

Heterogeneous impact of dust on tropospheric ozone: Sensitivity to season, species, and uptake rates

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Abstract. Heterogeneous chemistry on mineral dust particles causes significant reductions in important tropospheric trace gases such as O_3 , OH, and HNO_3 in dust-dominated regions such as the North African Tropical Atlantic region. We analyze the spatial and temporal modes of dust-induced heterogeneous ozone removal ($\Delta_H O_3$) using empirical orthogonal functions (EOFs) and principal components analysis. We use the results to attribute ozone removal to specific pathways, and to assess the sensitivity of ozone removal to uncertainties in key heterogeneous uptake rates. The first EOF mode dominates $\Delta_H O_3$ variance (93%) and shows that dust reduces O_3 through heterogeneous reactions globally and year-around with the maximum in July. The second mode explains only 4% of $\Delta_H O_3$ spatial variance yet accounts for most $\Delta_H O_3$ seasonality. With best-guess uptake coefficients, indirect ozone reduction due to HNO_3 uptake exceeds direct heterogeneous uptake of O_3 . However, uncertainties in uptake rates allow the possibility that direct O_3 uptake exceeds HNO_3 -induced O_3 uptake, especially in Northern Spring. Recently published HNO_3 uptake coefficients on authentic dust range from $10^{-5} < \gamma_{HNO_3} < 0.2$, and imply that dust destroys 0.5–5.2% of tropospheric O_3 , respectively. Improved γ_{HNO_3} measurements and correct model representation of global dust composition, deliquescence, and aging are required to further reduce these order-of-magnitude uncertainties.

1. Introduction

Heterogeneous chemistry on mineral dust aerosol is an important factor in determining tropospheric composition because mineral dust accounts for up to half of all aerosol surface area [Penner *et al.*, 2001] and heterogeneous uptake of many key oxidants (e.g., HNO_3 , OH) occurs quickly on dust [e.g., Dentener *et al.*, 1996]. Yet many gaps remain in our understanding of the role of dust heterogeneous chemistry in the tropospheric O_3 cycle. In particular, uptake coefficients for heterogeneous reactions are poorly constrained [e.g., Michel *et al.*, 2002], the specific pathways that dominate dust-induced O_3 changes are poorly understood [Bian and Zender, 2003], and the role of heterogeneous mineral

composition (and multi-component aerosols in general) on chemical processing is difficult to assess at global scales [Martin *et al.*, 2002; Rodriguez and Dabdub, 2003]. This paper quantifies our understanding of the first two of these problems, important reaction pathways and uptake uncertainty.

The impact of dust heterogeneous chemistry on tropospheric O_3 has been investigated on regional [Zhang and Carmichael, 1999; Galy-Lacaus *et al.*, 2002; Underwood *et al.*, 2001b; Martin *et al.*, 2002] and global scales [Dentener *et al.*, 1996; Liao *et al.*, 2003; Bian and Zender, 2003; Bauer *et al.*, 2004]. Dust reduces O_3 by 10–40% in dust storm conditions [Dentener *et al.*, 1996; Zhang and Carmichael, 1999]. Dust appears to play a minor role in

the distribution of tropical tropospheric ozone [Martin *et al.*, 2002; Bian and Zender, 2003]. Dust reduces global tropospheric ozone by 1–5% [Bian and Zender, 2003; Bauer *et al.*, 2004] depending on the uptake coefficients employed. Partitioning this ozone reduction between direct uptake of O₃ on mineral surfaces [Michel *et al.*, 2002; Hanisch and Crowley, 2003b] and precursor removal is the focus of this study.

