Mineral dust and global tropospheric chemistry: Relative roles of photolysis and heterogeneous uptake

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We investigate the influence of mineral dust on tropospheric chemistry in the present climate at the global scale. The analysis examines the effects of dust on photolysis and heterogeneous uptake, operating independently and together. In numerical experiments the size-resolved, time-varying mineral dust distribution predicted by the global Dust Entrainment and Deposition (DEAD) model perturbs the gas phase species in a global chemical transport model (University of California at Irvine (UCI) CTM). We find that the photolysis perturbation dominates limited regions in the low to middle troposphere, while heterogeneous uptake dominates the rest of atmosphere. Coupling of the photochemical and heterogeneous effects of dust is weak in the global mean but moderate in dusty regions, where coupling is sometimes responsible for more than 20% of local O3 changes. Ozone and odd-nitrogen concentrations are perturbed in opposite directions by photolysis and heterogeneous chemistry, resulting in a weak net change. However, both processes decrease the concentrations of OH and HO2. The global mean change due to dust is −0.7% for tropospheric O3, −11.1% for OH, −5.2% for HO2, and −3.5% for HNO3. Large seasonal signals are present near dust source regions. Over the North African region and tropical Atlantic Ocean downwind, OH decreases by −66.8%, six times more than the global mean reduction. Interestingly, net photolysis-induced annual mean O3 changes are greater in the Southern Hemisphere than in the Northern Hemisphere, where significantly more dust and O3 precursors reside. In polar regions, O3 change is dominated by transported O3 and is not sensitive to local dust concentration. O3 change due to photolysis depends not only on dust vertical structure but also on the availability of O3 precursors. O3 change due to heterogeneous reactions on dust is sensitive to dust vertical structure, mainly through the influence of temperature on uptake rates.

INDEX TERMS: 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 4801 Oceanography: Biological and Chemical: Aerosols (0305); KEYWORDS: tropospheric chemistry, mineral dust, photolysis impact, heterogeneous reaction

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1. Introduction

Aerosols impact the chemical composition of the atmosphere by providing a surface for heterogeneous chemistry, and for light scattering and absorption at photolytic wavelengths. Mineral dust is an important aerosol to consider in atmospheric chemistry because its natural and anthropogenic sources account for one-third to one-half of total annual aerosol emissions by mass [Penner et al., 2001]. On average, mineral dust contributes more than 60% of total aerosol optical depth in dusty regions, 15% in urban regions, and up to 10% in the southern

Hemisphere [Kinne et al., 2003]. Besides seasonal and annual dust variations, dust fluctuates on climatic timescales in both source regions and downwind [e.g., Ram and Koenig, 1997; Kohfeld and Harrison, 2001]. This work focuses on the current annual mean and seasonal cycle of global dust-chemistry interactions.

Convincing evidence that heterogeneous chemistry on mineral dust significantly alters the concentration of important atmospheric gases has been firmly established in field, lab, and model settings [Zhang et al., 1994; Dentener et al., 1996; Tabazadeh et al., 1998; Zhang and Carmichael, 1999; Goodman et al., 2000; Galy-Lacaux et al., 2001; Underwood et al., 2001; Michel et al., 2002]. Research also shows mineral dust significantly alters atmospheric photochemistry by absorption and scattering in photolytic wavelengths [Dickerson et al., 1997; Jacobson, 1998; He and Carmichael, 1999; Balis et al., 2002; Bian et al., 2003]. These previous three-dimensional chemical transport model
(CTM) simulations of the chemical influence of dust focus on the impact of one process (photochemical or heterogeneous) in isolation on atmospheric oxidants. Many of these efforts were conducted on regional spatial scales and/or event-based or synoptic timescales. Recent research on global tropospheric chemistry includes the dust impact through both processes [Martin et al., 2002; Liao et al., 2003] but does not thoroughly analyze or attribute the chemical forcing by dust. In this paper, we use a CTM framework to investigate the chemical alteration of the troposphere by dust through both photolysis rate forcing and heterogeneous uptake. We also highlight the non-linear interaction between dust photolysis rate forcing and heterogeneous uptake to determine the bias that arises from neglecting this interaction.

[4] Our objectives are as follows: (1) Estimate the perturbation by dust to global oxidant distributions due to the coupled effects of photolysis and heterogeneous uptake. (2) Isolate the effect of each process and learn whether there are non-linear interactions between them. (3) Identify regions and seasons where dust has its maximum influence on chemistry and compare these to selected observations. (4) Understand the influence of dust horizontal and vertical distributions on ozone production.

[5] The paper is organized as follows. Section 2 describes the two global models employed. Section 3 presents, in order, the results of the model simulations of the photochemical, heterogeneous uptake, and coupled effects of dust, and concludes with the effects of spatial distribution in selected regions. We discuss our main findings, their uncertainties, and implications for future studies follows in section 4.

2. Simulation Framework

2.1. CTM Description

[6] The University of California at Irvine (UCI) CTM [Wild and Akimoto, 2001] includes a detailed tropospheric photochemical scheme which uses the ASAD scheme [Carver et al., 1997] with an implicit solver. The chemical scheme includes complete treatment of inorganic plus methane chemistry and a lumped “family” treatment of hydrocarbon oxidation schemes for the representative species butane, propane, xylene and isoprene. This tropospheric O$_3$-NO$_x$-NMHC chemistry scheme contains 36 species, with 88 chemical reactions and 22 photochemical reactions [Wild and Prather, 2000; Bian and Prather, 2002]. Reaction rates are principally taken from DeMore et al. [1997] and from Atkinson et al. [1997], with additional rates from Hough [1991] and from the Leeds University Master Chemical Mechanism. Photolysis rates are calculated with an on-line treatment of molecular, aerosol, and water and ice cloud absorption and scattering using the Fast-J scheme [Wild et al., 2000; Bian and Prather, 2002]. For use in calculating photolysis rates, stratospheric ozone is taken from the Models and Measurements (M&M) climatology [Park et al., 1999] while tropospheric ozone is taken from the instantaneous CTM values.

[7] The meteorology driving the CTM is provided by the Goddard Institute for Space Studies (GISS) general circulation model version II$^+$ (4° × 5°, 9 vertical layers) based on the climatological sea surface temperature of the 1980s. The meteorological fields are supplied every 3 hours and linearly interpolated to the nearest time step. The advection scheme conserves second-order moments and considers not only gradients of tracer concentration but also the curvature in the tracer distribution [Prather, 1986].

