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Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols

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[1] We evaluate the sensitivity of tropospheric OH, O3, and O3 precursors to photochemical effects of aerosols not usually included in global models: (1) aerosol scattering and absorption of ultraviolet radiation and (2) reactive uptake of HO2,N O2, and NO3. Our approach is to couple a global 3-D model of tropospheric chemistry (GEOS-CHEM) with aerosol fields from a global 3-D aerosol model (GOCART). Reactive uptake by aerosols is computed using reaction probabilities from a recent review (\( \gamma_{HO2} = 0.2, \gamma_{NO2} = 10^{-4}, \gamma_{NO3} = 10^{-3} \)). Aerosols decrease the O3 → O(1D) photolysis frequency by 5–20% at the surface throughout the Northern Hemisphere (largely due to mineral dust) and by a factor of 2 in biomass burning regions (largely due to black carbon). Aerosol uptake of HO2 accounts for 10–40% of total HOx radical (OH + peroxy) loss in the boundary layer over polluted continental regions (largely due to sulfate and organic carbon) and for more than 70% over tropical biomass burning regions (largely due to organic carbon). Uptake of NO2 and NO3 accounts for 10–20% of total HNO3 production over biomass burning regions and less elsewhere. Annual mean OH concentrations decrease by 9% globally and by 5–35% in the boundary layer over the Northern Hemisphere. Simulated CO increases by 5–15 ppbv in the remote Northern Hemisphere, improving agreement with observations. Simulated boundary layer O3 decreases by 15–45 ppbv over India during the biomass burning season in March and by 5–9 ppbv over northern Europe in August, again improving comparison with observations. We find that particulate matter controls would increase surface O3 over Europe and other industrial regions.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; KEYWORDS: aerosols, ozone, heterogeneous chemistry, radiation, reactive uptake, OH


1. Introduction

[2] Understanding the radiative and heterogeneous chemical effects of aerosols on OH and O3, the main tropospheric oxidants, is a major issue for models of the oxidizing power of the atmosphere, radiative forcing, and surface air quality. The importance of NO3 hydrolysis in aerosols is well established [Heikes and Thompson, 1983; Dentener and Crutzen, 1993; Tie et al., 2001; Liao et al., 2003] and is included in all current-generation global models of tropospheric chemistry. Model calculations by Dentener and Crutzen [1993] indicate that this reaction reduces global tropospheric O3 and OH by 9%. Other aerosol effects have received far less study and are the focus of this paper.

[3] Scattering and absorption of ultraviolet (UV) radiation by aerosols modifies photolysis rates [He and Carmichael, 1999; Liao et al., 1999]. Reactive heterogeneous uptake of HO2, NO2, and NO3 by aerosols may be important as well [Jacob, 2000]. Including these photochemical effects of aerosols in global models could help resolve some long-standing discrepancies with measurements, such as the underestimate of the CO background in the Northern Hemisphere [Hauglustaine et al., 1998; Lawrence et al., 1999; Bergamaschi et al., 2000, 2001; Bey et al., 2001a] and the
overestimate of O₃ over India [Lal and Lawrence, 2001; Martin et al., 2002b].

Recent development of global simulations and observational databases for the major aerosol types (sulfate, black carbon, organic carbon, sea salt, and mineral dust) [Tegen et al., 1997; Takemura et al., 2000; Ghan et al., 2001; Chin et al., 2002; Chiang et al., 2002; Liao et al., 2003] facilitates a more detailed investigation of the photochemical effects of aerosols on tropospheric O₃ and OH. We present here such an investigation using a global 3-D model of tropospheric chemistry (GEOS-CHEM). Section 2 describes the implementation of aerosol photochemistry in GEOS-CHEM and section 3 examines its implications. Section 4 compares the results with observations for species and regions where the effects are particularly large. Global budgets of O₃ and OH are analyzed in section 5.

2. GEOS-CHEM Model

2.1. General Formulation

The GEOS-CHEM model was initially described by Bey et al. [2001a] and subsequent improvements are described by Martin et al. [2002b]. We use here GEOS-CHEM version 4.26 (http://www-as.harvard.edu/chemistry/trop/geo5/) with improved treatment of aerosol photochemical effects and a few other updates as described below. The model is driven by assimilated meteorological data from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO) [Schubert et al., 1993]. The meteorological data include 3-D fields updated every 3 hours for surface fluxes and mixing depths and every 6 hours for other relevant variables. We use for this study the GEOS data for 1996–1997, available with a resolution of 2° latitude by 2.5° longitude and 46 sigma levels in the vertical extending up to 0.1 hPa. For computational expedience we degrade the horizontal resolution to 4° latitude by 5° longitude and merge the vertical levels above the lower stratosphere, retaining a total of 26. There are five levels located below 2 km altitude (for a column based at sea level, these levels are centered at 50 m, 250 m, 600 m, 1100 m, and 1700 m).