Mineral dust affects the photochemical oxidant cycle by providing additional reaction pathways for species such as NO_y and H_xO_y [Underwood *et al.*, 2001b; Galy-Lacaus *et al.*, 2002; Hanisch and Crowley, 2003a]. These species, in turn, influence ozone production/destruction rates [Dentener *et al.*, 1996; Zhang and Carmichael, 1999]. Zhang and Carmichael [1999] studied the regional decrease in O₃ concentration by dust influence resulting from three paths: reduction in photolytic rates; direct O₃ uptake; and destruction of important precursors. They conclude that direct uptake of O₃ by dust is the dominant pathway in the change in O₃ by heterogeneous chemistry. However, dust-induced tropospheric O₃ reduction is highly sensitive to the assumed uptake coefficient [Dentener *et al.*, 1996; Bian and Zender, 2003; Bauer *et al.*, 2004]. As we will show, indirect heterogeneous chemistry mechanisms (especially uptake of HNO₃) dominate O₃ reduction by dust with our best guess uptake coefficients.

Our four specific objectives are to:

1. Characterize the spatial modes of tropospheric O₃ variation due to heterogeneous reactions on mineral dust
2. Identify the seasonality of dust heterogeneous impact on tropospheric O₃ change
3. Quantify the relative importance of O₃ change reaction paths assuming best-guess uptake rates
4. Quantify the sensitivity of tropospheric O₃ change to the measured uncertainty in uptake rates

To accomplish these objectives, we perform EOF analyses of a suite of model simulations of tropospheric O₃ variations caused by prescribed heterogeneous reactions on mineral dust.

The effect of each irreversible uptake reaction on the variance structures is evaluated with a particular emphasis on reduced or elevated individual uptake coefficients. The dominant variance structures help us associate the spatial and temporal modes with the atmospheric chemistry phenomena related to dust heterogeneous reactions. Understanding the variance patterns of these species and their causes is important for prioritizing future laboratory and field research to constrain on uptake rates.

The paper is organized as follows. Section 2 describes the

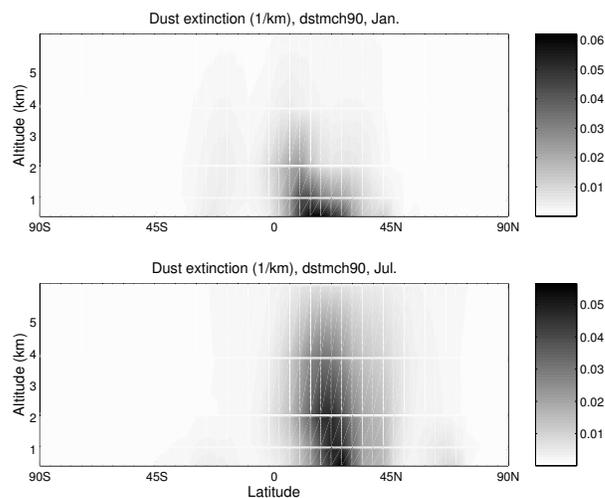


Figure 1. Zonal mean dust extinction [km^{-1}] at 340 nm in January and July.

simulated impact of mineral dust on tropospheric chemistry, and introduces the EOF analysis methodology. Section 3 presents the results of the EOF and sensitivity analyses. We discuss the uncertainties and implications of our findings in Section 4.

2. Models and Methods

2.1. Mineral Dust Distribution

The monthly-varying global 3-D dust concentrations used in this study are taken from the predictions of the mineral Dust Entrainment And Deposition (DEAD) model simulation of the 1990s [Zender *et al.*, 2003]. Figure 1 shows the predicted zonal mean mineral dust extinction [km^{-1}] at 340 nm in January and July. Maxima occur in the subtropical belts which contain Earth’s major deserts including North Africa, and the Saudi Arabian peninsula. Secondary maxima occur in Australia, and central and east Asia. In July, strong summertime convection lifts northern hemisphere dust higher than in January. This helps dust spread to remote regions. Dust centers around 10°N in January and shifts north to 20°N in July.

