Impacts of black carbon aerosol on photolysis and ozone

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[1] The regional distributions of black carbon aerosol (soot) are calculated and the impacts of black carbon aerosol on photolysis frequencies and ozone concentrations are evaluated in Houston, Texas, using a regional chemical transport model. Compared with measurements of the fine particle matter in the Houston area, the simulated daily mean black carbon aerosol concentration is in agreement with observations in the urban sites. Black carbon aerosol reduces the photolysis frequencies of \([O_3]([D])\) and \([NO_2]\) in the planetary boundary layer by 10–30% when air pollution is highest in the Houston area. As a result, the ground level ozone concentration in the Houston area decreases by 5–20%. Our study demonstrates that the impacts of black carbon aerosol on photochemistry are important in polluted urban atmospheres.


1. Introduction

[2] Atmospheric aerosols play an important role in the Earth-atmosphere system [Houghton et al., 2001; Prospero and Lamb, 2003; Zhang et al., 2004a]. Black carbon particles (soot) are formed as a result of incomplete combustion of coal, diesel fuels, biofuels, and outdoor biomass burning. An average global source of soot is estimated to be 8 Tg yr\(^{-1}\) [Penner et al., 1993; Bond et al., 2004]. Soot is of special interest because of its significant impact on global radiative balance and climate [Chameides and Bergin, 2002], both directly by absorbing solar and terrestrial radiation [Horvath, 1993; Ackerman et al., 2000] and indirectly by altering cloud formation since soot may serve as cloud condensation nuclei (CCN) [Jensen and Toon, 1997]. Also, soot particles are believed to exert deleterious impacts on health and visibility. Definitive studies have yet to be conducted that conclusively link soot to health problems, but various epidemiological and toxicological studies show that soot causes tissue irritation and the release of toxic chemical intermediates from scavenger cells [Lighty et al., 2000]. In addition, heterogeneous reactions on soot have the potential to play a major role in determining the chemical composition of the atmosphere [Calvert et al., 1994; Lei et al., 2004; Zhang and Zhang, 2005].

[3] Most aerosols cool the atmosphere by increasing Earth’s reflectivity, but soot warms the atmosphere by absorbing sunlight. The contribution of soot to global warming may be substantial, perhaps second only to that of CO\(_2\) [Jacobson, 2001; Hansen et al., 2000]. When considering the absorption of sunlight by soot, especially to ultraviolet (UV) radiation, the effect on photolysis frequencies in the troposphere needs to be taken into account. Dickerson et al. [1997] considered the effect of absorbing aerosol in the planetary boundary layer in model simulations and found that UV-absorbing aerosol reduced calculated ozone mixing ratios by up to 24 ppbv. Using a detailed one-dimensional radiative transfer model, Liao et al. [1999] evaluated the effects of aerosols on 14 tropospheric photolysis reactions under noncloudy and cloudy sky conditions. Martin et al. [2003] and Tie et al. [2005] used a global three-dimensional model of tropospheric chemistry to investigate the photochemical effects of aerosols on tropospheric chemistry, including the soot effects. These studies are mainly concerned with the global-scale effects of soot on photochemistry. A difficulty dealing with soot radiative properties lies in its mixing state [Posfai et al., 1999], which is characterized by two extreme scenarios: soot partially or entirely coated within other organic/inorganic constituents (internally mixed) and distinct soot particles mixed externally with other aerosol types (externally mixed). Model calculations indicated that soot could exert higher “positive” direct radiative forcing when associated with other scattering aerosols, e.g., sulfate, nitrate, and organic carbon [Jacobson, 2000]. In addition, internal mixture of soot with other aerosol ingredients appears significantly more absorptive than the external mixture counterpart [Jacobson, 2000]. The radiative effects of pure soot and internal and external mixtures of soot-containing aerosols were assessed in the work by Liao et al. [1999].

