SOAs at 405 and 532 nm were estimated based on the Mie theory (BH-

²⁵ MIE algorithm) assuming homogeneous spherical particles with a particle density of $1.4 \,\mathrm{g\,cm^{-3}}$ (Sato et al., 2007) and a constant $[NO_2]/[O_3]$ ratio during the formation of the SOAs. Usually, [NO] is significantly smaller than $[NO_2]$ during the daytime, when



(6)

the photooxidation of toluene occurs, because of the rapid conversion of NO to NO_2 due to the reaction with O_3 . Therefore, the constant [NO]/[NO₂] ratio (= 0.04) was assumed in the calculation. Figure 9 shows the [NO₂]/[O₃] dependence of the MACs of the SOAs with a diameter of 200, 400, and 600 nm, for the typical [NO₂]/[O₃] range be-

- tween 0.1 and 10 in an urban atmosphere during the daytime (e.g., Finlayson-Pitts and Pitts, 2000; Kondo et al., 2008). The ranges of the best estimates (upper and lower limits) of the MAC values at 405 and 532 nm for the toluene-SOA with diameters between 200 and 600 nm were estimated to be 0.11–0.33 (0.08–0.48) and 0.012–0.046 (0.002–0.081) m² g⁻¹, respectively. As shown in Fig. 8, the MAC values at 405 and 532 nm
 both increase 2.4 times on average with an increase in the [NO₂]/[O₃] ratio from 0.1
- to 10 and increase 1.2 and 1.6 times on average, respectively, with an increase in the particle diameter from 200 to 600 nm.

Several observational studies on wavelength dependence of the MAC values of brown carbon in urban aerosols (Barnard et al., 2008; Flowers et al., 2010; Zhang et al., 2011; Cheng et al., 2011) have been reported. Barnard et al. (2008) deter-15 mined the MAC values at wavelength between 300 and 500 nm for organic components of aerosols in the Mexico city and reported that the MAC steeply decrease from $\sim 6 \text{ m}^2 \text{g}^{-1}$ at 390 nm to $\sim 1 \text{ m}^2 \text{g}^{-1}$ at 410 nm. Flowers et al. (2010) reported the MAC values for organic carbon in various Asian pollution plumes, which were transported to Jeju, Korea, ranging between 2.1 and $3.4 \text{ m}^2 \text{ g}^{-1} \text{ C}$ at 405 nm and between 0 and 20 $1.0 \text{ m}^2 \text{ g}^{-1} \text{ C}$ at 532 nm. The MAC value at 405 nm for the toluene-SOA obtained in the present study $(0.08-0.48 \text{ m}^2 \text{ g}^{-1})$ is several times smaller than those reported values. The difference may be explained by contributions of other sources of brown carbon such as biomass burning, because the reported MAC values for combustion related organic aerosols (combustion-OA) are typically larger than those for water soluble or-25

ganic carbons (WSOC) (Sun et al., 2007 and references therein).

Very recently, SOAs generated from anthropogenic VOCs were reported to contribute to the light absorption of WSOC at near UV wavelengths (Zhang et al., 2011; Cheng et al., 2011). Zhang et al. (2011) compared the light absorption spectra of



WSOC in the Los-Angeles basin (LA) and Atlanta during the summer and reported a 4–6 times higher bulk absorption per soluble carbon mass at 365 nm (α (365 nm)/ ρ ; α is the bulk absorption coefficient, ρ is the density of the WSOC) in LA: 0.69 (weekdays) and 0.77 m²g⁻¹C (weekends) than those in Atlanta. They suggested that the light absorption observed in LA was due to freshly-formed anthropogenic SOAs, because the radio carbon analysis showed that the SOAs were mainly formed by fossil carbon, and the chemical analysis showed a positive correlation between the bulk absorption coefficients with nitro-aromatics in the WSOC. The bulk absorption per soluble carbon can be compared with the particulate absorption coefficients using the follow-10 ing relationship, assuming that the particles are small relative to the wavelength (Sun et al., 2007),