[8] Dry deposition is treated with a resistance-in-series scheme based on the surface meteorological properties, vegetation type and species solubility [Jacob et al., 1991; H. P. Hanson, unpublished manuscript, 2000]. Wet deposition of soluble species is allowed for during convective transport and in large-scale precipitation using Henry’s Law coefficients [Bian, 2001]. Washout in rainfall uses precipitation mass fluxes from the supplied meteorological data and the pH of the water droplets. Evaporation occurring in the lower atmosphere allows these processes to transport soluble trace gases down through the atmosphere rather than removing them entirely.

[9] We map the GEIA inventories of trace species emissions from $1^\circ \times 1^\circ$ resolution to the model grid, preserving the second-order moments of the emissions. Additional emissions for CO and biomass burning sources are from $4^\circ \times 5^\circ$ resolution are from Wang et al. [1998a]. Diurnal variations are provided for industrial and biogenic sources, and seasonal variations are provided for soil emissions, methane, and biomass burning sources. NO from lightning is based on the parameterization of Price and Rind [1992]. The vertical mass flux from the meteorological fields is used to define deep convective events to distribute the NO source. An NO source from aircraft is also included [Baughcum et al., 1996].

[10] The upper boundary for stratospheric ozone is calculated with the Synoz model [McLinden et al., 2000]. The global annual mean flux of ozone from the stratosphere is specified as 475 Tg yr$^{-1}$ based on observations [Murphy and Fahey, 1994]. Synoz allows the circulation to determine where and when O$_3$ enters the troposphere. A dynamical tropopause is diagnosed as the 120 ppb isopleth of this synthetic ozone. Below this level, the tropospheric chemistry scheme is applied, and above, a simplified stratospheric scheme is used.

2.2. Mineral Dust

[11] The usefulness of global chemical studies of mineral dust depends, in part, on the fidelity of the simulated dust distribution to observations. The climatological global 3-D dust concentrations used in the UCI CTM are predicted by the mineral Dust Entrainment and Deposition (DEAD) model [Zender et al., 2003]. Predictions from DEAD have been used and evaluated against field measurements in numerous aerosol studies [Rasch et al., 2001; Collins et al., 2001, 2002; Mahowald et al., 2002; Zender et al., 2003; Luo et al., 2003].

[12] DEAD predicts the size-resolved distribution of atmospheric dust in four size bins (0.1–1, 1–2.5, 2.5–5, and 5–10 μm). Mobilization processes include entrainment thresholds, moisture inhibition, drag partitioning, saltation feedback, and erodibility enhancements in sedimentary basins. Dry deposition processes include sedimentation and turbulent mix-out. Nucleation and collision scavenging in both stratiform and convective cloud types are simulated. DEAD simulations of 1994–1998 [Zender et al., 2003] in the NCAR MATCH model [Rasch et al., 1997] at T62
L28 resolution were averaged to create global 3-D monthly mean dust concentrations for the UCI CTM. These dust concentrations are then re-gridded to the spatial and temporal resolution of the UCI CTM.

Figure 1 depicts the predicted zonal mean mineral dust extinction \([\text{km}^{-1}]\) at 340 nm and horizontal distributions of dust optical thickness in January and July. Strong summertime convection lifts dust into higher atmosphere in July, and spreads more dust into remote region. Dust centers around \(10^\circ\text{N}\) in January and shifts north to \(20^\circ\text{N}\) in July. The annual mean atmospheric dust burden is \(29 \text{ mg m}^{-2}\). The geographic and seasonal variations of dust loading are shown and evaluated by Zender et al. [2003] and Luo et al. [2003]. These studies show that, in the 1980s and 1990s, DEAD broadly agrees with station observations of mass concentration, mass deposition, optical depth, and satellite-inferred dust distribution. The model captures the seasonal migration of the trans-Atlantic African dust plume and the spring maximum in Asian dust outflow. However, DEAD predicts emissions, burden, and optical depth are significantly \((10–50\%)\) less than predicted by Ginoux et al. [2001], largely because of differences in wet deposition. DEAD underestimates transport and deposition of East Asian and Australian dust to some regions of the Pacific Ocean. An underestimate of long range transport of particles larger than \(3 \mu \text{m}\) contributes to this common model bias [e.g., Ginoux, 2003; Colarco et al., 2003a].

3. Results and Discussion

[14] The results presented are taken from the final 12 months of CTM simulations of 1 July of year 1 through 31 January of year 3. These nineteen month runs include a seven-month spin-up time which allows for most chemically important trace gases, except \(\text{CH}_4\), to reach steady state. Throughout this paper, the influence of dust on atmospheric chemistry is isolated by subtracting the control run (without aerosol) from the perturbation run (with dust) and (for some quantities) dividing by the control run. The species changes reported refer only to tropospheric (i.e., not tropospheric + stratospheric) abundances.

3.1. Effects of Photochemical Forcing

[15] Aerosols manipulate the atmospheric radiance field in such an intricate way that outstanding problems remain in modeling the closure of even the clear sky radiative budget [Valero et al., 2003]. Sokolik et al. [2001] review current experimental and theoretical approaches used to quantify...
the dust radiative effects. They point out that despite recent advances, dust optical properties remain poorly quantified because of limited data and incomplete understanding of relevant physical and chemical properties. The reader is referred to the existing literature on the sensitivity of photochemistry to plausible ranges of dust optical properties [Liao and Seinfeld, 1998; He and Carmichael, 1999].

[16] The refractive index $n$ is an essential parameter required to derive the optical properties used in photolysis rate calculations. Specifically, Fast-J requires the single scattering albedo and the first 7 coefficients in the Legendre expansion of the scattering phase function for ultraviolet and visible wavelengths (300–600 nm) [Wild et al., 2000; Bian and Prather, 2002]. As given by Bian et al. [2003], we assume a wavelength independent refractive index, $n = 1.50 + 0.025i$, which is approximately the mean value of measurements by Patterson [1981] between 300–400 nm. For the lognormally distributed long range transport mode of dust with volume median diameter of 2.5 μm [Zender et al., 2003], the single scattering albedo at $\lambda = 300$ nm is 0.64. Previous observations and simulations agree that dust causes significant absorption in the key tropospheric photochemical wavelengths (300–400 nm) [Savoie et al., 2000; Diaz et al., 2001; Kaufman et al., 2001; Dubovik et al., 2002]. The influence of Relative Humidity (RH) on $n$ is neglected since the radiative properties of atmospheric dust are relatively insensitive to RH changes [Li-Jones et al., 1998; He and Carmichael, 1999].