[4] Two studies have also assessed the impact of soot on photolysis rates. Jacobson [1998] calculated that aerosol particles containing a black (elemental) carbon core coated by organic material and/or other material might reduce
ozone by 5–8% in Los Angeles. It was also found that strong absorption reduced photolysis coefficients of several gases in eastern Los Angeles, but the presence of strongly scattering (nonabsorbing) aerosols enhanced photolysis coefficients near the coast in western Los Angeles. Castro et al. [2001] found an even stronger reduction in photolysis coefficients in Mexico City due to absorbing aerosols than found previously in the Los Angeles study. Another study by Stockwell and Goliff [2004] suggested that the impact of photolysis on relative ozone concentrations varied depending on the VOC/NOx ratio.

[5] Houston is the fourth largest metropolitan area in the United States, and hosts one of the world’s largest petrochemical complexes and several large fossil-fueled electric power plants. Transportation and industry emit a great quantity of VOCs, NOx, and SO2, leading to distinct air chemistry over this area. As part of the Houston Supersite Project, measurements of chemical compositions of fine particle matter (PM2.5) were made at several sites in southeast Texas during 2000 by using a tapered element oscillating microbalance (TEOM) [Russell et al., 2004]. The measurements provided the daily mean of elemental carbon at seven sites in the Houston area. The Houston Supersite Project period was also associated with the 2000 Texas Air Quality Study (TexAQS) field campaign with extensive ground- and aircraft-based measurements of ozone and its precursors. Limited ground-based measurements of photolysis rate constants of several key chemical species were conducted in association with the TexAQS 2000 (B. Lefeber, private communications, 2005).

[6] In this paper we used a chemical transport model to simulate the distribution of soot in Houston, Texas. The modeled simulations of soot particles were compared to measurements from the TEOM during the 1999 Houston Supersite Project. An efficient radiation model (FTUV) was coupled to the chemical transport model [Tie et al., 2003] and used to evaluate the effects of clouds and aerosols on photolysis frequencies and chemical compounds. The model calculated photolysis frequencies of NO2 and O3 were compared to field measurements. The impacts of soot on the photolysis frequencies and ozone concentrations were assessed in the Houston area.

2. Methodology

[7] The chemical transport model (HANK) used in the present work was initially developed at the National Center for Atmospheric Research (NCAR) [Hess et al., 2000] and modified for photochemical modeling in the Houston area [Lei, 2003; Lei et al., 2004; Zhang et al., 2004b]. There were 38 layers in the vertical direction from the surface to 100 mbar in a terrain-following coordinate system with 7 layers in the lowest 500 m altitudes. The chemistry in the CTM included treatment of standard gas-phase and heterogeneous chemistry [Lei, 2003]. The organic part was based on the CB-4 mechanism used in the Comprehensive Air Quality Model with the extension version 3.1 (CAMx v3.1, available at http://www.camx.com/) [Gery et al., 1989; Simonaitis et al., 1997; ENVIRON, 2000]. The CB-4 mechanism was modified to represent both polluted and remote tropospheric atmosphere [Lei, 2003; Lei et al., 2004]. The isoprene oxidation mechanism was updated to accommodate the recent advances [Lei, 2003; Lei et al., 2001; Zhang and Zhang, 2002]. The heterogeneous reaction of N2O5 on sulfate aerosols was included in the model [Zhang et al., 1995]. The chemical initial and lateral boundary conditions were interpolated from Modeling Ozone and Related Chemical Tracers (MOZART v2), a global CTM [Horowitz et al., 2003]. The CTM was driven by the output circulation field from a meteorological model, the Penn State/NCAR Mesoscale Model, Version 5 (MM5) [Grell, 1993].

[8] We chose a 5-day episode from 25 August to 29 August 2000 in Houston, Texas. This period corresponds to typical summertime emissions and meteorological conditions in this region. Model simulations were initially performed with a 12 km horizontal resolution with 90 × 90 grid points in eastern Texas. We subsequently conducted model simulations using a 4 km horizontal resolution with 84 × 65 grid points in eastern Texas. The outputs with the 12 km resolution were used for the initial and boundary conditions in the simulations with the 4 km resolution. The meteorological field and emission inventory (EI) were provided by the Texas Commission of Environmental Quality (TCEQ) via a ftp site (ftp.tceq.state.tx.us). The surface EI was chemically speciated (based on the CB-4 mechanism), spatially gridded (4 × 4 km or 12 × 12 km), and temporally resolved (1-hour averaged). The VOC to NOx ratio was not uniform throughout the domain.