The GEOS-CHEM model includes a detailed description of tropospheric O₃–NOₓ–hydrocarbon chemistry. It solves the chemical evolution of about 120 species with a Gear solver [Jacobson and Turco, 1994] and transports 24 tracers. Photolysis frequencies are computed using the Fast-J radiative transfer algorithm [Wild et al., 2000] which includes Rayleigh scattering as well as Mie scattering by clouds and aerosols. Extensive evaluations of the GEOS-CHEM chemical fields with observations of tropospheric O₃ and its precursors in different regions of the world have been presented in a number of papers [e.g., Bey et al., 2001a, 2001b; Li et al., 2001, 2002a, 2002b; Palmer et al., 2001, 2003; Chandra et al., 2002; Fiore et al., 2002; Liu et al., 2003; Martin et al., 2002a, 2002b]. Observed monthly mean O₃ concentrations in different regions of the troposphere are usually reproduced to within 10 ppbv with no global bias, but there are some regional problems, most prominently a 20–30 ppbv positive bias over India [Martin et al., 2002b]. The seasonal and interannual variability of CO is well captured, but there is a general negative bias of 10–20 ppbv in the Northern Hemisphere. Consideration of aerosol photochemical effects alleviates these discrepancies, as discussed in section 4.

2.2. Aerosol Radiative and Chemical Effects

Previous versions of GEOS-CHEM have included heterogeneous reactions of HO₂, NO₂, NO₃, and N₂O₅ in sulfate aerosols [Bey et al., 2001a], and more recently these same reactions as well as radiative effects have been included for mineral dust aerosols [Martin et al., 2002b]. We include here a more comprehensive treatment of the photochemical effects of aerosols. To this end we use global 3-D monthly mean fields for 1996–1997 of dry aerosol mass from the GOCART model [Chin et al., 2000a, 2000b, 2002; Ginoux et al., 2001] which uses the same GEOS meteorological fields and transport algorithms as GEOS-CHEM. The GOCART data include sulfate, size-resolved mineral dust and sea salt, hydrophobic and hydrophilic black carbon, as well as hydrophobic and hydrophilic organic carbon. Nitrate aerosol is not included.

As described in detail elsewhere [Chin et al., 2000a, 2002; Ginoux et al., 2001], the GOCART model sulfate simulation includes oxidation of SO₂ emitted from industrial activity, biomass burning, biofuel, volcanic eruptions, and formed from dimethylsulfide (DMS) released from the ocean, as well as a small direct sulfate source. Oxidation rates in the GOCART model are calculated with offline fields of OH and aqueous H₂O₂. Organic and black carbon are emitted directly from biomass burning and industrial activity, with 80% of black carbon and 50% of organic carbon emitted as hydrophobic; the rest being hydrophilic. Organic carbon is also formed from volatile organic compounds. Hydrophobic carbonaceous aerosols age to become hydrophilic with an e-folding time of 1.2 days. Mineral dust emission is calculated as a function of the local probability of bare sediments, surface wind speed, and surface wetness. Sea-salt emission is calculated as a function of surface wind speed. All aerosols are subject to dry deposition and hydrophilic aerosols to wet deposition.

Simulation of the radiative and chemical effects of aerosols requires information on the relative humidity (RH) dependent aerosol size distribution. We obtain this information from Ginoux et al. [2001] for mineral dust, and from the Global Aerosol Data Set (GADS) [Köpke et al., 1997] and Chin et al. [2002] for other aerosols, and apply it to local RH from the GEOS fields. Table 1 shows the hygroscopic growth factors and Table 2 shows the effective radius of aerosols at 70% humidity. The effective radius is defined as

\[ r_e = \int r^2 f(r) dr / \int r f(r) dr \]

where \( f(r) \) is the fraction of pa-
particles with radius between \( r \) and \( r + dr \) [Hansen and Travis, 1974]. We cap aerosol growth above 90% RH; hygroscopic growth is very nonlinear at higher RH and cannot be adequately resolved in the GEOS fields because of sub-grid-scale variability, especially associated with clouds.

Calculation of the radiative effects of aerosols also requires information on the wavelength-dependent complex refractive index. We obtain this information from Patterson et al. [1977] for mineral dust, and for other aerosols as a function of RH from GADS. We assume an external mixture of the different aerosol types. Pósfai et al. [1999] found that soot and sulfate aerosols are often internally mixed; Liao et al. [1999] calculated that the absorbing effect of aerosols on photolysis frequencies is 5–15% larger for internally versus externally mixed sulfate-soot aerosols. A more physically realistic treatment of mixed sulfate-soot aerosols as a black carbon core surrounded by sulfate would have an intermediate effect [Jacobson, 2000].

We use a Mie algorithm [de Rooij and van der Stap, 1984; Mishchenko et al., 1999] to calculate for each aerosol type the single scattering albedo, the extinction efficiency, and the first eight terms in the Legendre expansion of the phase function, for input to the Fast-J radiative transfer code of Wild et al. [2000]. We tabulate the optical properties at the RH values in Table 1, and interpolate in the simulation. Table 2 shows the resulting optical properties at 0.4 \( \mu \text{m} \) and 70% RH. Sulfate and sea salt are purely scattering, black and organic carbon is moderately absorbing at UV and visible wavelengths. Organic carbon aerosols could be highly absorbing in the UV if they contain chromophore functional groups [Jacobson, 1999], but this is not considered here. Mineral dust is strongly absorbing in the UV and moderately absorbing at visible wavelengths. The extinction efficiencies of black carbon, organic carbon, and sulfate are about 20–60% larger at 300 nm than at 400 nm. The extinction efficiencies of supermicron mineral dust and sea-salt particles exhibit little wavelength sensitivity at UV and visible wavelengths.