[17] Figure 2 shows the change in photolysis rate coefficients ($J$ values) for O(1D) and NO2 due to scattering and absorption by mineral dust at three dusty locations. Points A (10°N, 15°E) and B (18°N, 5°W) are centers of dust emissions over west Africa in January and July, respectively. Point C (14°N, 32°W) is downwind in the tropical Atlantic. Dust significantly reduces $J_{O(1D)}$ and $J_{NO2}$ in the lower troposphere at all three points. A large seasonal shift is evident in the source regions (compare Figure 1).

[18] It is interesting to contrast our results at Point A to those of Martin et al. [2002], who also employ the Fast-J photolysis code but who use the Ginoux et al. [2001] dust distribution. Compared to Martin et al., we predict greater $J$-rate reductions due to dust in January, but smaller reductions at all altitudes in July. The discrepancy between dust-induced $J$-rate changes between these models is due to differences between the modeled dust distributions. In DEAD, dust emissions are maximum at Point A in January and then move to the northwest in July, leaving low column dust at Point A (compare Figure 1).

[19] To place the O3 response to mineral dust in context, we first show the unperturbed O3 abundance in Figure 3. This is the O3 abundance simulated with gas phase chemistry alone. Seasonal biomass burning forms the O3 maxima in sub-Saharan Africa in January. Industrial emissions of O3 precursors cause the O3 maxima in the United States, Europe, and downwind regions in July.

[20] Figures 4 and 5 show the effects of photolysis rate forcing by dust on O3 and OH, respectively, in January and July.
July. We show only O3 and OH because they represent the key tropospheric oxidants and drive tropospheric chemistry. The maximum perturbations are in dust source regions in the boundary layer and decrease with altitude. The perturbation patterns are consistent with dust abundance, and show that tropospheric chemistry responds quickly to photochemical forcing. January is characterized by decreased O3 at all levels in the African dust region, while a more diffuse O3 decrease occurs over Asia. In July, there is a striking change in the sign of the O3 perturbation due to African dust. The Asian dust O3 perturbation also changes from decreasing to increasing above the boundary layer.

Comparison of Figures 3 and 4 shows that in both January and July the maximum O3 reduction by dust occurs over continental, high-NOx, ozone-producing regions. Previous studies show that over low-NOx oceanic regions, photochemistry destroys O3 [Olson et al., 1997]. Dust absorption reduces photochemistry, and hence this loss, in low-NOx oceanic regions. This causes O3 to increase there [Bian et al., 2003]. The increased O3 perturbation in remote regions in July is associated with more background dust and higher ozone photochemical production and destruction rate due to the higher solar irradiance and precursor emissions in northern summer.

The tropical Atlantic ocean is an area of particular interest because of its proximity to dust sources. Here the O3 change is small in January, and increases by more than 3 ppb in July. The nearby upstream dust sources and biomass burning emissions (which provide high-NOx) are controlling factors in this seasonal change. Biomass burning in the Sahel in January (Figure 3) is close to dust emissions and transport paths in North Africa (Figure 1). However, the centers of dust and biomass burning emissions shift by about 10° in opposite directions in July, separating the dust from the biomass burning plumes. This leaves low-NOx in the tropical North Atlantic ocean in July. These results are consistent with previous studies which show that absorbing aerosol reduces ground level O3 in polluted environments [Dickerson et al., 1997; Jacobson, 1998; He and Carmichael, 1999] and that O3 increases or decreases in the upper atmosphere depending on the availability of NOx [He and Carmichael, 1999]. The OH decreases in Figure 5 are consistent with the spatial distribution of dust (Figure 1). The decreases are driven by reductions in O(1D) caused by reduced ultraviolet photolysis of O3. The OH decreases are exacerbated by chemical reduction of OH due to reduced NO and increased CO due to photolysis changes [Bian et al., 2003].

Table 1 lists the mean January, July and annual changes in O3 [%] and OH [%] due to light scattering and absorption by dust. The amplitude of the O3 perturbation in July in the Northern Hemisphere (NH) is much larger than the Southern Hemisphere (SH) perturbation. This is due to the three factors: absolute dust amount, proximity to O3 precursors, and relative land area, already mentioned. Interestingly, net photolysis-induced annual mean O3 changes are greater in the SH than in the NH because of negative O3 change in the NH winter time. The global annual mean perturbation of O3 and OH by dust via photolysis is 0.23% and −2.44%, respectively. The global O3 perturbation is a factor of four larger in July than in January. The perturbation of both gases is about a factor of larger in the NH than in the SH in both seasons and in the annual mean (for OH). The annual change in O3 is about 0.2% in each hemisphere, because the seasonal changes differ dramatically.

### 3.2. Effects of Heterogeneous Uptake

Direct measurements and theoretical research provide convincing evidence that mineral dust plays important roles in altering atmospheric chemistry through heterogeneous reactions [Goodman et al., 2000; Galy-Lacaux et al., 2001]. Once sequestered on mineral dust particles, oxidants such as HNO3 and SO2 appear to undergo fast neutralization reactions with alkaline material (e.g., CaCO3) in mineral dust [Dentener et al., 1996; Zhang and Carmichael, 1999; Underwood et al., 2001; Michel et al., 2002]. Dentener et al. [1996] estimated that at least 40% of total column nitrate is found on the mineral aerosol over vast regions of the NH. We simulate the net direct uptake on mineral dust of O3, odd-hydrogen (OH, HO2), odd-nitrogen (NO2, NO3, and HNO3), N2O5, and H2O2. Heterogeneous reaction of SO2 on dust is also an important uptake process [Dentener et al., 1996; Song and Carmichael, 2001]. However, we do not include the sulfur cycle in this study. Our results on heterogeneous uptake on dust for some species should be considered an upper bound on dust uptake since some of these species would be lost to heterogeneous reactions on other aerosol types.