2.2. Heterogeneous Dust Chemistry and Ozone

The UCI Chemical Transport Model (UCICTM) [Wild and Akimoto, 2001] is a global 3D chemical transport model including emission, transport, deposition, and gas-phase O₃-NO_x-NMHC chemistry. UCICTM has been described and evaluated in previous tropospheric and stratospheric chem-

istry studies [Avallone and Prather, 1997; Olsen et al., 2000; McLinden et al., 2000; Wild and Prather, 2000; Wild and Akimoto, 2001; Prather and Ehhalt, 2001; Bian, 2001; Bian et al., 2003]. Bian and Zender [2003] used UCICTM to study the relative roles of photolysis and heterogeneous chemistry in dust forcing tropospheric chemistry. We represented irreversible uptake of reactions of eight species on dust: O₃, OH, HO₂, H₂O₂, HNO₃, NO₂, NO₃, and N₂O₅. Here we use additional UCICTM simulations to determine the relative roles and spatial patterns of all eight mineral dust heterogeneous reaction represented.

The consequences of the large uncertainty in the uptake rate coefficients on the pathways of ozone reduction are determined by four distinct types of UCICTM simulation, using best-guess and end-member uptake coefficient values for each species of interest. The uptake coefficients in Bian and Zender [2003] are the best-guess coefficients. Type P simulations allow dust to influence chemistry only by altering photolysis (i.e., UV actinic fluxes) through its scattering and absorbing properties. We also call this photolysis forcing. Type PH simulations are Type P with the addition of heterogeneous chemistry from the eight important irreversible uptake reactions using the best-guess uptake rate coefficients [Bian and Zender, 2003]. Type PHOX simulations are Type PH except that the heterogeneous uptake of one particular species X is omitted. Type PHSX are Type PH except we reduce or increase the uptake coefficient of a particular species X by multiplying the best-guess value by an uncertainty factor S of 0.5, 1.0, or 2.0.

We accomplish Objectives 1 and 2 (Section 1) by EOF analysis of heterogeneous O₃ variation ($\Delta_{\text{H}}\text{O}_3$) derived by subtracting Type P from Type PH simulations. Similar EOF analyses are conducted for the heterogeneous O₃ variation due to irreversible uptake of each species X, $\Delta_{\text{H}}^{\text{X}}\text{O}_3$. The species-specific contribution to ozone reduction, $\Delta_{\text{H}}^{\text{X}}\text{O}_3$, is obtained by subtracting Type PHOX from Type PH (for Objective 3), and Type PHOX from Type PHSX (for Objective 4).

As before, dust distribution is from DEAD simulations of 1994–1998 [Zender et al., 2003] with NCEP meteorology [Kalnay, 1996] in the NCAR MATCH model [Rasch et al., 1997] (T62×L28 resolution) re-gridded to the UCICTM resolution (4° × 5°, 9 vertical layers). Each simulation spins up for six months before the one year period analyzed here.

2.3. EOF Analysis

Empirical orthogonal function (EOF) analysis is a useful tool for uncovering dominant variance structures within a gridded dataset evolving through time [e.g., Olsen, 2000]. The EOF structure and the principal components (PCs) help determine which processes control the data variance $v(\mathbf{r}, t)$

(e.g., perturbation of O₃ by dust). Here \mathbf{r} is the spatial coordinate, and t is time. We expand $v(\mathbf{r}, t)$ on an EOF basis. This is a diminishing series of time-evolving, spatially uniform PCs, $\text{PC}_i(t)$, and time-constant, spatially variable EOFs, $\text{EOF}_i(\mathbf{r})$ [Olsen, 2000]:

$$v(\mathbf{r}, t) = \sum_{i=1}^{N'} \text{PC}_i(t) \text{EOF}_i(\mathbf{r}) + \sum_{i=N'+1}^N \text{PC}_i(t) \text{EOF}_i(\mathbf{r}) \quad (1)$$

The eigenvalues and EOFs are ordered from largest to smallest. We retain $i \leq N'$ terms and discard the rest. The first two EOFs ($N' = 2$) suffice for our purposes. These EOFs highlight the dominant modes of variability while greatly reducing dataset size.

