



Heating rates and surface dimming due to black carbon aerosol absorption associated with a major U.S. city

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[1] In situ airborne measurements of actinic flux and the mass and mixing state of individual refractory black carbon (BC) particles were made in the lower troposphere around a major U.S. metropolitan area. These data were used to estimate atmospheric heating rates and surface dimming due to absorption of solar radiation by refractory BC. Direct absorption by ozone is also calculated and averages 10% of that of BC below 4 km but becomes dominant above this altitude. Variability in BC absorption is large due to source variability and clouds. Average BC heating rates are much smaller than those associated with BC and other absorbing aerosol components in global hotspot regions. These results, which are specific to refractory BC absorption, will help determine the value of short-term climate-change mitigation strategies involving BC emission reductions. They may also be used to estimate refractory BC contributions to total aerosol absorption. **Citation:** Schwarz, J. P., H. Stark, J. R. Spackman, T. B. Ryerson, J. Peischl, W. H. Swartz, R. S. Gao, L. A. Watts, and D. W. Fahey (2009), Heating rates and surface dimming due to black carbon aerosol absorption associated with a major U.S. city, *Geophys. Res. Lett.*, 36, L15807, doi:10.1029/2009GL039213.

1. Introduction

[2] The radiative forcing of anthropogenic black carbon (BC) aerosol is significant on a global scale [Forster *et al.*, 2007] and can be dramatic on local and regional scales [e.g., Tripathi *et al.*, 2005]. Direct radiative forcing from global fossil-fuel BC is estimated at 0.2 W/m², while regional surface forcing in India can easily exceed 30 W/m². Recent work suggests that BC contributions may dominate the estimated future impact of short-lived species [Levy *et al.*, 2008] and that reducing BC particulate emissions from specific sources in developing countries is an important short-term strategy in addressing both global [Bond and Sun, 2005; Sato *et al.*, 2003] and regional climate change [Shindell and Faluvegi, 2009].

[3] Here we present simultaneous in situ measurements of refractory BC (rBC) mass loadings and mixing state and actinic flux made in the lower troposphere (below 6 km) over a major USA metropolitan region (Houston, TX). The

data are used to quantify local heating rates in the atmosphere and atmospheric dimming due to rBC absorption of radiation in the wavelength band 280–2500 nm. Shortwave absorption by O₃, a short-lived yet important byproduct of anthropogenic emissions, is also presented to provide context for the rBC results. This work is specific to rBC aerosol, helping to separate its role from that of total aerosol (as in work by, e.g., Novakov *et al.*, [2008]) and organic aerosols including “brown carbon” [e.g., Barnard *et al.*, 2008]. Here rBC’s direct radiative effects on a local scale are founded on specific measurements of mass abundance and mixing state of rBC without sensitivity to other atmospheric absorbers.

2. Measurements and Results

[4] During the Texas Air Quality Study (TexAQS) the NOAA WP-3D research aircraft conducted 16 flights between 11 September 2006 and 12 October 2006 centering on southeastern Texas and Houston. Typically flights began in the late morning and ended with the waning sun at an airfield (Ellington Field) narrowly outside the metropolitan area. Overall the flights provided 85 hours of sampling from near the ground to 6 km altitude during periods where the solar zenith angle was less than 70 degrees. TexAQS targeted urban and industrial emission sources; however, since routine industrial emissions tend to be free of BC and are not sources of ozone, we do not consider this to have an important influence on this analysis. Periods when the aircraft was in the boundary layer (<1 km) within the Houston metropolitan area, defined as the area encompassed by the outer beltway (Beltway 8) highway that circumscribes the city, are assumed to characterize this major urban area because of the strong vertical mixing in this sampling region and the concentration of urban development within the beltway. Four hours of sampling occurred within this volume, which is bounded by latitudes ~29.6–29.95 N and longitude ~95.56–95.14W.