Using the method of Schwartz [1986] and Tie et al. [2001], the lifetime of species A associated with heterogeneous uptake on dust of NH, SH, and Global O3 and OH is

![Figure 5.](image)

**Table 1.** January, July, and Annual Mean Photochemical Perturbation by Dust of NH, SH, and Global O3 and OH

| Region | January | July | Annual |
|--------|---------|------|--------|
| O3     |         |      |        |
| NH     | −0.12   | 0.98 | 0.19   |
| SH     | 0.40    | 0.21 | 0.26   |
| Global | 0.14    | 0.59 | 0.23   |

| Region | January | July | Annual |
|--------|---------|------|--------|
| OH     |         |      |        |
| NH     | −2.51   | −4.82 | −4.07 |
| SH     | −0.68   | −1.03 | −0.82 |
| Global | −1.59   | −2.92 | −2.44 |

* Values are given in percent.
neous reactions on particles of radius \( R_p \), is provided by the inverse of the pseudo first-order heterogeneous rate constant \( k \) for diffusive and kinetic transport of \( A \) to the particle surface:

\[
k(A, R_p, T) = S[R_p/D_A + 4/(v_A \gamma)]^{-1}
\]

Here, \( v_A \) is the mean molecular speed of gas species \( A \) at temperature \( T \) [K]. We will discuss the \( T \)-dependence of \( k \) more thoroughly later in this section. \( D_A \) is the gas-phase diffusion coefficient of species \( A \) in air, and ranges from 1 to \( 2 \times 10^{-5} \) m\(^2\) s\(^{-1}\) for most species [Schwartz, 1986; Pruppacher and Klett, 1998]. Measurements of \( D_A \) have not been reported for many species modeled here, so we set \( D_A = 10^{-5} \) m\(^2\) s\(^{-1}\) for all species as given by Tie et al. [2001]. \( S \) [m\(^2\) m\(^{-2}\)] is the surface area density of the particles and is determined from the predicted mass mixing ratio of dust in four size bins using the specific area \( S \) [m\(^2\) kg\(^{-1}\)] shown in Table 2 of Zender et al. [2003]. The mass uptake coefficient of species \( A \) is \( \gamma \).

[26] The uptake coefficients of the eight species considered to undergo irreversible reactions on mineral dust surfaces in our model are summarized in Table 2. Uncertainties in \( \gamma \) are large, up to three orders of magnitude for certain species [Zhang and Carmichael, 1999; Goodman et al., 2000; Michel et al., 2002; Underwood et al., 2001]. For example, recent studies report \( 2.0 \times 10^{-6} < \gamma < 2.5 \times 10^{-3} \) for O\(_3\) [Michel et al., 2002] and \( 2.0 \times 10^{-3} < \gamma < 1.6 \times 10^{-2} \) for HNO\(_3\) [Goodman et al., 2000; Underwood et al., 2001]. We apply the values in Table 2 globally so that regional differences in \( \gamma \) due to dust mineralogy and RH are neglected.

[27] Figures 6 and 7 show the reduction of O\(_3\) [ppb] and OH [%], respectively, due to heterogeneous reactions on dust. Since the net uptake is irreversible, mineral dust uptake reduces O\(_3\) and OH globally. Heterogeneous uptake of O\(_3\) by dust (Figure 6) is broadly controlled by two factors: the O\(_3\) abundance (Figure 3) and the horizontal and vertical distributions of dust (Figure 1). In January, the maximum reduction occurs along the plume from western Africa to the tropical Atlantic ocean just above the boundary layer. In our simulations African dust that is lifted above the boundary layer in January is conveyed over the Atlantic ocean in a layer between 1–3 km known as the Saharan Air Layer (SAL) [Karyampudi et al., 1999]. The O\(_3\) change is greatest near the top of the boundary layer where the local maxima in O\(_3\) abundance (Figure 3) coincides with the SAL.
Table 3. January, July, and Annual Mean Decrease in NH, SH, and Global O₃ and OH Due to Heterogeneous Reactions on Dust

| Region | O₃ [%] | OH [%] |
|--------|--------|--------|
| NH     | −1.52  | −10.97 |
| SH     | −0.46  | −3.67  |
| Global | −0.99  | −7.32  |

*Values are given in percent.

and displaces the region of heterogeneous uptake to higher altitudes. It is interesting that the O₃ response to heterogeneous uptake increases with altitude in July, especially over Asia, while the photochemical response of O₃ to dust decreases with altitude (Figure 4).

Figure 7 shows that heterogeneous chemistry is important for OH over the dusty regions in both January and July. This is consistent with the OH photolytic perturbation (Figure 5). OH uptake favors lower altitudes than O₃ uptake (Figure 6). This reflects the quicker response of OH to indirect effects. The gas phase lifetime is only seconds for excessive OH uptake in very dusty regions by not allowing heterogeneous uptake coefficients (Table 2). We are quantifying these uncertainties in a separate study.

Table 3 lists the mean January, July, and annual changes in O₃ [%] and OH [%] due to heterogeneous chemistry on dust. Globally, O₃ decreases 0.9% and OH decreases nearly 10%. Regional reductions reach 8.5% for O₃ at the top of boundary layer over West Africa and the tropical Atlantic Ocean in January and in the mid-troposphere over the Arabian desert in July. OH decreases by 80% within the boundary layer in the zonally extensive tropical region from northern Africa to the Atlantic ocean in January and by 50% from India to the Caribbean in July. Our interpolated monthly mean dust fields contribute to excessive OH uptake in very dusty regions by not allowing dust-free periods during which OH could temporarily recover. The larger chemical perturbation occurs in the NH, where trace gas reductions are more than triple those in the SH. Heterogeneous uptake changes global O₃ and OH about four times more than photolysis rate forcing. This result is not quantitatively robust since our predicted changes in OH are large, as is the uncertainty in the uptake coefficients (Table 2). We are quantifying these uncertainties in a separate study.