The eigenvalue magnitude λ_i is the variance along EOF_i :

$$\text{Percent Variance Along EOF}_i = 100 \times \frac{\lambda_i}{\sum_{i=1}^N \lambda_i} \quad (2)$$

The denominator is the total variance in all modes. The Linear Algebra PACKage (LAPACK) [Anderson et al., 1999] routine `dgesvd` computes the singular value decompositions.

3. Results

3.1. Modes and Seasonality of Heterogeneous O₃ Reduction

Figure 2 shows the first and second EOFs and PCs of $\Delta_{\text{H}}\text{O}_3$. The primary EOF, EOF_1 , contributes 93% of the O₃ variance. This first mode shows that heterogeneous reactions on mineral dust suppress tropospheric O₃ globally, and that boreal summer dust causes most O₃ variance. The spatial distribution of EOF_1 is similar to the July zonal mean dust distribution (Figure 1) convolved with the ambient O₃ distribution (e.g., Figure 3 of Bian and Zender [2003]). The greatest O₃ reduction coincides with the July zonal dust maxima above 20°N caused by dust from North Africa and the Saudi Arabian peninsula.

Tropospheric O₃ formation and transport modulate the meridional extent and altitude of the ozone reduction signal. Tropospheric O₃ concentrations increase in northern polar regions and elevated altitudes, with minimal O₃ column near the equator. Thus O₃ concentration moves the $\Delta_{\text{H}}\text{O}_3$ signal north of the dust maxima, elongates the signal toward higher altitudes, and reduces the impact of southern hemispheric dust.

The continuously positive value of PC_1 indicates that EOF_1 continually reduces (rather than enhances) ozone year-round. The shape of PC_1 demonstrates that the O₃

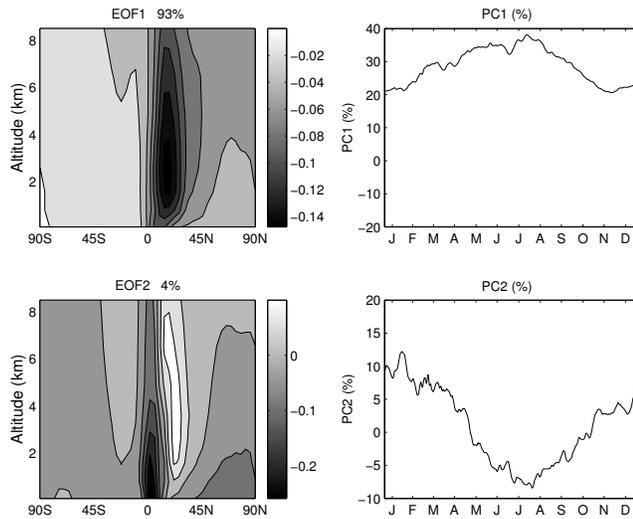


Figure 2. Variance of $\Delta_{\text{H}}\text{O}_3$ shown by EOF₁ (upper-left) and EOF₂ (bottom-left) for spatial patterns, and PC₁ (upper-right) and PC₂ (bottom-right) for seasonality. EOFs are labeled with percent variance explained by each.

reduction gradually intensifies from boreal winter to boreal summer to form an annual cycle with maximum in July. Strong boreal summer dust emission and convection [e.g., Zender *et al.*, 2003] and photochemistry [Bian and Zender, 2003] explain the $\Delta_{\text{H}}\text{O}_3$ seasonality.

EOF₂ contains a dipole feature in $\Delta_{\text{H}}\text{O}_3$. The negative pole occupies the Equator low to middle troposphere. Boreal winter African dust carried in tropical north-easterlies heavily influences this region. The positive pole is in the northern tropical mid- to upper-troposphere. We attribute this to boreal summer dust from North Africa and the Saudi Arabian peninsula. Though it accounts for only 4% of the global total O₃ variance, this second mode of $\Delta_{\text{H}}\text{O}_3$ reinforces the seasonality of $\Delta_{\text{H}}\text{O}_3$ seen in the first mode. The negative pole reduces O₃ in boreal winter and increases O₃ in boreal summer, as shown by PC₂. The positive pole has the opposite seasonality.