[9] We coupled a radiation model (FTUV) [Tie et al., 2003] into the chemical transport model to evaluate the effects of clouds and aerosols on photolysis frequencies and chemical compounds. The radiation model was online with the CTM. A soot module developed by Tie et al. [2001] was included in HANK. For the soot emission in the Houston area, we assumed that the emission rate was correlated to that of CO, as suggested from the study of Baumgardner et al. [2002] in Mexico City.

[10] The FTUV model employed the same physics process as the TUV model [Madronich and Weller, 1990], except that the wavelength bins between 121 and 750 nm were reduced from 140 bins to 17 bins. A correction method was used to reduce the error from FTUV due to its low wavelength resolution. The calculated J values from FTUV agreed within 5% with those calculated from TUV. Detailed descriptions of the FTUV model has been reported by Tie et al. [2003].

[11] In the soot module, the soot particles were separated into two types of aerosols. The first type was assumed to represent new and fresh particles, which were directly emitted from the sources. These particles were assumed to be hydrophobic (i.e., not mixed with other aerosols and not coated by water and acids). These particles were not subject to wet scavenging but were subject to dry deposition with a deposition velocity of 0.1 cm/s as suggested by Cooke and Wilson [1996]. The second type of soot particles represented aged particles, that were assumed to be coated with other aerosol components including liquid water and sulfates, and therefore hydrophilic. This type of aerosol was subject to both wet and dry deposition. The second type of soot was not directly emitted, but was converted from the first type with a rate of 1 day as suggested by Cooke and Wilson [1996]. We did not consider the effects of other aerosols, like sulfate, organic, etc., and scattering by those aerosol types. The soot module was not size resolved.
The simulation period generally corresponded to absence of major weather systems, mostly under clear-sky conditions. In addition, the MM5 failed to reproduce isolated cloud coverage during the simulation. Hence we were unable to include the cloud effects on photolysis rates in this work.

Several model sensitivity studies were performed, including (1) a base run without taking into account of the effect of soot on photolysis and (2) a control run taking into account of the effect of soot on photolysis. The impacts of soot on photolysis frequencies and chemical compounds, especially the ozone concentrations, were assessed by comparing the results from the two cases.

3. Modeled Soot Distribution and Comparison With Observations

Figure 1 illustrates the modeled ground level distributions of soot at 1300 local time (LT) (central daylight time (CDT)) from 25 to 29 August 2000. The calculated surface concentration of soot highlights the dominant impact of the anthropogenic emissions, mainly centered in the Houston urban area. The soot concentration is spatially inhomogeneous, with the highest concentration exceeding 1 $\mu$g m$^{-3}$ related to transportation emissions. Soot concentrations are significantly affected by thunderstorm activity (wet deposition of soot) and the field pattern of winds. We focused on a dry case in which wind (speed and direction) played important roles in controlling the soot concentration in the Houston area. On 25 August the surface wind in Houston was weak from the northeast in the morning, resulting in a high level of soot: more than 1.5 $\mu$g m$^{-3}$ at 1300 LT. The soot was transported to the northwest of the Houston area. On the following day (26 August), the midday wind was also weak, with the wind direction from the southeast. The soot concentration ranged from 0.5 to 1.0 $\mu$g m$^{-3}$ in the Houston area. On 27 and 28 August the noontime wind was stronger from the southeast. The soot concentration decreased to 0.3–0.7 $\mu$g m$^{-3}$ in the Houston area and soot was dispersed mainly to the north of the urban area. On 29 August the wind was generally light and disorganized throughout the Houston area in the early afternoon and the soot concentration was high near the emission source (about 1.0–1.5 $\mu$g m$^{-3}$).