MAC =
$$\xi \times \alpha / \rho$$

where ξ is defined by

15
$$\xi = \frac{9n}{\left(n^2 - k^2 + 2\right)^2 + 4n^2k^2}$$

Applying the n(405 nm) and k(405 nm) values estimated using Eqs. (5) and (6) for $[NO_2]/[O_3]$ ratios from 0.1 to 10, the ξ values were estimated to be 0.69–0.77. The MAC values at 405 nm were estimated from the reported $\alpha(365 \text{ nm})/\rho$ values to be 0.30–0.48 m²g⁻¹C, using the mean angstróm exponent, 3.2 ± 1.2 , for LA and the ξ values. The ranges of the best estimates (upper and lower limits) of the MAC values at 405 nm for the toluene-SOAs with a diameter of 200 nm estimated in the present study, 0.11–0.27 (0.08–0.36) m²g⁻¹, were converted to those per carbon mass, 0.22–0.57 (0.16–0.76) m²g⁻¹C, by taking into account the range of the O/C, H/C, and N/C ratios measured by the ToF-AMS during "runs A1–A4". These values are roughly consistent with the MAC values at 405 nm estimated based on the observations in LA by Zhang et al. (2011) (0.30–0.48 m²g⁻¹C).



(7)

(8)

The typical MAC values at 405 and 532 nm for the BC particles have been estimated to be 10.2 and $7.8 \text{ m}^2 \text{ g}^{-1}$, respectively, from the values reported by Bond and Bergstrom (2006) assuming an AAE of 1. The estimated MAC values for BC are 30–90 (20–130) and > 170 (> 100) times larger than the best estimates (upper and lower

- limits) of the MAC values determined in this study for the toluene-SOAs at 405 and 532 nm, respectively. In addition, the MAC values for combustion-OA may several times larger than those for the toluene-SOAs as discussed above. However, the temporal and spatial variations of the relative abundance of BC, combustion-OA, and anthropogenic SOAs should be large. Therefore, the light absorption by the anthropogenic SOAs potentially contributes to the radiation balance at UV wavelengths below ~ 400 nm, specification.
 - ically when the relative abundance of the anthropogenic SOAs is significant.

It should be noted that the presence of seed particles may enhance the light absorption of the toluene-SOAs by a factor of 2–3 as reported by Zhong and Jang (2011). Further studies on the contribution of other possible factors, such as the presence of seed particles and the generation of SOA from other anthropogenic VOCs, to the RI

15

6 Conclusions

values of the SOAs should also be important.

In the present study, the $[NO_x]_{ini}$ dependence of the complex RI values at 405, 532, and 781 nm for the toluene-SOAs was determined for the first time. The imaginary part of the RI value (*k*) for the toluene-SOAs was found to increase steeply to shorter wavelengths at < 405 nm, while the real part of the RI value (*n*) gradually increased to shorter wavelengths. The *k* value at 405 nm was found to increase from 1.8×10^{-3} to 7.2×10^{-3} with increasing $[NO_x]_{ini}$ from 109 to 571 ppbv. The HRNO₃/HROrg and O/C ratios of the SOAs determined using the H-ToF-AMS also increased with increasing $[NO_x]_{ini}$. Our results imply that nitro-aromatic compounds, probably nitro-cresols, are the main cause of light absorption by the toluene-SOAs and that oxidation processes of the precursors may also contribute to the enhancement of the light absorption of the



toluene-SOAs. The RI values of the 1,3,5-TMB-SOAs, generated under a high [NO_x]_{ini} condition, were also determined for the first time. The light absorption of the 1,3,5-TMB-SOAs was found to be negligible at all wavelengths (405, 532, and 781 nm). These results are explained by a suppression of formation of nitrophenols due to the instability

⁵ of the NO₂ adducts of the phenoxytype radicals produced from 2,4,6-trimethyphenol, which was formed from the reaction of the 1.3.5-TMB with OH.