3.2. Heterogeneous O₃ Reduction by Species

Figure 3 shows EOF₁ and PC₁ of $\Delta_{\text{H}}^{\text{X}}\text{O}_3$ for the seven species X whose irreversible uptake on dust is represented: O₃, OH, HO₂, HNO₃, NO₂, NO₃, and N₂O₅. H₂O₂ is omitted from the presentation due to its negligible impact. EOF₁ accounts for the greatest total variance of $\Delta_{\text{H}}\text{O}_3$ (Figure 2) and is extremely similar (spatial correlation $r = 0.97$) to EOF₁ of $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ (Figure 3). EOF₁ explains about 90% of each $\Delta_{\text{H}}^{\text{X}}\text{O}_3$ dataset, dominating the variance. PC₁

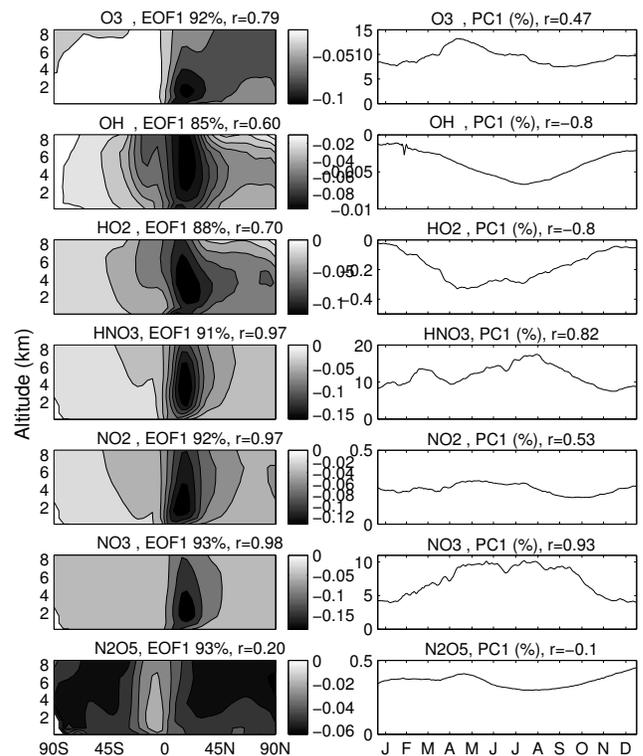


Figure 3. Zonal mean EOF₁ of $\Delta_{\text{H}}^{\text{X}}\text{O}_3$ variances due to irreversible uptake of seven reactive species on mineral dust (left) and the corresponding seasonal variation of PC₁ (right). Percent variances alone EOF₁ (2) are indicated. Correlation r between EOF₁ of $\Delta_{\text{H}}\text{O}_3$ and $\Delta_{\text{H}}^{\text{X}}\text{O}_3$ is shown for each species, as is the correlation between PC₁ of $\Delta_{\text{H}}\text{O}_3$ and $\Delta_{\text{H}}^{\text{X}}\text{O}_3$.

of $\Delta_{\text{H}}\text{O}_3$ and $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ are virtually identical with correlation $r = 0.82$. Both display strong seasonal cycles that peak in July.

EOF₁ of $\Delta_{\text{H}}\text{O}_3$ is also highly correlated with EOF₁ of both $\Delta_{\text{H}}^{\text{NO}_3}\text{O}_3$ and $\Delta_{\text{H}}^{\text{NO}_2}\text{O}_3$ ($r = 0.98$ and 0.97 , respectively). However, the temporal correlation is high between $\Delta_{\text{H}}\text{O}_3$ and $\Delta_{\text{H}}^{\text{NO}_3}\text{O}_3$ ($r = 93\%$), and low between $\Delta_{\text{H}}\text{O}_3$ and $\Delta_{\text{H}}^{\text{NO}_2}\text{O}_3$ ($r = 53\%$). Furthermore, PC₁ of $\Delta_{\text{H}}^{\text{NO}_2}\text{O}_3$ is one order of magnitude smaller than PC₁ of $\Delta_{\text{H}}^{\text{NO}_3}\text{O}_3$. Thus NO₂ uptake by mineral dust is a relatively minor contribution to $\Delta_{\text{H}}\text{O}_3$.