Russell et al. [2004] reported measurement of the chemical composition of fine particle matter at a variety of sites in southeast Texas during 2000 by using a tapered element oscillating microbalance (TEOM). They employed their daily mean measurements of elemental carbon from 25 to 29 August 2000 in the Houston area to compare with our model results. In the Houston area, there were seven sites with the elemental carbon measurements. Figure 2a displays a scatterplot of the measured data points versus the calculated values. The modeled values at the lowest model layer are linearly interpolated to a monitoring site from the four cells surrounding the monitoring station. A correlation coefficient ($R^2$) of 0.65 is obtained from the data shown in Figure 2, indicating a good agreement between the model simulations and measurements of the soot concentration. The comparison of the soot concentrations averaged over the available observation sites between the model simulations and measurements is depicted in Figure 2b. The model predicts the highest and lowest soot concentrations on 25 and 27 August, respectively, in agreement with measurements. Overall, the calculated average concentration in 5 days for all sites is about 0.39 $\mu$g m$^{-3}$, consistent with the observed value of 0.35 $\mu$g m$^{-3}$.

4. Impacts of Soot on Photolysis Frequencies and Ozone

4.1. Photolysis Frequencies

With the coupling of radiation model FTUV into the chemical transport model (HANK), the changes due to the soot on the photolysis rate constants were calculated and analyzed. Figure 3 demonstrates the diurnal variation of $J(O_3(1D))$ and $J(NO_2)$ at La Porte, Texas (−95.050, 29.667), where measurements of photolysis frequencies were available during this episode (B. Lefer, private communications, 2005). The measurements were based on downwelling $J$ values that included a downwelling diffuse radiation component and a direct solar actinic flux component. The total photolysis frequencies were obtained from the downwelling $J$ values using a factor of 1.04 (B. Lefer, private communications, 2005).

The calculated $J(O_3(1D))$ and $J(NO_2)$ diurnal variations are consistent with the measurements (B. Lefer, private communications, 2005). It is evident in Figure 3 that the calculated photolysis is slightly overestimated during the noontime. Inclusion of the soot effect generally yielded the calculated results closer to the observed values. Also, other differences between the calculation and measurement existed. The measured photolysis frequencies exhibited perturbations from 27 to 29 August, which were absent in the calculations. This is likely explained by the fact that the cloud may not be well represented in the dynamical inputs calculated from MM5.

Figures 4 and 5 show the percentage changes of $J(O_3(1D))$ and $J(NO_2)$ near the surface at 1300 LT due to the impact of soot. On 25 August, the soot concentration reached a maximum at 1300 LT during the episode. Consequently, the impacts of soot on $J(O_3(1D))$ and $J(NO_2)$ were the most significant. The values of $J(O_3(1D))$ and $J(NO_2)$ were reduced by as much as 10–30% in the Houston area. On 26 and 29 August the decrease in $J(O_3(1D))$ and $J(NO_2)$ was about 5–20% at 1300 LT. The reduction in $J(O_3(1D))$ and $J(NO_2)$ due to soot absorption was rather small on 27 and 28 August, less than 10%. The impacts of soot on photolysis in the Houston area are similar to those previously reported by Liao et al. [1999]. Their results indicated that soot had a significant impact on $J(O_3(1D))$ and $J(NO_2)$ in highly polluted urban areas, decreasing the average photolysis rates by 9 to 19% over the entire troposphere. However, the soot amount considered in the work of Liao et al. [1999] was considerably larger than that in this present work. Also, in this work we focused primarily on the surface effects of soot on photolysis rates.

4.2. Impacts of Soot on Ozone Concentrations

The photolysis frequencies of $J(O_3(1D))$ and $J(NO_2)$ strongly influence the formation of tropospheric ozone. The combination reaction between the ground state oxygen atom, produced from the photolysis of NO$_2$, and oxygen...
Figure 1. Modeled soot distribution at 1300 LT (CDT) from 25 to 29 August 2000 in Houston, Texas. The panels correspond to the dates during the episode.
molecules forms ozone, representing the only important source of ozone in the troposphere,

\begin{align}
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O}^{(3P)} \\
\text{O}^{(3P)} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align}

The photolysis of ozone by ultraviolet radiation leads to the production of electronically excited O\(^{(1D)}\) atom, which subsequently reacts with H\(_2\)O to form OH,

\begin{align}
\text{O}_3 + \text{hv} & \rightarrow \text{O}_2 + \text{O}^{(1D)} \\
\text{O}^{(1D)} + \text{H}_2\text{O} & \rightarrow 2\text{OH}
\end{align}