Unfortunately, field measurements which could confirm or deny our findings for climatological heterogeneous uptake of oxidant species on mineral surfaces in dusty regions are scarce [Bey et al., 2001]. Previous research has focused on the heterogeneous perturbation in dusty conditions. Using a global three-dimensional model, Dentener et al. [1996] estimated that heterogeneous uptake on dust leads to a ~10% reduction of O₃ in dust source regions during the dustiest season. Using a box model, Zhang and Carmichael [1999] estimated that spring dust storms in East Asia decrease O₃ by 11–40%, NOₓ (NOₓ + N₂O₅ + HNO₃) by 16–100%, and H₂O₂ (OH + HO₂ + H₂O₂) by 11–59% via heterogeneous uptake. Our simulations indicate global reductions due to heterogeneous uptake on dust of 0.9% for O₃, 3.9% for NOₓ, and 5.1% for H₂O₂. Thus our global estimates are an order of magnitude less than estimates from other models during dusty conditions. In dusty parts of North Africa during late winter and early spring, we predict boundary layer ozone reductions of ~10%, similar to Dentener et al. [1996]. In East Asia in spring, we predict the monthly mean O₃ decreases by about 2%. This is consistent with the 11–40% instantaneous O₃ reduction during spring dust events in East Asia reported by Zhang and Carmichael [1999]. (Dust concentrations during these events are an order of magnitude larger than the monthly mean concentrations.)

3.3. Photochemical and Heterogeneous Coupling

Sections 3.1–3.2 describe the photolytic and heterogeneous forcing of oxidants by dust, examining each process in isolation. We now quantify interactions between photolytic and heterogeneous forcing when those processes operate simultaneously, as in nature. We define the effects of the photolysis-rate-only, heterogeneous-only, and coupled (photolysis plus heterogeneous) forcing by Δₚ, Δₜ, and Δₚ+ₜ respectively. The degree of non-linear interaction between photolysis and heterogeneous effects of dust defines the coupling factor λ

\[ \lambda = \frac{\Delta_{P+H}}{\Delta_P + \Delta_H} \]

Values of λ near unity indicate that the individual Δₚ and Δₜ perturbations are additive (i.e., linear). Figure 8 shows the zonal mean \( \lambda_{O_3} \), \( \lambda_{OH} \), and \( \lambda_{HNO_3} \) in January and July. In most remote and upper tropospheric regions, λ is near unity. In these regions, feedbacks between the photolytic and heterogeneous perturbations are generally less than 10%. The interaction increases over the subtropics, especially in the NH, where most dust resides. Feedbacks of O₃ production and loss due to changes in O₃ precursors leads to the complicated structure of \( \lambda_{O_3} \). Involvement of O₃ in photolysis alteration is negligible in its contribution to \( \lambda_{O_3} \) magnitude and structure. Coupling amplifies O₃ reductions in most of the SH and suppresses it in the tropics and NH in January. The effect of coupling in July is similar except in the NH mid-to-high latitudes where coupling changes from a suppressing to an amplifying effect on O₃.

Figure 8. Zonal mean coupling factor λ between photolysis rate and heterogeneous dust forcing of O₃, OH, and HNO₃ in January (left column) and July (right).
coupling occurs in the boundary layer and lower troposphere from the equator to 50°S in January and in the NH subtropical boundary layer and high latitudes in July. Other species studied in this paper exhibit coupling patterns similar to OH or to HNO3.

We now examine the relative roles of \( \delta_P \) and \( \delta_H \) in determining \( \Delta P+H \), and how the vertical structure of dust affects this relationship. We define the relative contribution of photolysis, \( \delta_P \), to \( \Delta P+H \), the net species change by dust, as

\[
\delta_P = \frac{\Delta P}{|\Delta P| + |\Delta H|}
\]  

Thus \( 0 < |\delta_P| < 1 \) and \( |\delta_P| = 0.5 \) where the magnitudes of the photolysis-only effect and the heterogeneous-only effect of dust are equal. Strictly, this definition is only valid where \( \lambda = 1 \). We take this definition approximately due to the weak nonlinear interaction on global scale (Figure 8). The relative contribution of heterogeneous reactions, \( \delta_H \) (not shown) is defined analogously to equation (3). Heterogeneous uptake is negative definite, so that \( \delta_H \equiv -1 + |\delta_P| \). Thus \( |\delta_H| \) is small where \( |\delta_H| \) is large, and visa versa.

Figures 9 and 10 show the zonal mean \( \delta_P \) for six of the species in Table 2 in January and July, respectively.

[35] Most regions dominated by photolysis perturbation (i.e., \( |\delta_P| > 0.5 \)) are confined to low-to-mid altitudes. This is consistent with our results in the previous section that heterogeneous forcing by dust is almost four times larger than the photolysis rate forcing. Patterns of \( \delta_P \) for \( \text{O}_3 \) and odd-nitrogen are similar. All show large values in the SH midlatitude boundary layer in January and in tropics and the NH high latitudes in July. Among these species, \( \text{NO}_2 \) is most changed by photolysis, with extensive vertical and meridional regions of large \( |\delta_P| \). Odd-hydrogen (OH and \( \text{HO}_2 \)) shows large \( |\Delta P| \) in polar regions in both seasons.

Table 4 summarizes the annual mean changes due to photolysis-only \( \Delta P \), heterogeneous-only \( \Delta H \), and the coupled forcing of dust, \( \Delta P+H \). The NH change dominates the SH change for most species, in accord with the hemispheric asymmetry of dust mass. Global annual mean tropospheric \( \text{O}_3, \text{H}_2\text{O}_2, \text{NO}_2, \) and \( \text{N}_2\text{O}_5 \) change less than or around 1%; \( \text{HNO}_3, \text{HO}_2, \) and \( \text{NO}_3 \) change 3–6%, and OH changes by \(-11.1\%\). OH and \( \text{HO}_2 \) are the most sensitive species in our study because photolysis rate and heterogeneous forcing by dust both decrease their abundance. In contrast, the individual changes \( \Delta P \) and \( \Delta H \) are of opposite signs for \( \text{O}_3 \), odd-nitrogen, \( \text{N}_2\text{O}_5 \), and \( \text{H}_2\text{O}_2 \). Thus cancellation by...
opposing responses to dust results in smaller net changes $\Delta_{PH}$ for these species.

Table 4 also lists the global mean coupling factors $\lambda$ (equation (2)). In the global mean, OH is the most sensitive to coupling: 7% of its change is due to the interaction of the photochemical and heterogeneous responses to dust forcing. O$_3$ exhibits no sensitivity to coupling ($\lambda_{O_3} = 1$) in the global mean because of mutual cancellation of regions of positive and negative coupling (Figure 8). On regional scales, however, O$_3$ exhibits moderate coupling.