We calculate the aerosol optical depth locally in the model from the mass concentration, extinction efficiency, and particle mass density for each particle type and wavelength. Figure 1 shows the modeled aerosol optical depth at 400 nm during March and August. Extensive evaluation of the GOCART fields with in situ, ground based, and satellite observations have been presented in a number of papers [Chin et al., 2000b, 2002; Ginoux et al., 2001; Penner et al., 2001; S. Kinne et al., Monthly averages of aerosol properties: A global comparison among models, satellite data and AERONET ground data, submitted to Journal of Geophysical Research, 2002]. The GOCART aerosol fields are generally consistent with observations to within a factor of 2. Mineral dust and sulfate dominate the background optical depth in the Northern Hemisphere. Mineral dust optical depth reaches a seasonal maximum during boreal summer, associated with surface cyclones that erode particles from topographic depressions in desert regions and with intense solar heating that transports particles into the free troposphere through dry convection [Ginoux et al., 2001]. The mineral dust optical depth of greater than 0.5 over much of northern Africa during summer is consistent with measurements from AERONET [Holben et al., 2001] and retrievals from TOMS [Torres et al., 2002], as shown by Ginoux et al. [2001] and Chin et al. [2002]. Mineral dust over the tropical Pacific is biased high by a factor of 2–5 [Ginoux et al., 2001]. Sulfate optical depth is maximum during summer due to higher \( \text{SO}_2 \) oxidation rates, and is most important over the eastern United States, eastern Asia, and Europe [Chin et al., 2000a, 2000b]. Modeled sulfate concentrations over the eastern United States are a factor of 1.5 lower than observations from the Eulerian Model Evaluation Field Study (EMEFS) [Chin et al., 2000b]. Black and organic carbon aerosols from biomass burning contribute to seasonal enhancements in optical depth over South Asia during March and southern Africa during August [Kuhlbusch et al., 1996; Chowdhury et al., 2001; Holben et al., 2001; Leon et al., 2001]. The GOCART model optical depths are generally within 0.3 of AERONET measurements over African biomass burning regions, but are about 2–3 times lower than AERONET measurements over the biomass burning region of South America [Chin et al., 2002]. Black carbon is also notable over northern Europe (diesel engines) and East Asia (biofuels). Sea-salt

Table 1. Hygroscopic Growth Factors for Aerosols

<table>
<thead>
<tr>
<th>Aerosol Type</th>
<th>Density, g cm(^{-3})</th>
<th>( r_s, \mu\text{m} )</th>
<th>Refractive Index</th>
<th>( \varpi_r )</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>1.7</td>
<td>0.24</td>
<td>1.36 – 10(^{-4})</td>
<td>1.00</td>
<td>1.95</td>
</tr>
<tr>
<td>Black carbon</td>
<td>1.0</td>
<td>0.04</td>
<td>1.75 – 0.46i</td>
<td>0.27</td>
<td>0.76</td>
</tr>
<tr>
<td>Organic carbon</td>
<td>1.8</td>
<td>0.10</td>
<td>1.42 – 0.0022</td>
<td>0.98</td>
<td>0.74</td>
</tr>
<tr>
<td>Sea salt</td>
<td>2.2</td>
<td>1.3</td>
<td>1.37 – 10(^{-3})</td>
<td>1.00</td>
<td>2.43</td>
</tr>
<tr>
<td>Accumulation</td>
<td>2.2</td>
<td>10.1</td>
<td>1.37 – 10(^{-3})</td>
<td>1.00</td>
<td>2.09</td>
</tr>
<tr>
<td>Mineral dust( ^b )</td>
<td>0.1 – 0.18 ( \mu\text{m} )</td>
<td>2.5</td>
<td>0.15</td>
<td>1.58 – 0.014i</td>
<td>0.94</td>
</tr>
<tr>
<td>0.18 – 0.3 ( \mu\text{m} )</td>
<td>2.5</td>
<td>0.25</td>
<td>1.58 – 0.014i</td>
<td>0.91</td>
<td>3.10</td>
</tr>
<tr>
<td>0.3 – 0.6 ( \mu\text{m} )</td>
<td>2.5</td>
<td>0.4</td>
<td>1.58 – 0.014i</td>
<td>0.86</td>
<td>2.82</td>
</tr>
<tr>
<td>0.6 – 1 ( \mu\text{m} )</td>
<td>2.5</td>
<td>0.8</td>
<td>1.58 – 0.014i</td>
<td>0.76</td>
<td>2.43</td>
</tr>
<tr>
<td>1.8 – 1 ( \mu\text{m} )</td>
<td>2.65</td>
<td>1.5</td>
<td>1.58 – 0.014i</td>
<td>0.68</td>
<td>2.27</td>
</tr>
<tr>
<td>1.8 – 3 ( \mu\text{m} )</td>
<td>2.65</td>
<td>2.5</td>
<td>1.58 – 0.014i</td>
<td>0.62</td>
<td>2.19</td>
</tr>
<tr>
<td>3 – 6 ( \mu\text{m} )</td>
<td>2.65</td>
<td>4.0</td>
<td>1.58 – 0.014i</td>
<td>0.58</td>
<td>2.14</td>
</tr>
</tbody>
</table>

\( ^a \) Effective radius \( r_s \), single scattering albedo \( \varpi_r \), and extinction efficiency Q are calculated using refractive index and lognormal size distribution data available from the Global Aerosol Data Set (GADS) [Köpke et al., 1997] and Chin et al. [2002] with the following exceptions. We use a geometric standard deviation of 2.0 for all aerosol types except mineral dust. The calculations for mineral dust use complex refractive indices from Patterson et al. [1977], and assume a standard gamma particle size distribution with effective variance of 0.2.

\( ^b \) Size ranges were resolved in the GOCART simulation and used as input to GEOS-CHEM.
optical depths are highest near ±60° where strong surface winds increase emissions [Gong et al., 1997].