The impact of direct O₃ uptake on ozone levels, $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$, is weaker than $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ except in April. $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ is comparable to $\Delta_{\text{H}}^{\text{NO}_3}\text{O}_3$ in boreal summer. Direct O₃ uptake produces lower correlations of EOF₁ and PC₁ with $\Delta_{\text{H}}\text{O}_3$ ($r = 0.79$ and 0.47 , respectively) than do $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ and

$\Delta_{\text{H}}^{\text{NO}_3}\text{O}_3$. Direct O₃ uptake exerts maximal influence on O₃ in April, three months earlier than the July peak in $\Delta_{\text{H}}\text{O}_3$ (Figure 2). These results show that direct O₃ uptake is a significant, but not dominant, pathway for O₃ reduction with the best-guess uptake coefficients. Figure 3 also shows that direct uptake of N₂O₅, HO₂, and OH on mineral dust cause only negligible reductions in tropospheric O₃.

Dentener et al. [1996] investigated O₃ impact of N₂O₅, O₃, and HO₂-radical uptake on dust using $\gamma_{\text{O}_3} = 5 \times 10^{-5}$. They found tropospheric ozone decreases up to 10% in and nearby dust source areas. Most of their O₃ reduction (2–6%) was due to direct uptake of O₃ destruction on mineral aerosol. Our EOF analysis supports their conclusion when we consider only N₂O₅, O₃, and HO₂-radicals.

Zhang and Carmichael [1999] show that direct uptake of O₃ on dust significantly decreases O₃ concentrations if $\gamma_{\text{O}_3} \gtrsim 1 \times 10^{-4}$. They find that $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ dominates $\Delta_{\text{H}}\text{O}_3$ if $\gamma_{\text{O}_3} = 1 \times 10^{-4}$. The significant difference in the importance of direct ozone uptake between *Zhang and Carmichael* [1999] and ours study clearly demonstrates that the relative importance of $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ depends on γ_{O_3} . More recent studies of O₃ uptake on authentic Asian and African dust samples find $\gamma_{\text{O}_3} = 2\text{--}6 \times 10^{-5}$ [*Michel et al.*, 2002; *Hanisch and Crowley*, 2003b]. These confirm our use of $\gamma_{\text{O}_3} = 5 \times 10^{-5}$ [*Bian and Zender*, 2003].

The main nitrogen oxide reservoir species, NO_x and HNO₃, strongly affect tropospheric O₃ through complex photochemical cycles [e.g., *Seinfeld and Pandis*, 1997]. According to *Underwood et al.* [2001b], initial uptake coefficients for NO₂ and HNO₃, adjusted for roughness effects, must exceed 10⁻⁴ to significantly impact global NO_x, HNO₃, and O₃ concentrations. Box-model calculations show that $\gamma_{\text{NO}_2} = 1 \times 10^{-5}$ is sufficient to reduce HNO₃ concentrations [*Underwood et al.*, 2001b]. Thus our best-guess uptake coefficient for NO₂ on dry surface, $\gamma_{\text{NO}_2} = 4.4 \times 10^{-5}$, is slightly too low to significantly impact the global photochemical oxidant cycle,

With our best-guess uptake coefficient of $\gamma_{\text{HNO}_3} = 1.1 \times 10^{-3}$, irreversible uptake of HNO₃ has the most significant effect on O₃. Yet, this choice may still be conservative [e.g., *Hanisch and Crowley*, 2001a, b] and will be discussed further below. In any case, the mechanism by which HNO₃ affects O₃ is important. In dusty regions, coarse particles adsorb HNO₃ and sediment to the planetary surface at a rate that exceeds gas phase HNO₃ removal. Consequently, heterogeneous uptake of HNO₃ on mineral dust substantially reduces the O₃ precursor NO_x, and makes HNO₃ the most important species for dust-induced heterogeneous O₃ variation. Field and laboratory studies confirm that a large fraction of gas-phase nitric acid is neutralized and removed by alkaline mineral aerosol [*Tabazadeh et al.*, 1998; *Zhang*