We demonstrate this by examining the effects of dust on atmospheric chemistry in a dust-dominated region. This is Northern Africa and Tropical Atlantic (NATA) region downwind (80°W to 30°E, 0°–30°N). This NATA region carries the largest dust burden on the planet because of African dust sources [e.g., Zender et al., 2003]. Figure 11 shows the seasonal cycles of the dust forcing ($\Delta_{PH}$, $\Delta_{PH}$, and $\Delta_{PH+H}$) of each species in Table 2. The photolysis rate forcings peak in spring for OH, HNO$_3$, and HO$_2$, and in summer for O$_3$, NO$_3$, NO$_2$, N$_2$O$_5$. This seasonal change is also consistent with regional seasonality of dust burden from observations [Savoie et al., 1992; Holben et al., 1998] and simulations [Ginoux et al., 2001; Zender et al., 2003]. The net dust forcing of atmospheric chemistry is substantially

![Figure 10. Same as Figure 9, except for July.](image)

Table 4. Annual Mean Changes of Eight Species Due to Effects of Dust

| Species | NH | SH | Global | NATA | Photolysis $\Delta_P$ | Heterogeneous $\Delta_H$ | Coupled $\Delta_{PH}$ | $\lambda$ |
|---------|----|----|--------|------|------------------------|-------------------------|------------------------|--------|
| O$_3$   | 0.2| 0.3| 0.2    | 0.9  | –1.5                   | –0.3                    | –0.9                   | –5.0   | 1.00  | 0.93 |
| OH      | –4.0| –0.8| –2.4   | –15.0| –16.4                   | –2.9                    | –9.6                   | –64.0  | –18.5 | 0.93 | 0.85 |
| HNO$_3$ | 0.4| 0.3| 0.3    | 0.8  | –6.1                   | –1.5                    | –3.8                   | –28.3  | –5.8  | 0.95 | 1.00 |
| HO$_2$  | –1.0| 0.2| –0.4   | –6.0  | –9.1                   | –1.1                    | –5.1                   | –43.5  | –9.6  | 0.95 | 1.00 |
| NO$_3$  | 1.9| 0.8| 1.3    | 5.4  | –10.2                   | –1.5                    | –5.9                   | –47.2  | –8.7  | 0.95 | 1.00 |
| NO$_2$  | 3.2| 0.7| 1.4    | 9.8  | –0.5                   | –0.2                    | –0.3                   | –6.9   | 1.6 | 0.95 | 0.92 |
| N$_2$O$_5$ | 1.0| 1.0| 2.2    | 12.0 | –3.4                   | –0.8                    | –2.1                   | –19.6  | –0.3  | 0.95 | 0.92 |
| H$_2$O$_2$ | 0.3| 0.5| 0.5    | –0.6 | –0.4                   | 0.1                     | –0.2                   | –2.2   | –0.2  | 0.95 | 0.92 |

Values are given in percent. Shown are $\Delta_{PH}$, $\Delta_{PH}$, and $\Delta_{PH+H}$ in NH, SH, global mean, and North Africa and the Tropical Atlantic (NATA) region downwind (80°W to 30°E, 0°–30°N), and global mean and NATA-region coupling factors $\lambda$ (equation (2)).
larger in this region (see Table 4) than in the global mean. For instance, OH reduction in this region reaches ~66.8%, six times the global mean OH change. Table 4 shows that the influence of photolysis-heterogeneous coupling is much stronger in the NATA region than in the global mean. Coupling accounts for 7%, 15%, and 24% of the change of O3, OH, and N2O5, respectively, in the NATA region.

[39] Our results are consistent with previous regional studies of dust-chemistry interactions in Asia. [Zhang et al., 1994] observed short term anti-correlations of O3 and dust concentrations in Happo, Japan. They estimated O3 decreases about 3–10% per 10 μg m⁻³ dust. Our simulated annual mean boundary layer dust concentration in Happo, Japan is about 1.2 μg m⁻³ [Zender et al., 2003]. We estimate ΔP+H O3 is about −1.2% in fall, −1.3% in winter, and −1.5% in spring (consistent with Zhang et al.), and +0.4% in summer.

[40] Figure 12 compares our modeled O3 profile to observations at Abidjan (5°N, 4°W) made during the MOZAIC aircraft program from 1994–1999 [Martin et al., 2002]. The January simulation improves in the lower troposphere when we account for the effects of mineral dust on chemistry. The simulated influence of dust on the O3 profile in July is not obvious because of the cancellation of positive photolysis forcing and negative heterogeneous forcing over this station.

[41] Tabazadeh et al. [1998] propose heterogeneous chemistry on mineral dust and biomass burning aerosols irreversibly removes gaseous HNO3. If so, then representing this process should help reduce high biases in HNO3 common to gas-phase-only models. For example, previous studies of the nitrogen cycle simulated summertime HNO3 levels 2–10 times larger than observed in the upper troposphere over the east China coast [Hauglustaine et al., 1998; Wang et al., 1998b]. The UCI CTM summertime HNO3 bias in this region is also close to a factor of two. We find that dust reduces HNO3 by about 60% in the mid-to-upper troposphere in and downwind of dust source regions in summer, and by about 40% in winter. Based on our best estimate uptake rates (Table 2), therefore, dust explains a significant portion of HNO3 biases as proposed by Tabazadeh et al. [1998]. Remaining model-observation differences could be further, but probably not completely, reconciled if we are underestimating uptake rates and/or dust surface area in this region. Dust and NOx are often in the same plume and it is possible that interpolated monthly mean dust used here underestimates the impact of dust on HNO3. Further investigation is needed to quantify these uncertainties.

3.4. Sensitivity to Dust Spatial Distribution

[42] In this section we examine the sensitivity of column ozone change to dust horizontal, vertical, and geographic distribution. Our goal here is to link the efficiency with which dust alters important oxidants like O3 to physical processes, so that we understand where and why oxidants are most sensitive to marginal changes in dust emissions. We define the net O3 forcing efficiency of dust $\epsilon_{P-H}$ as the change in tropospheric column O3 [%] normalized by the column mass of dust in mg m⁻². The analogous forcing
forcing/C15 is inverted during transport from source regions to high latitudes. Dust near 45°N that normally resides between 2–4 km is located between 5–8 km in the inverted dust scenario, upper tropospheric dust mixed with NH subtropical dust from northern Africa lies beneath the mid-to-upper troposphere where scavenging processes for these clay-sized ($D < 2.5$ μm) particles are inefficient [Zender et al., 2003]. Thus the vertical structure of dust is inverted during transport from source regions to high latitudes.