[5] Refractory black carbon aerosol mass mixing ratio, size distribution, and mixing state were measured with a Single Particle Soot Photometer (SP2), which has been described elsewhere [Schwarz *et al.*, 2008a, and references therein]. Briefly, the instrument uses an intense intracavity laser (1064 nm) to heat the refractory carbon (*i.e.* rBC) component of fine-mode aerosols to vaporization (~3500 C). Analysis of the thermal radiation emitted by the hot material determines its mass and constrains its composition. The instrument detects rBC cores in the size range of 90–600 nm volume equivalent diameter (VED, assuming a density of 2.0 g/cc) irrespective of morphology or internal mixing with organic or non-organic materials. rBC mass is

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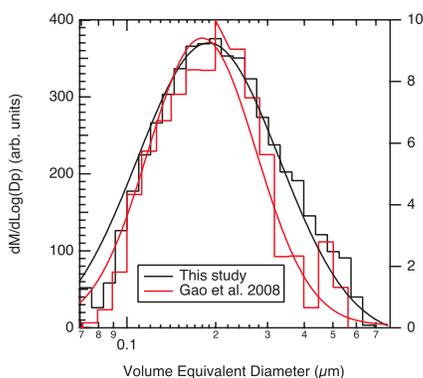


Figure 1. Mass distributions of rBC particles measured in tropospheric flights over Texas (black histogram) with its lognormal distribution fit (smooth black line). The distribution of rBC cores is constructed of 120,000 rBC-containing particles randomly selected from approximately 34 million contained in this data set. For comparison, the average mass distribution in the tropical lower stratosphere (red histogram) is shown with its lognormal distribution fit (smooth red line); this distribution was used to test Rayleigh-Debye-Gans theory against Mie theory calculations of rBC solar absorption [Gao *et al.*, 2008].

determined with an accuracy of 15% [Slowik *et al.*, 2007]. Thus the term “refractory black carbon” (“rBC”) is used here to refer specifically to the refractory carbon detected by the SP2, and does not include the mass of organic carbon typically associated with soot particles. Particle-by-particle rBC mass values are integrated over 1-s intervals and corrected by 10% to provide mass loadings with a combined uncertainty of 30% for the accumulation mode of rBC. Smaller size modes of rBC are not expected to contribute significantly to total rBC mass in the air masses measured here [Schwarz *et al.*, 2008b]. Size distributions of rBC are built from individually detected particle masses. Analysis of the time evolution of the scattered-light signal detected as a rBC-containing particle is heated identifies internal mixtures of rBC with non-refractory material. The ensemble rBC mixing state is represented by the number fraction of detected rBC particles associated with additional materials as measured over 1-s sampling periods. The detection limit of this approach is estimated to be equivalent to a sulfate coating thickness of ~ 25 nm [Schwarz *et al.*, 2008a].

[6] Spectrally resolved solar actinic flux from 280 to 690 nm was measured with 1-nm resolution in situ using a combination of two spectrometers that allow separation of upwelling and downwelling radiation [Stark *et al.*, 2007]. Actinic flux was extended to 2.5- μm wavelength using a pseudospherical version of the Discrete Ordinates Radiative Transfer Code (DISORT), as implemented in the libRadtran software package [Mayer and Kylling, 2005] at a single solar zenith angle (SZA). The flux measurements contribute 7% uncertainty in calculated energy deposition rates. Satellite measurements from the Ozone Monitoring Instrument (OMI) were used to constrain model assumptions about the surface albedo as well as ozone column amounts. Because the OMI albedo measurements are in the ultraviolet and visible wavelength bands, they are not fully appropriate to

the short-wave IR heating considered here. However, the model results were scaled to match upward- and downward-welling measurements from the spectrometers in the wavelength range of 655–690, reducing modeling errors in actinic-flux magnitudes to the level of $\sim 20\%$. The extended wavelength range of 0.7–2.5 μm represents only 35% of the net energy deposition to BC and contributes an estimated 10% uncertainty to calculated heating rates and atmospheric dimming values, while having only negligible dependence on SZA.

[7] Ozone was measured with 3% uncertainty on a 1-s time base using NO-induced chemiluminescence [Ryerson *et al.*, 1998]. Measured ozone mixing ratios ranged from 11–147 ppbv with an average of 54 ppbv. This variability is reflected in the heating rates calculated below. The ozone absorption cross-section for heating rate calculations was taken from the MODTRAN database for a temperature of 300 K [Berk *et al.*, 1998].