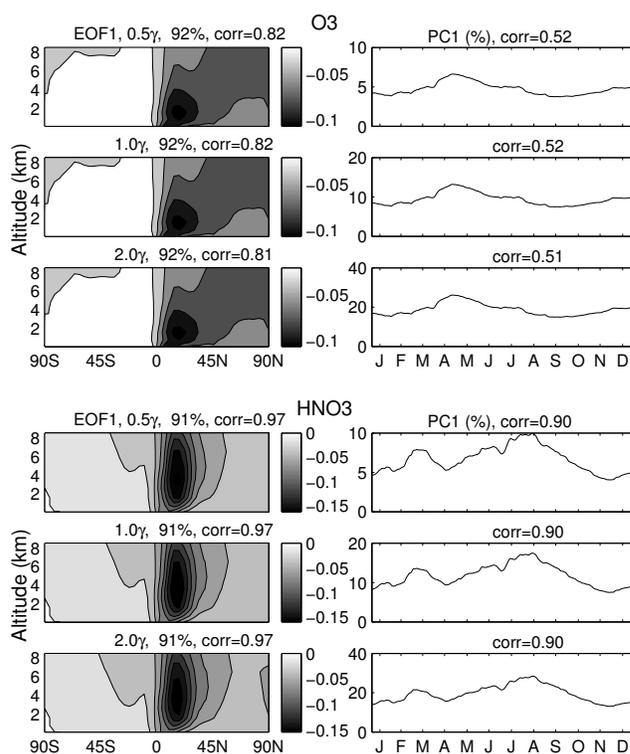


Figure 4. As in Figure 3 but for spatial distribution (EOF₁) and temporal behavior (PC₁) of $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ and $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ simulated using uptake coefficients of 0.5, 1.0, and 2.0 times the best-guess γ_{O_3} and γ_{HNO_3} .

and *Carmichael*, 1999; *Goodman et al.*, 2000; *Song and Carmichael*, 2001; *Bey et al.*, 2001].

3.3. Sensitivity to Assumed Uptake Coefficients

Given the uncertainty in the uptake coefficients, it is natural to ask how sensitive our results are to the uptake coefficients assumed. We focus on uncertainty in γ_{HNO_3} and γ_{O_3} since they dominate O₃ reduction (Figure 3). We multiply the best-guess values for γ_{HNO_3} and γ_{O_3} by uncertainty factors of 0.5, 1.0, and 2.0. Figure 4 shows the resulting primary modes of $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ and $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$. The O₃ reduction is linearly related to γ_{O_3} . $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ is more sensitive to γ_{O_3} than $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ is to γ_{HNO_3} . Therefore, the importance of HNO₃ in $\Delta_{\text{H}}\text{O}_3$ decreases while the importance of O₃ increases for the same relative elevation in γ . If our assumed γ_{HNO_3} (1.1×10^{-3}) is too high and our assumed γ_{O_3} (5.0×10^{-5}) is too low, then O₃ uptake might be more important for O₃ reduction than HNO₃ uptake. On the other hand, direct O₃ uptake is not the dominant pathway in heterogeneous O₃ variation unless our best guess coefficients are significantly

in error globally. For our best guess coefficients, $\Delta_{\text{H}}^{\text{O}_3}\text{O}_3$ exceeds $\Delta_{\text{H}}^{\text{HNO}_3}\text{O}_3$ only in Spring.