Using the obtained RI values, the MACs of the toluene-SOAs at 405 and 532 nm were estimated to be 0.08–0.48 and 0.002–0.081 $m^2 g^{-1}$, respectively, under typical conditions in urban atmospheres during the daytime. These results indicate that light absorption by the SOAs potentially contributes to the radiation balance at UV wave-

- 10 lengths below \sim 400 nm, specifically when the relative abundance of the anthropogenic SOAs are significant compared with those of BC and combustion-OA. The estimated MAC values at 405 nm for the toluene-SOA are roughly consistent with those estimated based on the bulk light absorption of WSOC observed in LA by Zhang et al. (2011).
- This study suggests that the optical properties of the SOAs generated from aro-15 matic hydrocarbons depend on the concentration of NO_x and O₃ during SOA formation and the chemical structure of the precursors. Therefore, further studies of the optical properties of SOAs generated from a variety of aromatic hydrocarbons (including their isomers) and their [NO_v]_{ini} dependence are required for the precise understanding of
- the atmospheric implications of light-absorbing anthropogenic SOAs.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/14551/2012/ acpd-12-14551-2012-supplement.pdf.

Acknowledgement. We would like to thank Y. Goto and Y. Ikeda (Nagoya Univ.) for their assistance with the experiments. This study was supported by the global environmental research 25 fund of the Japanese Ministry of the Environment (RF-1008), the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (KAKENHI 20120007, 21710007, 22310015),



Steel Foundation for Environmental Protection Technology, and the joint research program of the Solar-Terrestrial Environment Laboratory, Nagoya University.

References

5

10

- Adler, G., Abo Riziq, A., Erlick, C., and Rudich, Y.: Effect of intrinsic organic carbon on the optical properties of fresh diesel soot, P. Natl. Acad. Sci. USA, 107, 6699–6704, 2010.
- Akimoto, H., Hoshino, H., Inoue, G., Sakamaki, F., Washida, N., and Okuda, M.: Design and characterization of the evacuable and bankable photochemical smog chamber, Environ. Sci. Technol., 13, 471–475, 1979.

Alexander, D. T. L., Crozier, P. A., and Anderson, J. R.: Brown carbon spheres in East Asian outflow and their optical properties, Science, 321, 833–836, 2008.

Andreae, M. O. and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131–3148, doi:10.5194/acp-6-3131-2006, 2006.

Atkinson, R., Aschmann, S. M., and Arey, J.: Reactions of OH and NO₃ radicals with phenol,

cresols, and 2-nitrophenol, at 296 ± 2 K, Environ. Sci. Technol., 26, 1397–1403, 1992.
 Barnard, J. C., Volkamer, R., and Kassianov, E. I.: Estimation of the mass absorption cross section of the organic carbon component of aerosols in the Mexico City Metropolitan Area, Atmos. Chem. Phys., 8, 6665–6679, doi:10.5194/acp-8-6665-2008, 2008.

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H.,

- 20 Worsnop, D. R., and Jimenez, J. L.: Measurements of secondary organic aerosol from oxidation of cycloalkenes, terpenes, and m-xylene using an Aerodyne aerosol mass spectrometer, Environ. Sci. Technol., 39, 5674–5688, 2005.
 - Bohren, C. F. and Huffman, D. R., Absorption and Scattering of Light by Small Particles, John-Wiley & Sons Inc., New York, 1983.
- ²⁵ Bond, T.: Spectral dependence of visible light absorption by carbonaceous particles emitted from coal combustion, Geophys. Res. Lett., 28, 4075–4078, 2001.
 - Bond, T. C. and Bergstrom, R. W.: Light absorption by carbonaceous particles: an investigative review, Aerosol Sci. Technol., 40, 27–67, 2006.

Bones, D. L., Henricksen, D. K., Mang, S. A., Gonsior, M., Bateman, A. P., Nguyen, T. B., Cooper, W. J., and Nizkorodov, S. A.: Appearance of strong absorbers and fluorophores in



limonene- O_3 secondary organic aerosol due to NH_4^+ -mediated chemical aging over long time scales, J. Geophys. Res., 115, D05203, doi:10.1029/2009JD012864, 2010.

- Cappa, C. D., Che, D. L., Kessler, S. H., Kroll, J. H., and Wilson, K. R.: Variations in organic aerosol optical and hygroscopic properties upon heterogeneous OH oxidation, J. Geophys. Res., 116, D15204, doi:10.1029/2011JD015918, 2011.
- Chang, J. L. and Thompson, J. E.: Characterization of colored products formed during irradiation of aqueous solutions containing H_2O_2 and phenolic compounds, Atmos. Environ., 44, 541–551, 2010.