[8] The initial heating-rate calculation follows the approach of Gao *et al.* [2008], which was applied to lower stratospheric tropical rBC aerosol. Briefly, a theoretical estimate of the wavelength-dependent absorption cross section of rBC aerosol or ozone is multiplied by actinic flux and integrated over wavelength to obtain energy deposition rates in sampled air masses per unit rBC mass or ozone, respectively. Gao *et al.* [2008] showed that the Raleigh-Debye-Gans (RDG) approximation of the rBC absorption cross section gives a result equivalent to that of Mie theory for a typical size distribution of externally mixed rBC mass. We assume that rBC particles are composed of 50 nm primary nodules with refractive index (2, 1) and density 2 g/cc. The size distribution of rBC particles obtained here, peaking near 200-nm VED, agrees well with that used in the Gao *et al.* study (Figure 1). SP2 observa-

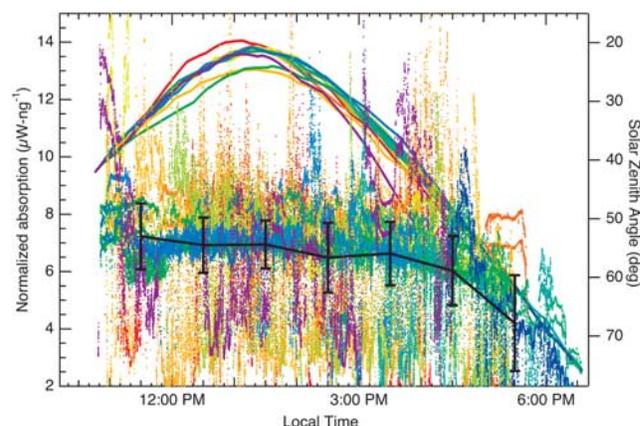


Figure 2. Solar absorption (0.3–2.5 μm) per unit rBC-mass (points, 1-s data) and solar zenith angle (colored lines) plotted against local time and colored by flight number. Average absorption of rBC is shown in black with whiskers denoting average deviation from the mean. A total of 16 flights occurred from Sept. 11 to Oct. 12 2006. Extreme values of the normalized solar absorption are due to the presence of clouds near the flight path, which either enhance or decrease actinic flux. Local surface albedo and column extinction will also influence the actinic flux. SZA varies with time of day, date, and aircraft location.

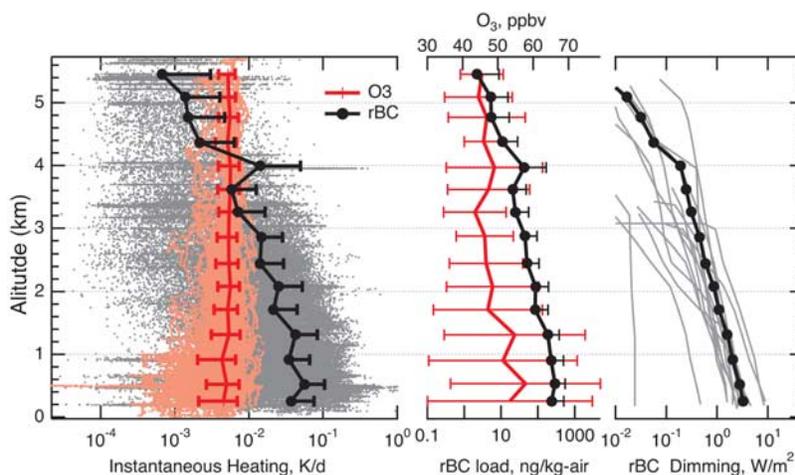


Figure 3. (left) Average vertical profiles of heating rates due to solar absorption calculated for ozone and rBC aerosol as observed in this data set (points represent 1-s values). Whiskers represent one standard deviation in each altitude bin (~ 0.4 km). BC whiskers to low values are not shown because of the log scale. (middle) Average vertical profiles of rBC and ozone concentrations. Whiskers represent one standard deviation. (right) Atmospheric dimming as a function of altitude calculated from integrated rBC absorption of downwelling radiation ($0.3\text{--}2.5\ \mu\text{m}$ wavelength). Values are shown for individual flights (grey) and for the average of all flights (red).