[14] We implement heterogeneous chemistry on aerosol surfaces in GEOS-CHEM following a standard reaction probability formulation. We neglect heterogeneous chemistry in clouds which would be difficult to constrain in our coarse resolution model; its effect on O₃ and OH is limited in any case by the small fraction of atmospheric volume occupied by clouds [Liang and Jacob, 1997]. As pointed out by Jacob [2000] it is the atmospheric volume fraction occupied by clouds, rather than the frequency of cloud processing, that limits the effect of cloud chemistry on the global budgets of O₃ and OH.

[15] In the reaction probability formulation, the rate constant $k$ for chemical loss of a gas with mean molecular speed $v$ and gas-phase molecular diffusion coefficient $D_g$ on an aerosol of particle radius $a$ is given by

$$k = \left( \frac{a}{D_g + \gamma v} \right)^{-1} A$$  \hspace{1cm} (1)

where $\gamma$ is the reaction probability, i.e., the probability that a molecule impacting the aerosol surface undergoes reaction [Ravishankara, 1997], and $A$ is the aerosol surface area per unit volume of air. We calculate $D_g$ as a function of

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Figure 1. Modeled monthly mean optical depth at 400 nm of different aerosol types for March 1997 (left column) and August 1997 (right column). Values are calculated from mass concentration fields from Ginoux et al. [2001] for mineral dust and from Chin et al. [2002] for the other aerosol types. See color version of this figure at back of this issue.
molecular weight, temperature, and air density following Dentener [1993]. We include the four heterogeneous reactions $\text{HO}_2 \rightarrow 0.5 \text{H}_2\text{O}_2$, $\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3$, $\text{NO}_3 \rightarrow \text{HNO}_3$, and $\text{N}_2\text{O}_5 \rightarrow 2 \text{HNO}_3$ with reaction probabilities of $0.2$, $10^{-3}$, $10^{-5}$, and $0.1$, respectively, as recommended by Jacob [2000]. The products have long lifetimes relative to the timescales for gas-particle exchange and are therefore released into the gas phase. Uptake of NO$_2$ on dry dust surfaces may be less ($10^{-6}$–$10^{-4}$) [Grassian, 2001], but the phase of mineral dust surfaces in the atmosphere is unclear [Martin, 2000]. For the range of $r_v$ and $\gamma$ values used here, the chemical rate constant $k$ may be limited either by free molecular collision ($4/v\gamma r$ term in equation (1)) or by diffusion ($a/D_g$ term). Figure 2 shows the aerosol surface area in the lower troposphere (~600 m). The spatial distribution is similar to that of optical depth but features stronger maxima in regions where submicron aerosols dominate.

[16] We do not include reactive uptake of O$_3$ by aerosols, for which Jacob [2000] cites no conclusive laboratory or field evidence. Dentener et al. [1996] postulated direct uptake of O$_3$ by dust with an assumed $\gamma_{03}$ of $10^{-4}$–$10^{-5}$ based on analogy with measured O$_3$ deposition to bare soil. However, O$_3$ deposition to soil most likely involves reaction with unsaturated organics. Laboratory measurements show that O$_3$ uptake by organic aerosol surfaces is rapidly quenched as surface reaction sites are oxidized [Moise and Rudich, 2000]. Recent laboratory measurements on dry mineral dust surfaces reveal $\gamma_{03} \sim 10^{-5}$ with no apparent surface saturation, but with a factor of 2–3 decrease over several hours of exposure [Michel et al., 2002]. A model study of an African dust layer over the Atlantic by De Reus et al. [2000] indicates that reactive uptake of O$_3$ ($\gamma = 5 \times 10^{-3}$) would reduce simulated O$_3$ concentrations in the layer by 11 ppbv, improving agreement with observations. Further work is evidently needed on this issue.

[17] We also do not include reactive uptake of CH$_3$O$_2$, HCHO, HNO$_3$, or H$_2$O$_2$ by aerosols. Current evidence is that uptake of CH$_3$O$_2$ and HCHO is too slow to be of atmospheric significance [Jacob, 2000]. Uptake of HNO$_3$ by alkaline dust particles is important for the partitioning of HNO$_3$ between the aerosol and gas phase, but should have little impact on oxidant concentrations since both HNO$_3$(g) and nitrate aerosols are removed by wet deposition. De Reus et al. [2000] calculated that uptake of HNO$_3$ had a large role only if the HNO$_3$ in the aerosol phase was not permitted to regenerate NO$_3$ through photolysis. Uptake of H$_2$O$_2$, if determined by reaction with SO$_2$, is significant only in clouds and has little overall effect on HO$_x$ [Tie et al., 2001].

[18] We use a March 1996 to August 1997 simulation period. The first 6 months are used to achieve proper initialization and we present results for September 1996 to August 1997. Biomass burning emissions for that period are specified from satellite observations [Duncan et al., 2003] (the large fires in Oceania associated with El Niño have not yet begun). The standard simulation is as described above. A sensitivity simulation is conducted that excludes both the radiative effects of aerosols and the heterogeneous uptake of HO$_2$, NO$_2$, and NO$_3$ (but retains the uptake of N$_2$O$_5$). Additional simulations focused on the effects of mineral dust for the same time period were presented by Martin et al. [2002b]. We also perform 1-month sensitivity simulations (following a 1-month spin-up) for March and August 1997 to compare the relative importance of radiative and chemical effects of aerosols.