Figure 13a shows the zonal mean column dust burden [mg m$^{-2}$] in July. The vertical scale is logarithmic and shows the dramatic variation of dust with latitude. Figure 13b shows the July change in tropospheric O$_3$ [%] due to the photolysis-only and the heterogeneous-only effects of dust. Figure 13c shows the forcing efficiencies $\epsilon_P$ and $\epsilon_H$ (i.e., the ratio of Figure 13b to Figure 13a). The significant separation between $\epsilon_P$ and $\epsilon_H$ (the scale is logarithmic), as well as between $\epsilon_{P\,H}$ and $\epsilon_{H\,H}$, shows the strong vertical sensitivity of the O$_3$ forcing efficiency.

The largest discrepancy between $\epsilon_P$ and $\tilde{\epsilon}_P$ occurs near 45°N. Dust near 45°N that normally resides between 2–4 km is located between 5–8 km in the inverted experiment. European emissions of O$_3$ precursors in NH summer create a strong O$_3$ band in the Erasing mentalities and subtropics. Consequently, O$_3$ change at high latitudes appears to be insensitive to model biases in high latitude dust.

Figure 13c shows both the photolysis and heterogeneous forcing efficiencies derived from the realistic dust vertical distribution, $\epsilon_P$ and $\epsilon_{P\,H}$, and the efficiencies of the inverted dust distribution, $\tilde{\epsilon}_P$ and $\epsilon_{H\,H}$. In our gas-phase-only simulation, horizontal advection is an order of magnitude more important than the local chemistry in determining O$_3$. With dust, the change of O$_3$ in this region due to horizontal advection is about five times more than the change from local chemistry. Thus O$_3$ change in non-dusty Northern high latitudes is controlled by transport of perturbed O$_3$ from the NH mentalities and subtropics. Consequently, O$_3$ change at high latitudes appears to be insensitive to model biases in high latitude dust.

Figure 13a shows the zonal mean column dust burden [mg m$^{-2}$], (b) tropospheric O$_3$ change [%] due to normal dust distribution broken down into $\Delta_P$ (thin line) and $\Delta_H$ (thick line), (c) O$_3$ forcing efficiencies of dust by photolysis forcing $\epsilon_P$ (thin line) and heterogeneous uptake $\epsilon_H$ (thick line). Dashed lines show corresponding $\tilde{\epsilon}_P$ and $\epsilon_{H\,H}$ for the inverted dust distribution. (d) Normalized vertical distribution of dust.

**Figure 13.** July zonal mean (a) column dust burden [mg m$^{-2}$], (b) tropospheric O$_3$ change [%] due to normal dust distribution broken down into $\Delta_P$ (thin line) and $\Delta_H$ (thick line), (c) O$_3$ forcing efficiencies of dust by photolysis forcing $\epsilon_P$ (thin line) and heterogeneous uptake $\epsilon_H$ (thick line). Dashed lines show corresponding $\tilde{\epsilon}_P$ and $\epsilon_{H\,H}$ for the inverted dust distribution. (d) Normalized vertical distribution of dust.

In July, total dust burden decreases monotonicity away from the NH subtropical source region (Figure 13a). The O$_3$ forcing peaks in the NH sub tropics with slight variations in the other latitudes (Figure 13b). To determine the relative importance of transport and local chemistry in the polar regions, we diagnosed separately the adjective and local chemical contributions to the O$_3$ budget in the region 72°–90°N. In our gas-phase-only simulation, horizontal advection is an order of magnitude more important than the local chemistry in determining O$_3$. With dust, the change of O$_3$ in this region due to horizontal advection is about five times more than the change from local chemistry. Thus O$_3$ change in non-dusty Northern high latitudes is controlled by transport of perturbed O$_3$ from the NH mentalities and subtropics. Consequently, O$_3$ change at high latitudes appears to be insensitive to model biases in high latitude dust.

[45] The strong meridional gradient in $\epsilon_P$ is also a function of the meridional gradient in the vertical structure of dust. Figure 13b shows the normalized vertical structure of dust. This is obtained by dividing the dust column by the local mass (so the values in each column sum to unity). Dust in source regions is concentrated in the lower troposphere in July (compare the upper right panel of Figure 1). At the same time, dust reaching the remote high latitudes is concentrated in the upper troposphere where scavenging processes for these clay-sized ($D < 2.5$ μm) particles are inefficient [Zender et al., 2003]. Thus the vertical structure of dust is inverted during transport from source regions to high latitudes.

[46] We studied the sensitivity of ozone forcing to the vertical distribution of dust by inverting the vertical profile of the dust while fixing the total dust column amount. In this sensitivity study, therefore, high-latitude dust is concentrated near the surface, while NH subtropical dust is concentrated in the upper troposphere. Figure 13d shows the normalized vertical structure of dust. This is obtained by dividing the dust column by the local mass (so the values in each column sum to unity). Dust in source regions is concentrated in the lower troposphere in July (compare the upper right panel of Figure 1). At the same time, dust reaching the remote high latitudes is concentrated in the upper troposphere where scavenging processes for these clay-sized ($D < 2.5$ μm) particles are inefficient [Zender et al., 2003]. Thus the vertical structure of dust is inverted during transport from source regions to high latitudes.

[47] Dust high in the atmosphere alters column O$_3$ through photolysis more than the same amount of dust in the lower atmosphere. However, $\tilde{\epsilon}_P < \epsilon_P$ in the NH sub tropics. As discussed in section 3.1, dust in low-NO$_x$ environments increases O$_3$ by reducing photochemical destruction of O$_3$. In the normal dust vertical distribution, lower tropospheric dust is concentrated near the surface, while NH subtropical dust is concentrated in the upper troposphere. Figure 13d shows the normalized vertical structure of dust. This is obtained by dividing the dust column by the local mass (so the values in each column sum to unity). Dust in source regions is concentrated in the lower troposphere in July (compare the upper right panel of Figure 1). At the same time, dust reaching the remote high latitudes is concentrated in the upper troposphere where scavenging processes for these clay-sized ($D < 2.5$ μm) particles are inefficient [Zender et al., 2003]. Thus the vertical structure of dust is inverted during transport from source regions to high latitudes.