4. Discussion and Conclusions

We use EOF techniques to analyze the species and uptake rate dependence of tropospheric O₃ reductions due to heterogeneous uptake on mineral dust particles. The first EOF is produced by boreal summer dust and the tropospheric O₃ distribution. It dominates O₃ variation and has relatively weak seasonality. EOF₂ includes the signature of boreal winter dust, and accentuates the seasonality of dust-induced O₃ variation. With the best-guess uptake coefficients, the most important heterogeneous path leading to O₃ variation is HNO₃ uptake, followed in importance by direct uptake of O₃ itself. NO₃ is also important in boreal summer. In general, dust-induced heterogeneous O₃ variation depends on assumed uptake rate γ , season, and presence of O₃ precursors.

HNO₃, NO₃, and O₃ are most important in modulating dust-induced O₃ variation. Thus the mechanisms and uptake rates of HNO₃, O₃, and NO₃ deserve priority in laboratory and field experiments. Direct O₃ uptake is more important than HNO₃ uptake only if $\gamma_{\text{O}_3} > 5.0 \times 10^{-5}$ and $\gamma_{\text{HNO}_3} < 1.1 \times 10^{-3}$ globally.

The value of γ_{HNO_3} is both the most uncertain and important parameter in our study. Our assumed value of $\gamma_{\text{HNO}_3} = 1.1 \times 10^{-3}$ [Underwood *et al.*, 2001b] is a hundred times larger than measurements of authentic Chinese dust and Saharan sand showing $\gamma_{\text{HNO}_3} = 1\text{--}2 \sim 10^{-5}$ [Underwood *et al.*, 2001a; Grassian, 2002], and a hundred times smaller than measurements of other samples from the same regions which find $\gamma_{\text{HNO}_3} = 0.1\text{--}0.2$ [Hanisch and Crowley, 2001a, b, 2003a]. The disparity between these measurements must be reconciled by careful procedural analysis, intercomparison, and replication of results. Factors which may contribute to this large discrepancy in measurements include dust composition, surface area, relative humidity, and anthropogenic contamination. The larger values are similar to HNO₃ uptake into liquid cloud droplets [Seinfeld and Pandis, 1997, e.g.], suggesting that deliquescence, and thus CaCO₃ [Krueger *et al.*, 2003], plays a key role in γ_{HNO_3} . If this is the case, then particle mineralogy must be known and traced in models before reliable predictions of dust-induced heterogeneous O₃ destruction are possible. Tropospheric O₃ reduction reaches 0.9% by dust photolytic and heterogeneous influence with the best guess uptake coefficients (Table 4 of Bian and Zender [2003]). Using $\gamma_{\text{HNO}_3} = 0.1$ in our model instead of $\gamma_{\text{HNO}_3} < 1.1 \times 10^{-3}$ reduces global tropospheric O₃ by 5.2%, over five times our best-guess estimate. Thus, if high values of HNO₃ uptake coefficient are

valid globally, HNO₃ uptake (and O₃ reduction) are significantly greater than presented in Bian and Zender [2003] and this study.

Re-noxification of HNO₃ on dust may reduce the importance of HNO₃ on tropospheric O₃ [Zhang and Carmichael, 1999]. This effect, however, could be partially compensated for by NO_x recycled from heterogeneous reaction of HNO₃ on dust surfaces. Further investigation is needed to understand the role of HNO₃ re-noxification on mineral dust.

Other aerosol types compete with mineral dust as heterogeneous reaction sites, reducing the impact of dust. This competition depends on the amount, composition, and mixing-state (internal or external) of the other species. A unified model which represents all important atmospheric aerosols is required to better quantify heterogeneous O₃ reduction due to mineral dust. We have implemented dust, sea salt, biomass, sulfate, nitrate, and ammonium using an aerosol thermodynamic equilibrium model [Metzger *et al.*, 2002] in UCICM. Our preliminary results show that the additional nitrogen aerosol reservoir acts to decrease the HNO₃ uptake on mineral dust by about 15%. We anticipate the inclusion of these anthropogenic aerosols will help improve our understanding of the global O₃ and nitrogen budgets and the role of dust in removing these biogeochemically important species from the atmosphere to the surface.

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