3. Photochemical Effects of Aerosols

[19] Figure 3 shows that aerosols reduce UV photolysis frequencies near the surface throughout a large part of the world. The noontime O$_3$ $\rightarrow$ O($^1$D) photolysis frequency, $J$(O($^1$D)) (300–320 nm), decreases by more than 5% over most of the Northern Hemisphere, largely due to mineral
The effect on J(NO₂) (340–400 nm) is similar to that on J(O(1D)) and about 10% weaker. Removing sulfate from the aerosol mixture generally causes a slight increase (<2%) in J(O(1D)) relative to the standard simulation near the surface; 1-D calculations by Liao et al. [1999] similarly showed that in the presence of absorbing aerosols, sulfate aerosols have a small effect on photolysis frequencies. Mineral dust reduces J(O(1D)) by 15–30% over and downwind of northern Africa throughout the year [Martin et al., 2002b]. Black carbon causes most of the 15–25% decrease in J(O(1D)) over northern Europe during August. Aerosols from biomass burning and other sources in the Ganges Valley reduce J(O(1D)) near the surface by a factor of 2, largely due to black carbon with smaller contributions from organic carbon and mineral dust. Similar features are observed over southern Africa during August. The reduction in photolysis frequencies may be 5–15% greater for internally mixed aerosols than for the external mixture assumed here [Liao et al., 1999]. Measurements of J(O(1D)) over the northern Indian Ocean during March showed reductions of 40% due to absorbing aerosols (J. Burkert et al., Trace gas and radical diurnal behavior in the marine boundary layer during INDOEX 1999, submitted to Journal of Geophysical Research, 2002), consistent with the results presented here.

Heterogeneous chemistry also contributes to the photochemical effects of aerosols. Figure 4 shows the fraction of total HOx loss in the lower troposphere (~600 m above the surface) contributed by uptake of HO₂ by aerosols. Values are monthly mean model results for March and August 1997. See color version of this figure at back of this issue.

Figure 4. Fraction of total HOx loss in the lower troposphere (~600 m above the surface) contributed by uptake of HO₂ by aerosols. Values are monthly mean model results for March and August 1997. See color version of this figure at back of this issue.

dust. The effect on J(NO₂) (340–400 nm) is similar to that on J(O(1D))) and about 10% weaker. Removing sulfate from the aerosol mixture generally causes a slight increase (<2%) in J(O(1D))) relative to the standard simulation near the surface; 1-D calculations by Liao et al. [1999] similarly showed that in the presence of absorbing aerosols, sulfate aerosols have a small effect on photolysis frequencies. Mineral dust reduces J(O(1D))) by 15–30% over and downwind of northern Africa throughout the year [Martin et al., 2002b]. Black carbon causes most of the 15–25% decrease in J(O(1D))) over northern Europe during August. Aerosols from biomass burning and other sources in the Ganges Valley reduce J(O(1D))) near the surface by a factor of 2, largely due to black carbon with smaller contributions from organic carbon and mineral dust. Similar features are observed over southern Africa during August. The reduction in photolysis frequencies may be 5–15% greater for internally mixed aerosols than for the external mixture assumed here [Liao et al., 1999]. Measurements of J(O(1D))) over the northern Indian Ocean during March showed reductions of 40% due to absorbing aerosols (J. Burkert et al., Trace gas and radical diurnal behavior in the marine boundary layer during INDOEX 1999, submitted to Journal of Geophysical Research, 2002), consistent with the results presented here.

Heterogeneous chemistry also contributes to the photochemical effects of aerosols. Figure 4 shows the fraction of total HOx loss in the lower troposphere (~600 m altitude) contributed by aerosol uptake of HO₂. Here we define total HOx loss as the sum of the main loss pathways [Frost et al., 1998; Jaeglé et al., 2001]: 2(OH + HO₂) + 2(HO₂ + HO₂) + 2(HO₂ + CH₄O₂) + (NO₂ + OH) + 2(HNO₄ + OH) + aerosol uptake of HO₂. Aerosols are responsible for more than 70% of HOx loss over biomass burning regions. The abundance of fine aerosol over biomass burning regions [Anderson et al., 1996] and industrial regions [ten Brink et al., 1997] leads to high aerosol surface area and rapid gas-particle mass transfer (this transfer is not diffusion-limited, unlike with supermicron particles). Aerosol uptake of HO₂ is responsible for over 50% of HOx loss over Eastern Europe during August, due to high surface areas from organic carbon (anthropogenic and biogenic) and sulfate, both of which peak in the summer. Black carbon constitutes less than 20% of total surface area over Eastern Europe, despite playing a dominant role in the reduction of photolysis rates. Uptake of HO₂ by aerosols accounts for over 20% of HOx loss over much of northern Africa, the Atlantic Ocean, and Asia, and over 50% of HOx loss in the Arctic during March.

Figure 5 shows the fraction of total NOx loss to HNO₃ contributed by aerosol uptake of NO₂ and NO₃ in the lower troposphere for March and August. This fraction is 15–30% in regions with high concentrations of biomass burning, mineral dust, and sea-salt aerosols. Over land, heterogeneous NOx loss is mainly NO₂ uptake. Over oceans, uptake of NO₂ and NO₃ have comparable roles. We do not include reaction of NO₃ with marine DMS in the model, and as a result may exaggerate the importance of NO₃ heterogeneous uptake over the oceans.