tions show, in general, only small variability in mass-weighted size distributions of rBC [e.g., Shiraiwa *et al.*, 2008; Schwarz *et al.*, 2008a], although this is not the case when sampling very fresh emissions. The power deposited into a unit mass of rBC aerosol or ozone is scaled to the measured amount of rBC or ozone in a volume of air and divided by the specific heat of the air to obtain an instantaneous heating rate, here presented as a diurnal average. rBC absorption cross sections were scaled upward from the RDG value to account for the internal mixtures with rBC that increase its absorption. Schwarz *et al.* [2008b] calculated theoretical enhancements for dried rBC particles associated with biomass burning and urban sources measured in this same dataset; their values are used here as follows. If the number fraction of coated rBC particles observed within 1 s was less (more) than 60%, then an enhancement factor of 23% (41%) was applied to the heating rate determined for that second. 20% of the air masses sampled were associated with the larger enhancement value, resulting in a campaign average mass-specific absorption (MSA) of $7.3 \pm 2.2\ \text{m}^2/\text{g}$ at 532 nm, generally consistent with estimates of MSA for BC in the literature. The enhancement factors bracket the range observed in the campaign and contribute an additional 10% uncertainty in the rBC absorption cross-section. The internal mixing state measured by the SP2 in this data set is representative of low relative humidity conditions due to heating of ambient air during sampling into the aircraft. Ambient relative humidity, which averaged 58% during these measurements, could increase estimated rBC absorption further because ambient water uptake may increase coating thicknesses depending on the composition of the coating. The net systematic uncertainty in heating rates is 35% for individual known error sources summed in quadrature.

[9] Atmospheric dimming values are based on integrating the downwelling radiative flux absorbed by rBC as measured from the upper altitude of measurements (6 km). The downwelling flux only was multiplied by the rBC absorp-

tion cross-section to calculate the amount of radiation blocked from reaching lower altitudes. This value was integrated to the ground to provide a surface dimming value. Surface dimming values specific to the metropolitan area are not available because vertical profiles were not flown over the city. Based on calculations of Rayleigh scattering, the difference between downwelling flux and solar irradiance (the quantity ideally measured for dimming) at an SZA of 20 degrees is 10% increasing to 30% at 45 degrees. Thus the atmospheric dimming values here are most representative of high noon.

[10] Heating rates due to rBC are found to be largely insensitive to SZA, varying only 25% for SZAs in the range 20–60 degrees because rBC absorbs energy primarily in a wavelength range ($\sim 350\text{--}700$ nm) relatively free of atmospheric absorption by trace gases. In contrast, ozone absorption shows a stronger dependence due to its sensitivity to UV radiation, dominated by ozone absorption and Rayleigh scattering. Ozone absorption changes 40% over the same SZA range. Figure 2 shows rBC solar absorption normalized by rBC mass mixing ratio, and SZA as functions of time of day. The large scatter in absorption rate at a given SZA is mainly due to clouds that can both enhance and decrease actinic flux. Due to the expected increase in planetary albedo with altitude, actinic flux and hence rBC absorption increased weakly with altitude equivalent to a 25% increase from the ground to 6 km. Examination of the underlying clear-sky rBC-normalized solar absorption shows that it can be generally approximated for this study region as $7 \pm 2.5\ \mu\text{W}(\text{ng-rBC})^{-1}$ for most daylight hours. Model tests indicate that the likely global variability of actinic flux in the context of extrapolating the clear-sky rBC heating rates to other areas is generally less than a factor 2 over typical ranges of altitude, SZA, albedo, water vapor, and ozone in the troposphere. Comparison of normalized absorption between flight legs over the Gulf of Mexico and the urban area show they agree, in cloud-free conditions, within 15%.

[11] Vertical profiles of in situ heating rates and concentrations of rBC and O₃, and the atmospheric dimming associated with rBC aerosol from all flights are shown in Figure 3. In situ heating rates are largely proportional to the local daytime mixing ratio and mass loading of O₃ and rBC respectively. Averaged below 4 km, rBC heating is larger than that of O₃ by a factor 10. rBC heating rates (1-s average) vary over more than three orders of magnitude, with the largest values from sampled plumes associated with biomass burning emissions. In biomass burning plumes the instantaneous heating rate peaked at 1 K d⁻¹ (diurnal average). Over the entire campaign region rBC heating rates averaged 0.045 ± 0.02 K d⁻¹, roughly half of the value in the urban region defined above, where they averaged 0.1 ± 0.04 K d⁻¹. In the urban area rBC heating was a factor 20 higher than that due to O₃ absorption of solar radiation. Surface dimming due only to rBC absorption of down-welling solar radiation averaged 3.3 ± 1 W m⁻² during the day, with day-to-day variability of roughly a factor of three within a very large range.