5

10

- Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, Atmos. Chem. Phys., 10, 1773–1787, doi:10.5194/acp-10-1773-2010, 2010.
- Chen, J., Wenger, J. C., and Venables, D. S.: Near-ultraviolet absorption cross section of nitrophenols and their potential influence on tropospheric oxidation capacity, J. Phys. Chem. A, 115, 12235–12242, 2011.

Cheng, Y., He, K.-B., Zheng, M., Duan, F.-K., Du, Z.-Y., Ma, Y.-L., Tan, J.-H., Yang, F.-M., Liu, J.-

M., Zhang, X.-L., Weber, R. J., Bergin, M. H., and Russell, A. G.: Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China, Atmos. Chem. Phys., 11, 11497–11510, doi:10.5194/acp-11-11497-2011, 2011.

Coeur-Tourneur, C., Henry, F., Janquin, M.-A., and Brutier, L.: Gas-phase reaction of hydroxyl radicals with *m*-, *o*- and *p*-cresol, Int. J. Chem. Kinet., 38, 553–562, 2006.

- ²⁰ Dinar, E., Abo Riziq, A., Spindler, C., Erlick, C., Kissc, G., and Rudich, Y.: The complex refractive index of atmospheric and model humic-like substances (HULIS) retrieved by a cavity ring down aerosol spectrometer (CRD-AS), Faraday Discuss., 137, 279–295, 2008.
 - Drewnick, F., Hings, S. S., DeCarlo, P. F., Jayne, J. T., Gonin, M., Fuhrer, K., Weimer, S., Jiminez, J. L., Demerjian, K. L., Borrmann, S., and Worsnop, D. R.: A new time-of-flight
- aerosol mass spectrometer (ToF-AMS) instrument description and first field deployment, Aerosol Sci. Tech., 39, 637–658, 2005.
 - Favez, O., Alfaro, S. C., Sciare, J., Cachier, H., and Abdelwahab, M. M.: Ambient measurements of light-absorption by agricultural waste burning organic aerosols, J. Aerosol Sci., 40, 613– 620, 2009.
- ³⁰ Finlayson-Piits, B. J. and Pitts Jr., J. N.: Chemistry of the Upper and Lower Atmosphere, Academic Science Press, New York, 2000.
 - Flowers, B. A., Dubey, M. K., Mazzoleni, C., Stone, E. A., Schauer, J. J., Kim, S.-W., and Yoon, S. C.: Optical-chemical-microphysical relationships and closure studies for mixed



carbonaceous aerosols observed at Jeju Island; 3-laser photoacoustic spectrometer, particle sizing, and filter analysis, Atmos. Chem. Phys., 10, 10387-10398, doi:10.5194/acp-10-10387-2010, 2010.

Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: molecular composition, Aerosol Sci. Technol., 31, 5 1345-1358, 1997.

Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331-3345. doi:10.5194/acp-9-3331-2009. 2009.

10

Graber, E. R. and Rudich, Y.: Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, Atmos. Chem. Phys., 6, 729-753, doi:10.5194/acp-6-729-2006, 2006.

- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claevs, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., linuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maen-15 haut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155-5236, doi:10.5194/acp-9-5155-2009, 2009.
- Henze, D. K., Seinfeld, J. H., Ng, N. L., Kroll, J. H., Fu, T.-M., Jacob, D. J., and Heald, C. L.: 20 Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: highvs. low-yield pathways, Atmos. Chem. Phys., 8, 2405–2420, doi:10.5194/acp-8-2405-2008, 2008.

Hoffer, A., Gelencser, A., Guyon, P., Kiss, G., Schmid, O., Frank, G. P., Artaxo, P., and Andreae, M. O.: Optical properties of humic-like substances (HULIS) in biomass-burning

- 25 aerosols, Atmos. Chem. Phys., 6, 3563-3570, doi:10.5194/acp-6-3563-2006, 2006.
 - Jacobson, M. Z.: Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption, J. Geophys. Res., 104, 3527–3542, 1999.

Jang, M. and Kamens, R. M.: Characterization of secondary aerosol from the photooxidation

of toluene in the presence of NO_v and 1-propene, Environ. Sci. Technol., 35, 3626–3639, 30 2001.