We examine the vertical distribution of the photochemical effects of aerosols over two regions where the effects are large: during March over India where carbonaceous aerosols are particularly important and during August over the Sahara where mineral dust dominates. The vertical profile of the radiative effect is shown in the top panels of Figure 6. The effect decreases rapidly with altitude following the distribution of aerosols. The small enhancement in J(NO₂) in the upper troposphere over India results from scattering by aerosols below. The middle panels of Figure 6 show the vertical profiles of the chemical effect of aerosols. Uptake of HO₂ on aerosol surfaces is responsible for about 80% of HOx loss through the depth of the boundary layer over India, and 20–40% of HOx loss throughout most of the troposphere over the Sahara. Almost 20% of the HNO₃ production in the boundary layer over India results from uptake of NO₂ by aerosols. The bottom panels in Figure 6 show that over India the radiative and chemical properties of aerosols

Figure 5. Fraction of total HNO₃ production in the lower troposphere (~600 m above the surface) contributed by uptake of NO₂ and NO₃ by aerosols. Values are monthly mean model results for March and August 1997. See color version of this figure at back of this issue.
Aerosols have comparable effects on OH near the surface, but chemical effects dominate at higher altitudes where the overhead aerosol column is smaller. Over the Sahara the radiative effects of mineral dust are about twice as important as the chemical effects, reflecting the absorbing nature of mineral dust at UV wavelengths [Sokolik et al., 1993] and the large size of the dust particles.

Figure 7 shows the combined photochemical effects of aerosols on OH, CO, NOx, and O3 concentrations in March. Here we compare the standard simulation to a simulation excluding radiative effects of aerosols and the heterogeneous reactions of HO2, NO2, and NO3 (hydrolysis of N2O5 is included in both simulations). The top panel shows that OH is reduced by 25–50% over northern Africa and South Asia, largely due to mineral dust, organic carbon, and black carbon. Over northern India near Calcutta, OH decreases by a factor of 4 reflecting comparable contributions from radiative and chemical effects. Over much of the Northern Hemisphere OH concentrations decrease by 5–25%; about half of this decrease is from the radiative effects of mineral dust. The depletion of OH increases the lifetime of CO and other trace gases such as NOx and non-methane hydrocarbons, increasing their export from regions of emissions. As a result, CO increases by 5–15 ppbv (5–10%) throughout much of the Northern Hemisphere, with local increases downwind of biomass burning regions of 20–75 ppbv (10–15%). Ship and aircraft measurements during the March winter monsoon found elevated CO concentrations in the marine boundary layer off the coast of India [Rhoads et al., 1997; Lelieveld et al., 2001]; our analysis suggests that depletion of OH by aerosols contributed to the observed enhancement. Over the tropical Atlantic downwind of the Sahara, CO increases by 10–20 ppbv (7–13%).

The photochemical effects of aerosols generally result in a slight increase of NOx over continental regions due to OH depletion. Over the oceans the effect is more often a slight decrease (up to 20%) as NO2 and NO3 uptake are relatively more important (Figure 5). The bottom panel
shows that the effect on $O_3$ is confined largely to regions with intense emissions of both aerosols and $O_3$ precursors. Ozone is reduced by $10-40\%$ or $15-45$ ppbv over and downwind of the biomass burning region of northern India during March. Ozone also is reduced by $5-10$ ppbv ($10-15\%$) over northeastern China and the Yellow Sea, a region where industrial activity is collocated with high aerosol loading from anthropogenic and mineral dust aerosols [Zhang et al., 1994; Zhang and Carmichael, 1999]. Phadnis and Carmichael [2000] previously used a regional 3-D model to calculate a reduction in boundary layer $O_3$ of about $5\%$ over the region during May due to uptake of $HO_2$ (γ = 0.1), $H_2O_2$ (γ = 0.1), $N_2O_5$ (γ = 0.1), and $HNO_3$ (γ = 0.1) on mineral dust.

Figure 7. Changes in OH, CO, NOx, and $O_3$ concentrations in the lower troposphere ($\sim600$ m above the surface) from scattering and absorption by aerosols, and from uptake of $HO_2$, $NO_2$, and $NO_3$ by aerosols, as determined by difference with a simulation that did not include these effects. Values are model monthly means during March. White circles show the locations of observations compared to the model in section 4. Also shown is the change in the CO flux due to the above aerosol effects. See color version of this figure at back of this issue.
half of the reduction of 5–25% over most of the Northern Hemisphere is from the radiative effects of mineral dust. Concentrations of CO increase by 5–10 ppbv throughout much of the Northern Hemisphere, with local increases of more than 10 ppbv over Europe and the Mediterranean. Concentrations of NOx generally increase by less than 10%, with local increases of up to 30% over Europe, and local decreases of up to 20% over tropical oceans. As for March the effect on O3 is localized to photochemically active regions where aerosols are collocated with anthropogenic emissions of O3 precursors. Aerosols reduce O3 in the boundary layer by 5–9 ppbv over northern Europe during August 1997. We find a smaller reduction in July 1997 (3–5 ppbv) due to lower aerosol loadings, which in the model are due to higher precipitation. The photochemical effects of aerosols are smaller over the eastern United States where concentrations of absorbing aerosols are lower. The combined photochemical effects of aerosols decrease O3 in the boundary layer over the eastern United States by up to 3 ppbv and over East Asia by up to 5 ppbv. [26] Comparison of our results with previous global model studies of sensitivity to aerosol photochemistry is
difficult because of differences in the aerosol processes and aerosol types examined. Table 3 shows these differences. Liao et al. [2003] find that the radiative effects of aerosols change O₃ concentrations by less than 1 ppbv anywhere in a global 3-D model with substantially smaller aerosol loadings than used here. Dickerson et al. [1997] calculated that the radiative effects of aerosols increase surface O₃ over regions of scattering aerosols such as the eastern United States, and decrease O₃ over regions of absorbing aerosols. We find that the combined radiative and chemical effects of aerosols lead to small net decreases in O₃ over the eastern United States, and larger decreases in O₃ over Europe and Asia where aerosols are more absorbing. Tie et al. [2001] calculated that uptake of HO₂ (γ = 0.2) by sulfate aerosols decreases zonal mean OH by 5–10% during June north of 45°N. Over this region sulfate aerosols are the largest contributor to the aerosol load; our results are comparable to those of Tie et al. [2001] and indicate that consideration of radiative effects would about double the impact on OH. Dentener et al. [1996] found that uptake of HO₂ (γ = 0.1) by mineral dust decreased HO₂ concentrations over northern Africa and the Gobi Desert by up to 10% during February, March, and April, but had little effect on O₃ due to low NOₓ concentrations. Over this region mineral dust dominates the total aerosol load, we calculate an effect on HO₂ four times as large as using γHO₂ of 0.2 and accounting for scattering and absorption of UV radiation by mineral dust. The effect on O₃ is still small.