3. Discussion and Conclusion

[12] The weak dependence of rBC shortwave absorption on solar zenith angles observed here suggests that the energy deposition to dry rBC of 7 ± 2.5 μW-(ng-rBC)⁻¹ during daylight hours may be generally appropriate to other geographic regions with comparable mass size distributions of rBC and similar clear sky conditions. This value will be an underestimate if ambient conditions result in significant uptake of water on the particles, or an over estimate if actinic flux (as weighted by rBC spectral absorption) is significantly reduced e.g. by clouds. Estimates of absorption of internally mixed rBC aerosol in the lower stratosphere suggest that aging of rBC particles increases dry absorption by only ~20% above that observed for the mixtures in this data set [Schwarz et al., 2008a]. The fact that rBC heating rates are not strongly dependent on solar zenith angle (unlike solar irradiance) suggests that its relative contribution to atmospheric instability will be largest in the morning and evening.

[13] The radiative impact of rBC on the Houston urban region is small compared to the impact of absorbing aerosol in developing countries such as China, where surface dimming estimates attributed to absorbing aerosols are more than an order of magnitude higher than the 3.3 ± 1.2 W m⁻² estimated here [Wendisch et al., 2008]. The rBC heating rate estimated for the Houston urban area of 0.1 ± 0.04 K d⁻¹ is a factor of ten larger than the direct radiative impact of lower tropospheric ozone, but is still unlikely to significantly influence local atmospheric stability [Feingold et al., 2005].

[14] These results are best examined in the context of all absorbing aerosols, of which rBC is only one component. They are unique to rBC, and are unaffected by the presence of other absorbing species such as dust or light-absorbing organics [Andreae and Gelencser, 2006]. In contrast, Ramanathan et al. [2007] link absorption coefficient measurements made with a miniaturized aethalometer to a radiative transfer model. By coupling their modeled heating rate due to the elemental carbon and organic in soot with the measured black carbon loadings in the Maldives, we obtain a diurnal heating rate per unit black carbon mixing ratio of

0.6 ± 0.4 K/d/(μg-BC/kg-air). This is close to three times larger than the value of 0.23 ± 0.09 K/d/(μg-rBC/kg-air) derived here for the Maldives based on assuming that the 7 ± 2.5 μW-(ng-rBC)⁻¹ energy deposition rate to dry rBC is constant when SZA is greater than 70 degrees, and zero otherwise. The difference in the results (which agree within large uncertainty) may be attributable in part to absorption by organic carbon supporting the idea that brown carbon may have an even more significant role than presently estimated [Barnard et al., 2008]. Although the uncertainty in this comparison is large, it highlights the importance of source-specific absorption information for interpreting aerosol radiative impacts and strategizing climate change mitigation [Shindell et al., 2008].