Jaoui, M., Edney, E. O., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Suratt, J. D., and Seinfeld, J. H.: Formation of secondary organic aerosol from irradiated α -pinene/toluene/NO_v



mixtures and the effect of isoprene and sulfur dioxide, J. Geophys. Res., 113, D09303, doi:10.1029/2007JD009426, 2008.

- Kim, H., Barkey, B., and Paulson, S. E.: Real refractive indices of α and β -pinene and toluene secondary organic aerosols generated from ozonolysis and photo-oxidation, J. Geophys.
- Res., 115, D24212, doi:10.1029/2010JD014549, 2010. 5
- Kirchstetter, T. W., Novakov, T., and Hobbs, P. V.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, J. Geophys. Res., 109, D21208, doi:10.1029/2004JD004999.2004.

Kleindienst, T. E., Conver, T. S., McIver, C. D., and Edney, E. O.: Determination of secondary

- organic aerosol products from the photooxidation of toluene and their implications in ambient 10 PM_{2.5}, J. Atmos. Chem., 47, 79–100, 2004.
 - Klotz, B., Sørensen, S., Barnes, I., Becker, K. H., Etzkorn, T., Volkamer, R., Platt, U., Wirtz, K., and Martín-Reviejo, M.: Atmospheric oxidation of toluene in a large-volume outdoor photoreactor: in situ determination of ring-retaining product yields, J. Phys. Chem. A, 102, 10289-10299, 1998.
- 15
 - Koch, R., Knispel, R., Elend, M., Siese, M., and Zetzsch, C.: Consecutive reactions of aromatic-OH adducts with NO, NO₂ and O₂: benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline, Atmos. Chem. Phys., 7, 2057-2071, doi:10.5194/acp-7-2057-2007, 2007.
- Kondo, Y., Morino, Y., Fukuda, M., Kanaya, Y., Miyazaki, Y., Takegawa, N., Tanimoto, H., McKen-20 zie, R., Johnston, P., Blake, D. R., Murayama, T., and Koike, M.,: Formation and transport of oxidized reactive nitrogen, ozone, and secondary organic aerosol in Tokyo, J. Geophys. Res., 113, D21310, doi:10.1029/2008JD010134, 2008.

Laskin, J., Laskin, A., Roach, P. J., Slysz, G., Anderson, G. A., Nizkorodov, S. A., Bones, D. L.,

- and Nguyen, L. Q.: High-resolution desorption electrospray ionization mass spectrometry for 25 chemical characterization of organic aerosols, Anal Chem., 82, 2048–2058, 2010.
 - Moosmüller, H., Chakrabarty, R. K., and Arnott, W. P.: Aerosol light absorption and its measurement: a review, J. Quant. Spectrosc. Ra., 110, 844-878, 2009.
- Moosmüller, H., Chakrabarty, R. K., Ehlers, K. M., and Arnott, W. P.: Absorption Angstróm coefficient, brown carbon, and aerosols: basic concepts, bulk matter, and spherical particles, 30 Atmos. Chem. Phys., 11, 1217–1225, doi:10.5194/acp-11-1217-2011, 2011.
 - Nakayama, T., Matsumi, Y., Sato, K., Imamura, T., Yamazaki, A., and Uchiyama, A.: Laboratory studies on optical properties of secondary organic aerosols generated during the



Chem. Phys., 12, 4667-4682, doi:10.5194/acp-12-4667-2012, 2012.

trimethylbenzene in the presence of NO_v: effects of chemical structure on SOA aging, Atmos.

Schnaiter, M., Schmid, O., Petzold, A., Fritzsche, L., Klein, K.-F., Andreae, M. O., Helas, G., 30 Thielmann, A., Gimmler, M., Möhler, O., Linke, C., and Schurath, U.: Measurement of wavelength resolved light absorption by aerosols utilizing a UV-VIS extinction cell, Aerosol Sci. Technol., 39, 249-260, 2005.

der, W. F., and Sehested, J.: Atmospheric chemistry of the phenoxy radical, $C_6H_5O(\bullet)$: UV spectrum and kinetics of its reaction with NO, NO₂, and O₂, J. Phys. Chem. A, 102, 7964– 15 7974, 1998.

- Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, Atmos. Chem. Phys., 10, 997-1016, doi:10.5194/acp-10-997-2010, 2010.
- Sato, K., Hatakeyama, S., and Imamura, T.: Secondary organic aerosol formation during the 20 photooxidation of toluene: NO_x dependence of chemical composition, J. Phys. Chem. A, 111, 9796–9808, 2007.
 - Sato, K., Takami, A., Isozaki, T., Hikida, T., Shimono A., and Imamura, T.: Mass spectrometric study of secondary organic aerosol formed from the photo-oxidation of aromatic hydrocar-
- bons, Atmos. Environ., 44, 1080-1087, 2010. 25 Sato, K., Takami, A., Kato, Y., Seta, T., Fujitani, Y., Hikida, T., Shimono, A., and Imamura, T.: AMS and LC/MS analyses of SOA from the photooxidation of benzene and 1,3,5-

- Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H., and Mocanu, R.: FT-IR study of the ring-10 retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, Atmos. Environ., 36, 3685–3697, 2002.
- 5 comparison with conventional techniques, Atmos. Environ., 44, 3034–3042, 2010b.
- Nakayama, T., Hagino, R., Matsumi, Y., Sakamoto, Y., Kawasaki, M., Yamazaki, A.,

Uchiyama, A., Kudo, R., Moteki, N., Kondo, Y., and Tonokura, K.: Measurements of aerosol

optical properties in Central Tokyo during summertime using cavity ring-down spectroscopy:

photooxidation of toluene and the ozonolysis of α -pinene, J. Geophys. Res., 115, D24204,

- Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.:
 - Secondary organic aerosol formation from *m*-xylene, toluene, and benzene, Atmos. Chem.

Phys., 7, 3909–3922, doi:10.5194/acp-7-3909-2007, 2007.

doi:10.1029/2010JD014387, 2010a.

Paper **Complex refractive Discussion** Paper Platz, J., Nielsen, O. J., Wallington, T. J., Ball, J. C., Hurley, M. D., Straccia, A. M., Schnei-**Title Page** Abstract Conclusions **Discussion** Paper Tables

Discussion Paper

Discussion



ACPD

12, 14551–14589, 2012

- Schnaiter, M., Gimmler, M., Llamas, I., Linke, C., Jäger, C., and Mutschke, H.: Strong spectral dependence of light absorption by organic carbon particles formed by propane combustion, Atmos. Chem. Phys., 6, 2981–2990, doi:10.5194/acp-6-2981-2006, 2006.
- Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd edn., Wiley Interscience, New York, 2006.
- Shama, S. A.: Vacuum ultraviolet absorption spectra of organic compounds in gaseous and liquid state, Thesis of Faculty of Science, Zagazig University, Egypt, 1991.
- Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R., and McNeill, V. F.: Lightabsorbing secondary organic material formed by glyoxal in aqueous aerosol mimics, Atmos. Chem. Phys., 9, 2289–2300, doi:10.5194/acp-9-2289-2009, 2009.
- Chem. Phys., 9, 2289–2300, doi:10.5194/acp-9-2289-2009, 2009.
 Smith, D. F., McIver, C. D., and Kleindienst, T. E.: Primary product distribution from the reaction of hydroxyl radicals with toluene at ppb NO_v mixing ratios, J. Atmos. Chem., 30, 209–228,

5

15

- of hydroxyl radicals with toluene at ppb NO_x mixing ratios, J. Atmos. Chem., 30, 209–228, 1998.
- Sun, H., Biedermann, L., and Bond, T. C.: Color of brown carbon: a model for ultraviolet and visible light absorption by organic carbon aerosol, Geophys. Res. Lett., 34, L17813, doi:10.1029/2007GL029797, 2007.
- Tao, Z. N. and Li, Z. J.: A kinetics study on reactions of C_6H_5O with C_6H_5O and O_3 at 298 K, Int. J. Chem. Kinet., 31, 65–72, 1999.