4. Comparison With Observations

We compared our model results with a suite of aircraft, sonde, and satellite observations to determine if inclusion of the photochemical effects of aerosols described here improves or degrades the simulation. Again these effects include (1) absorption and scattering of ultraviolet radiation and (2) reactive uptake of HO₂, NO₂, and NO₃. We present here selected comparisons for locations where the model exhibits large discrepancies with observations and where aerosol effects are large. Large decreases in O₃ are found over South Asia in March and northern Europe in August due to photochemical effects of aerosols (Figures 7 and 8). Figure 9 compares monthly modeled O₃ profiles over South Asia with measurements from commercial aircraft as part of the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) program [Marenco et al., 1998] during 1995–1999. The photochemical effects of aerosols improve the simulation at all three sites by decreasing O₃ concentrations in the lower troposphere, although they have minimal effect at higher altitudes (above 600 hPa) where the model is still too high. The magnitude of the lower tropospheric correction, although insufficient to bring model results in agreement with observations, is correlated with the magnitude of the model bias. The low O₃ values observed at Madras in surface air likely reflect local titration. Lal and Lawrence [2001] found a model overestimate of comparable magnitude at the surface during February and March at Ahmadabad (23°N, 73°E). Our black carbon emissions from fossil fuels in India [from Cooke et al., 1999] may be a factor of 2–3 too low [Dickerson et al., 2002], so that aerosols may reduce O₃ over India throughout the year and may lead to a greater O₃ reduction during March. However, it does not appear that aerosols could correct the model overestimate above 600 hPa.

5. Global Budgets of O₃ and OH

Table 4 shows annual mean global O₃ production and loss rates computed in the model, as well as the lifetime of methylchloroform (CH₂CCl₃) against oxidation by tropospheric OH. The latter is a standard index of the global mean tropospheric OH concentration [Spivakovsky et al., 2000]. The photochemical effects of aerosols beyond N₂O₅ hydrolysis reduce global O₃ production and loss by 6% and 7%, respectively. The global O₃ burden is unchanged
because the large regional decreases in boundary layer O₃ are compensated by small increases throughout the tropical troposphere. The global O₃ production and loss rates calculated here are still at the high end of the current generation of global 3-D models, an issue discussed by Bey et al. [2001a].

Dentener and Crutzen [1993] previously found that N₂O₅ hydrolysis decreases the global mean tropospheric OH concentration (as measured by the lifetime of CH₃CCl₃) by 9%. We find here that the additional photochemical effects of aerosols globally decrease OH by an additional 9%. The radiative effects of mineral dust explain 60% of this decrease. The OH decrease is much larger in the Northern Hemisphere (13%) than the Southern Hemisphere (4%). The resulting global CH₃CCl₃ lifetime of 5.6 years against oxidation by tropospheric OH is consistent with estimates from observations of 5.7 ± 0.7 years [Spivakovsky et al., 2000] and 6.0 (+1.0, −0.7) years [Prinn et al., 2001].

6. Conclusions

We have evaluated the sensitivity of tropospheric OH, O₃, and O₃ precursors to aerosol effects not usually included in global models: (1) aerosol scattering and absorption of ultraviolet radiation and (2) reactive uptake of HO₂, NO₂, and NO₃. We used for this purpose a global 3-D model of tropospheric chemistry (GEOS-CHEM) with specified global 3-D fields of sulfate, black carbon, organic carbon, sea salt, and mineral dust aerosol concentrations from a global model (GOCART) driven by the same meteorological fields. We did not examine the role of N₂O₅ hydrolysis in aerosols, whose importance is well established [Dentener and Crutzen, 1993] and which is included in all current-generation tropospheric chemistry models.

We find important aerosol effects from reduction in photolysis frequencies and reactive uptake of HO₂ (γ = 0.2). Perturbations to photolysis frequencies are largely from absorbing aerosols; sulfate has little effect. Aerosols decrease the O₃ → O¹D) photolysis frequency, J(O¹D), at the surface by 5–15% throughout most of the Northern Hemisphere, largely due to mineral dust, and by a factor of 2 in biomass burning regions, largely due to black carbon.