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References

- Andreae, M. O., and A. Gelencser (2006), Black or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, *6*, 3131–3148.
- Barnard, J. C., R. Volkamer, and E. I. Kassianov (2008), 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.
- Berk, A., L. S. Bernstein, G. P. Anderson, P. K. Acharya, D. C. Robertson, J. H. Chetwynd, and S. M. Adler-Golden (1998), MODTRAN cloud and multiple scattering upgrades wit application to AVIRIS, *Remote Sens. Environ.*, *65*(3), 367–375, doi:10.1016/S0034-4257(98)00045-5.
- Bond, T. C., and H. Sun (2005), Can reducing black carbon emissions counteract global warming?, *Environ. Sci. Technol.*, *39*(16), 5921–5926, doi:10.1021/es0480421.
- Feingold, G., H. Jiang, and J. Y. Harrington (2005), On smoke suppression of clouds in Amazonia, *Geophys. Res. Lett.*, *32*, L02804, doi:10.1029/2004GL021369.
- Forster, P., et al. (2007), Changes in atmospheric constituents and in radiative forcing, in *Climate Change 2007: The Physical Science Basis—Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon et al., pp. 129–233, Cambridge Univ. Press, New York.
- Gao, R. S., S. R. Hall, W. H. Swartz, J. P. Schwarz, J. R. Spackman, L. A. Watts, D. W. Fahey, K. C. Aikin, R. E. Shetter, and T. P. Bui (2008), Calculations of solar shortwave heating rates due to black carbon and ozone absorption using in situ measurements, *J. Geophys. Res.*, *113*, D14203, doi:10.1029/2007JD009358.
- Levy, H., II, M. D. Schwarzkopf, L. Horowitz, V. Ramaswamy, and K. L. Findell (2008), Strong sensitivity of late 21st century climate to projected changes in short-lived air pollutants, *J. Geophys. Res.*, *113*, D06102, doi:10.1029/2007JD009176.
- Mayer, B., and A. Kylling (2005), Technical note: The libRadtran software package for radiative transfer calculations—Description and examples of use, *Atmos. Chem. Phys.*, *5*, 1855–1877.
- Novakov, T., T. W. Kirchstetter, S. Menon, and J. Aguiar (2008), Response of California temperature to regional anthropogenic aerosol changes, *Geophys. Res. Lett.*, *35*, L19808, doi:10.1029/2008GL034894.
- Ramanathan, V., M. V. Ramana, G. Roberts, D. Kim, C. Corrigan, C. Chung, and D. Winkler (2007), Warming trends in Asia amplified by brown cloud solar absorption, *Nature*, *448*, 575–578, doi:10.1038/nature06019.
- Ryerson, T. B., et al. (1998), Emission lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, *103*, 22,569–22,583, doi:10.1029/98JD01620.
- Sato, M., J. Hansen, D. Koch, A. Lacis, R. Ruedy, O. Dubovik, B. Holben, M. Chin, and T. Novakov (2003), Global atmospheric black carbon inferred from AERONET, *Proc. Natl. Acad. Sci. U. S. A.*, *100*(11), 6319–6324, doi:10.1073/pnas.0731897100.
- Schwarz, J. P., et al. (2008a), Coatings and their enhancement of black carbon light absorption in the tropical atmosphere, *J. Geophys. Res.*, *113*, D03203, doi:10.1029/2007JD009042.

- Schwarz, J. P., et al. (2008b), Measurement of the mixing state, mass, and optical size of individual black carbon particles in urban and biomass burning emissions, *Geophys. Res. Lett.*, *35*, L13810, doi:10.1029/2008GL033968.
- Shindell, D. T., and G. Faluvegi (2009), Climate response to regional radiative forcing during the twentieth century, *Nat. Geosci.*, *2*, 294–300, doi:10.1038/NGEO473.
- Shindell, D. T., H. Levy II, M. D. Schwarzkopf, L. W. Horowitz, J.-F. Lamarque, and G. Faluvegi (2008), Multimodel projections of climate change from short-lived emissions due to human activities, *J. Geophys. Res.*, *113*, D11109, doi:10.1029/2007JD009152.
- Shiraiwa, M., Y. Kondo, N. Moteki, N. Takegawa, L. K. Sahu, A. Takami, S. Hatakeyama, S. Yonemura, and D. R. Blake (2008), Radiative impact of mixing state of black carbon aerosol in Asian outflow, *J. Geophys. Res.*, *113*, D24210, doi:10.1029/2008JD010546.
- Slowik, J. G., et al. (2007), An inter-comparison of instruments measuring black carbon content of soot particles, *Aerosol Sci. Technol.*, *41*(3), 295–314, doi:10.1080/02786820701197078.
- Stark, H., B. M. Lerner, R. Schmitt, R. Jakoubek, E. J. Williams, T. B. Ryerson, D. T. Sueper, D. D. Parrish, and F. C. Fehsenfeld (2007), Atmospheric in situ measurement of nitrate radical (NO_3) and other photolysis rates using spectroradiometry and filter radiometry, *J. Geophys. Res.*, *112*, D10S04, doi:10.1029/2006JD007578.
- Tripathi, S. N., S. Dey, V. Tare, and S. K. Satheesh (2005), Aerosol black carbon radiative forcing at an industrial city in northern India, *Geophys. Res. Lett.*, *32*, L08802, doi:10.1029/2005GL022515.
- Wendisch, M., et al. (2008), Radiative and dynamic effects of absorbing aerosol particles over the Pearl River Delta, China, *Atmos. Environ.*, *42*, 6405–6416, doi:10.1016/j.atmosenv.2008.02.033.
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