[48] The largest discrepancy between $\epsilon_P$ and $\tilde{\epsilon}_P$ occurs near 45°N. Dust near 45°N that normally resides between 2–4 km is located between 5–8 km in the inverted experiment. European emissions of O$_3$ precursors in NH summer create a strong O$_3$ band in the Erasing mentalities and subtropics. Consequently, O$_3$ change at high latitudes appears to be insensitive to model biases in high latitude dust.
weakens toward the poles. Thus O₃ change in remote regions is more sensitive to global O₃ transport than to dust vertical structure.

The difference between $\epsilon_H$ and $\epsilon_I$ tracks the normalized dust distribution in Figure 13d. Where dust normally resides in the lower troposphere, $\epsilon_H > \epsilon_I$, and visa versa. In the troposphere, inverting the dust has little effect on the amount of O₃ the dust is exposed to because the zonal mean vertical distribution of O₃ is relatively homogeneous. Thus the discrepancy between $\epsilon_H$ and $\epsilon_I$ is largely explained by the increase of heterogeneous uptake with temperature, $v_\lambda \propto \sqrt{T}$ in equation (1).

In a box model study, He and Carmichael [1999] reported that surface O₃ decreases slightly by dust photochemical forcing when the aerosol layer is raised within the boundary layer, but that O₃ stops changing as the aerosol layer is raised further. Our results indicate that in the real atmosphere the sensitivity of O₃ to the vertical location of dust is more complicated than this and can change signs depending on the presence of O₃ precursors. We find that in dusty regions, O₃ is sensitive not only to the height of the dust layer but also to NOₓ availability. In remote regions O₃ transport is more important than local dust vertical structure.

4. Conclusions

We simulated and analyzed the influence of mineral dust on tropospheric chemistry through its impact on atmospheric photolysis and heterogeneous chemistry. The global annual mean change due to dust is on the order of several percent for most species considered, except for OH (−11.1%) (Table 4). As expected the largest changes occurred in and downwind of dust source regions, e.g., northern Africa, the tropical Atlantic, and the Arabian peninsula (Figures 4, 5, 6, and 7). Changes in O₃ and OH due to dust are more than five times greater in the NH than in the SH (Table 4).

To examine the coupling between photolysis rate forcing and heterogeneous forcing, we defined a coupling factor $\lambda$ (equation (2)) as the ratio of the forcing by both processes acting simultaneously to the sum of the forcings of each process acting alone (section 3.3). Photolysis forcing and heterogeneous forcing by dust are weakly coupled in the atmosphere the sensitivity of O₃ to the vertical location of dust is raised further. Our results indicate that in the real atmosphere the sensitivity of O₃ to the vertical location of dust is more complicated than this and can change signs depending on the presence of O₃ precursors. We find that in dusty regions, O₃ is sensitive not only to the height of the dust layer but also to NOₓ availability. In remote regions O₃ transport is more important than local dust vertical structure.

At least two studies report that indirect forcing by sulfate aerosol decreases by 20% when the aerosol is simulated interactively rather than interpolated from monthly means [Feichter et al., 1997; Roistayn and Lohmann, 2002]. The sulfate indirect effect depends strongly on non-linear relationships between aerosols, clouds, and radiative fluxes. Mineral dust is not as efficient a CCN as sulfate, therefore the non-linear relation between dust and clouds may be weaker than that of sulfate. However, dust and NOₓ are often in the same plume, e.g., in east Asia in spring and in west Africa in northern winter. Our model predicts NOₓ dynamically with a full chemistry scheme, but uses interpolated monthly mean dust abundances. This artificially suppresses dust concentration during dust events and promotes the concentration between events. We showed that the presence of O₃ precursors like NOₓ significantly affects the chemical forcing by dust. Thus non-linear relationships between dust, O₃ precursors, and their chemical responses may be biased in our model simulations. Further investigation is needed to quantify these potential biases.

The uncertainty in our estimates of the photochemical forcing of mineral dust stems from the choice of refractive index $n$ compounded by regional biases in the size and vertical distribution [Bian et al., 2003]. Previous studies show that dust strongly absorbs in the near ultraviolet, and that $n$ varies with wavelength [Savoie et al., 2000; Diaz et al., 2001; Kaufman et al., 2001; Dubovik et al., 2002]. Although the constant dust refractive index adopted in this study (section 3.1) results in strong absorption at key tropospheric photochemical wavelengths (300–400 nm), it should have a strong wavelength dependence.

The uptake coefficients in Table 2 are taken to be globally uniform, although the mineralogical composition of dust varies with sources [Sokolik et al., 2001; Michel et al., 2002]. We emphasize that our results are sensitive to our...
choice of uptake coefficient values which have large uncertainties. An analysis of the sensitivity our results to these uncertainties in γ is underway and we hope it will help prioritize future laboratory research on γ. Gaseous uptake may also vary with Relative Humidity through two mechanisms. First, high RH may significantly increase surface area on deliquescent particles [Hanel, 1976]. Second, RH may increase γ for some gases, such as HNO₃, but not others, such as NO₂ [Underwood et al., 2001]. Unfortunately, γ(RH) for most interesting species is unknown. The resulting biases may be small since RH is low in arid source regions, and particle surface area is low in most ocean regions except the tropical North Atlantic.

[55] Because of these uncertainties in model inputs, this study should be regarded as exploratory and subject to further improvements, including improved model evaluation. Unfortunately, field data to evaluate modeled dust photochemical and heterogeneous effects are limited. Few comprehensive measurements of O₃ have been performed in dusty regions, and the available observations, being for limited field experiments, do not provide representative climatologies. Records for other photochemically active species are also sparse. Recent field campaigns such as ACE-Asia and ITCT 2K2 will greatly facilitate future studies since these campaigns were conducted in and downwind of dust source region during Asian dust outbreaks. Fully evaluating the seasonality, geographic location, and vertical structure of dust perturbation predicted by our model, however, will require sustained measurements in dusty regions.

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