Trainic, M., Abo Riziq, A., Lavi, A., Flores, J. M., and Rudich, Y.: The optical, physical and

- chemical properties of the products of glyoxal uptake on ammonium sulfate seed aerosols, Atmos. Chem. Phys., 11, 9697–9707, doi:10.5194/acp-11-9697-2011, 2011.
 - Zhang, X., Lin, Y.-H., Surratt, J. D., Zotter, P., Prévôt, A. S. H., and Weber, R. J.: Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: a contrast in secondary organic aerosol, Geophys Res. Lett., 38, L21810, doi:10.1029/2011GL049385, 2011.
- ²⁵ Zhong, M. and Jang, M.: Light absorption coefficient measurement of SOA using a UV-visible spectrometer connected with an integrating sphere, Atmos. Environ., 45, 4263–4271, 2011.



Discussion Paper	AC 12, 14551– Complex index of to	ACPD 12, 14551–14589, 2012 Complex refractive index of toluene-SOA			
Discu	T. Nakay	T. Nakayama et al.			
ssion P	Title	Title Page			
aper	Abstract	Introduction			
	Conclusions	References			
Discu	Tables	Figures			
loissi	۱۹	►I			
n Pap	•	•			
oer	Back	Close			
—	Full Scr	een / Esc			
Discussion	Printer-frie Interactive	Printer-friendly Version Interactive Discussion			
Paper	œ	ву			

Table 1. Experimental conditions, mass concentrations, and surface mean diameters of the SOAs used for determination of the RI values.

Run number ^a	Compounds	[HC] _{ini} (ppmv)	[NO _x] _{ini} b (ppbv)	${M_{ m p}}^{ m c}$ (μg m ⁻³)	${ar{D}_{ extsf{s}}}^{ extsf{d}}$ (nm)
A1	Toluene	3.9	109	31–34	133–149
A2	2 Toluene 3 Toluene		167	40–60	119–170
A3			289	81–113	153–218
A4	Toluene	4.0	571	119–160	211–270
B1	1,3,5-TMB	2.4	571	78–117	370–429
A2 A3 A4 B1	Toluene Toluene Toluene 1,3,5-TMB	3.9 4.0 4.0 2.4	167 289 571 571	40–60 81–113 119–160 78–117	119–17(153–218 211–27(370–429

^a No seed particles were added in the present study.

^b NO was used for all experimental runs. ^c Range of mass concentrations of the SOAs estimated from the size distributions measured by the SMPS assuming a particle density of 1.4 g cm⁻³ (Sato et al., 2007). Effects of dilution and wall loss were not taken into account. ^d Range of surface mean diameters of the SOAs measured by the SMPS.

Run	λ	b_{abs}^{a}	$b_{\rm sca}$ or $b_{\rm ext}^{b}$	Refractive index	
number	(nm)	$(M m^{-1})$	$(M m^{-1})$	(<i>m</i> = <i>r</i>	1 – ki)
				m	k (×1000)
A1	405	1.1–2.9	61.2–71.8	$1.449^{+0.026}_{-0.025}$	1.8 ^{+1.3} _{-1.3}
	532	< 0.8	22.1–27.3	1.431 ^{+0.016} _0.017	0 ^{+2.3}
	781	< 0.6	4.4–6.1	$1.389^{+0.049}_{-0.054}$	0 ^{+1.5}
A2	405	2.0–5.3	67.5–166.5	$1.467^{+0.026}_{-0.027}$	$3.0^{+1.0}_{-1.0}$
	532	< 2.1	26.2–70.5	1.457 ^{+0.015} _0.016	$0.4^{+1.5}_{-0.4}$
	781	< 1.9	4.5–14.5	$1.403^{+0.032}_{-0.034}$	0 ^{+1.6}
A3	405	6.7–10.8	247.5–411.4	$1.468^{+0.025}_{-0.026}$	$3.6^{+0.7}_{-0.7}$
	532	< 1.9	101.5–180.8	1.447 ^{+0.014} _0.017	$0.3^{+0.9}_{-0.3}$
	781	< 0.4	21.6–41.5	1.387 ^{+0.024} _0.025	0 ^{+0.6} _0
A4	405	24.8–43.0	762.8–1263.3	$1.567^{+0.035}_{-0.034}$	$7.2^{+1.0}_{-1.0}$
	532	1.2-4.0	454.2–546.8	1.498 ^{+0.015} _0.014	$1.0^{+0.7}_{-0.8}$
	781	< 0.8	72.1–146.7	$1.452^{+0.027}_{-0.025}$	0 ^{+0.6} _0
B1	405	< 1.3	722.2–953.5	$1.485^{+0.025}_{-0.024}$	$0.2^{+0.4}_{-0.2}$
	532	< 1.1	529.3–679.3	$1.459^{+0.016}_{-0.017}$	0 ^{+1.0}
	781	< 1.3	186.8–191.0	$1.423^{+0.015}_{-0.016}$	$0.2^{+0.7}_{-0.2}$