OH-initiated oxidation of volatile organic compounds (VOCs) produces organic peroxy (RO\(_2\)) radicals, which facilitate the conversion of NO to NO\(_2\),

\begin{align}
\text{OH} + \text{VOCs} + \text{O}_2 & \rightarrow \text{RO}_2 + \text{others} \\
\text{RO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{NO}
\end{align}

VOCs are emitted into the atmosphere from anthropogenic and natural sources. Hence VOC oxidation in the presence of nitrogen oxides (NO\(_x = \text{NO} + \text{NO}_2\)) considerably enhances ozone production in the troposphere. The reduction of \(J[\text{O}_3 (1\text{D})]\) and \(J[\text{NO}_2]\) due to soot absorption can lead to an important impact on O\(_3\) concentrations.

[20] Figure 6 illustrates the relative change (percent) in ozone concentrations when the effect on the photolysis frequencies due to soot is included. The results presented are the ground level ozone concentrations at 1300 LT (CDT) from 25 to 29 August 2000. On 25 August the impacts of soot on ozone were the highest; the ozone concentration was reduced by about 5–20% in the Houston area. On 26 and 29 August the ozone level was reduced by less than 10%. On 27 and 28 August the ozone decrease was minimal, less than 3%. It is apparent that the effect of soot on O\(_3\) concentrations is dependent on the soot concentration, which is linked to emissions and sensitive to the meteorological conditions, especially the wind. In polluted urban areas, soot can have significant impact on O\(_3\) concentrations.

[21] The work by Castro et al. [2001] reported larger reduction of photolysis rates by aerosols in Mexico City than those found in the present work, but the work of Jacobson [1998] found smaller effects of aerosols on photolysis rates in Los Angeles.

[22] It should be pointed out that in this study we only included a soot module in the chemical transport model that did not differentiate mixing of soot with other types of aerosols. Black carbon aerosol can be internally or exter-
Figure 4. Calculated relative changes (percent) in $J(O_3(1D))$ due to the soot effect at 1300 LT (CDT) from 25 to 29 August 2000 in the Houston area. The panels correspond to the dates during the episode.
Figure 5. Same as Figure 4 except for $J[\text{NO}_2]$. 
Figure 6. Calculated relative changes (percent) in ozone concentrations due to the soot effect at 1300 LT (CDT) from 25 to 29 August 2000 in the Houston area. The panels correspond to the dates during the episode.
nally mixed with other aerosol constituents (such as sulfate and organics) in the atmosphere. The work by Liao et al. [1999] calculated that the absorbing effect of aerosols on photolysis frequencies was 5–15% larger for internally mixed soot-sulfate aerosols compared to the externally mixed particles. There is a lack of field measurements of the mixing state of soot in the Houston area. Furthermore, few experimental studies are available concerning the optical properties of soot containing particles as a function of chemical coatings. Clearly, more physically realistic treatment of mixing state of soot with other aerosol types should be included in further model simulations to assess the impact of soot-containing particles on photolysis frequencies and ozone concentrations.

5. Conclusions

A case study (from 25 to 29 August 2000) was performed to assess the impact of soot on photolysis frequencies and ozone concentrations in Houston, Texas. The calculated daily mean of the soot concentration was in agreement with measurements in seven urban sites associated with the 1999 Houston Superstice Project. The highest soot concentration occurred on 25 August, more than 1.0 μg m⁻³. Geographical distributions of soot in the Houston area were inhomogeneous, and the soot concentration was determined by emissions and dispersed by wind. A radiation model (FTUV) was coupled to the chemical transport model to evaluate the effects of clouds and aerosols on photolysis frequencies and chemical compounds. The calculated photolysis frequencies of \([O_3(1D)]\) and \([NO_2]\) were compared with ground-based measurements, showing a good agreement between the calculated and measured values. Inclusion of soot effect yielded better agreement between the calculated and measured values. On the most polluted day (25 August 2000), the impacts of soot on photolysis frequencies were significant. The calculated \(J[D(1D)]\) and \(J[NO_2]\) values were reduced by 10–30%. The decrease in photolysis frequencies led to a decrease in the surface ozone concentration by about 5–20% in the Houston area. Our results suggest that soot can exert an important effect on photolysis frequencies and ozone concentrations in polluted urban cites.

References


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