Uptake of HO₂ by aerosols accounts for more than 10% of total HO₂ (≡ OH + peroxy) loss in the boundary layer of most continental regions. The heterogeneous chemical effects of aerosols are largest where high concentrations...
of fine aerosols enable efficient gas-particle mass transfer. Uptake of HO₂ on aerosols accounts for up to 50–70% of HOx loss over polluted regions of Eastern Europe (largely due to sulfate and organic carbon), and more than 70% over biomass burning areas of the tropics (largely due to organic carbon). Aerosols decrease boundary layer OH concentrations by 5–35% in most of the Northern Hemisphere, by a factor of 2 over northern Europe during August, and up to a factor of 4 over India during March.

Reactive uptake of NO₂ (γ = 10⁻⁴) and NO₃ (γ = 10⁻³) have relatively small effects. These processes account for more than 10% of HNO₃ production only over the tropical North Atlantic, the Sahara, and the southern oceans. Over continental regions, the net effect of the aerosol processes considered here is to slightly increase NOₓ due to OH depletion.

We examined the implications of the above aerosol effects on the global model budgets of OH, O₃, and CO. Annual mean OH concentrations decrease by 9% globally (comparable to the effect of N₂O₅ hydrolysis) and by 13% in the Northern Hemisphere. About 60% of the global decrease is due to the radiative effects of mineral dust. The resulting CH₃CCl₃ lifetime against oxidation by tropospheric OH (5.6 years) is in better agreement with estimates constrained by observations. Annual mean global O₃ chemical production decreases by 6%, but the tropospheric O₃ burden remains unchanged. Concentrations of CO increase by 5–15 ppbv in most the Northern Hemisphere, improving agreement with observations at remote sites. Boundary layer O₃ decreases by 15–45 ppbv over South Asia during the biomass burning season in March, improving the comparison to aircraft observations (MOZAIC) although the model is still too high. Summertime boundary layer O₃ is reduced by 5–9 ppbv over northern Europe, and by 1–3 ppbv over the United States, again improving the model simulation with respect to observations over both regions. We conclude that surface O₃ concentrations over Europe and other industrial regions will increase if emissions of aerosols are reduced without corresponding reductions in O₃ precursors.

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Table 4. Global Tropospheric O₃ Budget and CH₃CCl₃ Lifetime

<table>
<thead>
<tr>
<th></th>
<th>Full Aerosol Photochemistry</th>
<th>N₂O₅ Hydrolysis Onlyb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical production, Tg O₃ yr⁻¹</td>
<td>4924</td>
<td>5263</td>
</tr>
<tr>
<td>Chemical loss, Tg O₃ yr⁻¹</td>
<td>4377</td>
<td>4693</td>
</tr>
<tr>
<td>Burden, Tg O₃</td>
<td>322</td>
<td>323</td>
</tr>
<tr>
<td>Global CH₃CCl₃ lifetime, yr</td>
<td>5.6</td>
<td>5.2</td>
</tr>
<tr>
<td>NH CH₃CCl₃ lifetime, yr</td>
<td>5.4</td>
<td>4.8</td>
</tr>
<tr>
<td>SH CH₃CCl₃ lifetime, yr</td>
<td>5.8</td>
<td>5.6</td>
</tr>
</tbody>
</table>

aThe production, loss, and burden of O₃ are actually for the extended odd oxygen family defined as O₃ + NO₂ + 2 * NO₃ + peroxyacylnitrates + HNO₃ + 3 * N₂O₅. They are calculated for the column extending up to the local model tropopause. The CH₃CCl₃ lifetime is calculated as the ratio of the total burden of atmospheric CH₃CCl₃ to the tropospheric loss rate against oxidation by OH [Spivakovsky et al., 2000]. Values are annual means for September 1996 to August 1997 from the GEOS-CHEM model.

bThis is the same as full aerosol photochemistry simulation but without radiative effects or uptake of NO₂, NO₃, and HO₂ by aerosols.

References


Figure 1. Modeled monthly mean optical depth at 400 nm of different aerosol types for March 1997 (left column) and August 1997 (right column). Values are calculated from mass concentration fields from Ginoux et al. [2001] for mineral dust and from Chin et al. [2002] for the other aerosol types.
Figure 2. Modeled monthly mean total aerosol surface area in the lower troposphere (~600 m above the surface) for March and August 1997. Values are calculated from mass concentration fields from Ginoux et al. [2001] for mineral dust and from Chin et al. [2002] for the other aerosol types.

Figure 3. Sensitivity to aerosols of the O$_3$ → O(1D) photolysis frequency ($J$(O(1D))) in surface air. Values are monthly mean model results for March and August 1997.
Figure 4. Fraction of total HO\textsubscript{x} loss in the lower troposphere (~600 m above the surface) contributed by uptake of HO\textsubscript{2} by aerosols. Values are monthly mean model results for March and August 1997.

Figure 5. Fraction of total HNO\textsubscript{3} production in the lower troposphere (~600 m above the surface) contributed by uptake of NO\textsubscript{2} and NO\textsubscript{3} by aerosols. Values are monthly mean model results for March and August 1997.
Figure 7. Changes in OH, CO, NOx, and O3 concentrations in the lower troposphere (~600 m above the surface) from scattering and absorption by aerosols, and from uptake of HO2, NO2, and NO3 by aerosols, as determined by difference with a simulation that did not include these effects. Values are model monthly means during March. White circles show the locations of observations compared to the model in section 4. Also shown is the change in the CO flux due to the above aerosol effects.
Figure 8. As in Figure 7, but for August.