Table 2. Absorption, scattering, and extinction coefficients used for the analyses and the RI values determined in the present study.

^a Ranges of the absorption coefficients at 405, 532, and 781 nm measured using the PASS-3 instrument (12 min average).

^b Ranges of the scattering coefficients at 405 and 781 nm and those of the extinction coefficients at 532 nm measured using the PASS-3 and CRDS instruments, respectively (12 min average).



Discussion Pa	AC 12, 14551–	PD 14589, 2012				
iper	Complex index of to	Complex refractive index of toluene-SOA				
Discu	T. Nakay	T. Nakayama et al.				
ssion F	Title	Title Page				
aper	Abstract	Introduction				
_	Conclusions	References				
Disc	Tables	Figures				
ussio	I	►I				
n Pal	•	•				
per	Back	Close				
_	Full Scr	Full Screen / Esc				
Discuss	Printer-frie	Printer-friendly Version				
ion F	Interactive	Interactive Discussion				
aper	CC O					

Table 3. Effective concentrations of NO_2 , NO, and O_3 during SOA formation and the chemical properties of the SOAs.

Run number	[NO ₂] _{eff} ^a (ppbv)	[NO] _{eff} ^a (ppbv)	[O ₃] _{eff} ^a (ppbv)	Y _{NO2} ^b	HRNO ₃ /HROrg ^c	O/C ^c
A1	13	0.7	178	0.34	0.023 ± 0.002	0.64 ± 0.01
A2	2	0.4	205	0.41	0.026 ± 0.005	0.66 ± 0.02
A3	45	1.9	261	0.55	0.025 ± 0.004	0.70 ± 0.02
A4	97	2.5	301	0.69	0.037 ± 0.008	0.73 ± 0.02
B1	43	1.1	277	_	0.019 ± 0.001	0.49 ± 0.01

^a Effective NO₂, NO, and O₃ concentrations during the SOA formation, which were estimated using Eq. (4), see text for details.

^b Effective yield of the methyl phenoxy radials with NO₂ during the SOA formation, which were estimated using Eq. (3), see text for details.

^c Average $(\pm 1\sigma)$ of the HRNO₃/HROrg and O/C ratios of the SOAs measured by the H-ToF-AMS during the periods used for the determination of the RI values.



Fig. 1. Schematic diagram of the experimental setup. SMPS, scanning mobility particle sizer; PASS-3; 3λ -photoacoustic soot spectrometer; CRDS, cavity ring-down spectrometer; FT-IR, fourier transform infrared spectrometer; H-ToF-AMS: high-resolution time-of-flight aerosol mass spectrometer.







Fig. 2. Temporal profiles of **(a)** toluene (open circles), NO (open inverted triangles), NO_2 (open triangles), O_3 (open squares), **(b)** mass concentrations (filled circles), and surface mean diameters (filled triangle) during "run A4". A bar indicates the period used for analysis of optical properties.



























Fig. 7. One of the significant reaction schemes for the formation of nitro-cresols during photoxidation of toluene in the presence of NO_x . The bold arrows indicate the major reaction path leading to formation of 4-nitro-*o*-cresol under our experimental conditions.













Fig. 9. $[NO_2]/[O_3]$ dependence of the MAC values at **(a)** 405 and **(b)** 532 nm for the toluene-SOAs with particle diameters of 200, 400, and 600 nm, assuming a constant $[NO]/[NO_2]$ (= 0.04). The solid and dashed lines are the best estimation and upper (or lower) limit values, respectively.