Impact of air pollution on wet deposition of mineral dust aerosols

Song-Miao Fan, Larry W. Horowitz, Hiram Levy II, and Walter J. Moxim

NOAA Geophysical Fluid Dynamics Laboratory, Princeton University, Princeton, New Jersey, USA

[1]   Mineral dust aerosols originating from arid regions are simulated in an atmospheric global chemical transport model. Based on model results and observations of dust concentration, we hypothesize that air pollution increases the scavenging of dust by producing high levels of readily soluble materials on the dust surface, which makes dust aerosols effective cloud condensation nuclei (CCN). This implies that air pollution could have caused an increase of dust deposition to the coastal oceans of East Asia and a decrease by as much as 50% in the eastern North Pacific.   *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0330 Atmospheric Composition and Structure: Geochemical cycles; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry. **Citation:** Fan, S.-M., L. W. Horowitz, H. Levy II, and W. J. Moxim (2004), Impact of air pollution on wet deposition of mineral dust aerosols, *Geophys. Res. Lett.*, *31*, L02104, doi:10.1029/2003GL018501.

[2]   A large amount of mineral dust is lifted during windstorms over deserts and semi-arid regions, and transported over long distances in the atmosphere. Dust aerosols are removed from the atmosphere by gravitational settling followed by dry deposition to the surface, and are scavenged by seeding cloud condensation and colliding with falling rain drops and snow. Mineral dust can become wet but is insoluble [*Rosenfeld et al.*, 2001]. However, aged dust aerosols are often coated with soluble materials such as sulfate and nitrate resulting from heterogeneous chemical reactions [*Dentener et al.*, 1996]. Dust aerosols are effective ice nuclei in the atmosphere [*Pruppacher and Klett*, 1978]. Whether they are good droplet nuclei depends on the content of ions on the particle surface and the competition of other cloud condensation nuclei such as sea-salt and sulfate aerosols [*Pruppacher and Klett*, 1978; *Rosenfeld et al.*, 2001]. Here we present modeling results that, in combination with observations, suggest dust aerosols coated with sulfate and nitrate ions are effective droplet nuclei (hydrophilic), but non-reacted ones are not (hydrophobic, or droplets form but do not grow to the size threshold for onset of precipitation).

[3]   The Geophysical Fluid Dynamics Laboratory (GFDL) global chemical transport model (GCTM) [*Mahlman and Moxim*, 1978] was used for this study. It has equal-area horizontal grids with 265 km resolution. The model was adapted to use NCEP reanalysis winds, archived every 6 hours, on the same 28 vertical (sigma) levels [*Kalnay*,

1996]. The NCEP winds were linearly interpolated horizontally to the center point of GCTM grid-cells. Vertical velocities are calculated from horizontal mass divergence and the surface pressure tendency.

[4]   Sub-grid scale vertical mixing is parameterized by a diffusion coefficient (K_z) [*Levy et al.*, 1982]. In the surface mixed layer, K_z is calculated from the surface momentum flux and vertical wind shear, both of which are derived from the NCEP reanalysis, using an approximation that momentum flux is constant with altitude [*Zhang and Anthes*, 1982]. The boundary layer height is diagnosed from the gradient Richardson number ($Ri < 1.0$). Diffusion is enhanced for deep convection whose height is diagnosed from the moist Richardson number ($Ri < 0.25$) [*Levy et al.*, 1982]. Grid-scale advection is calculated using a finite difference scheme [*Mahlman and Moxim*, 1978]. The advection time step is 26 minutes, and the vertical diffusion time step is 2.6 minutes. Model transport has been evaluated by comparing model results to observed SF_6, CO_2, and ^{222}Rn in the atmosphere.

[5]   Dust entrainment (E, kg m^{-2} s^{-1}) is predicted in the model from surface friction velocity (u*, m s^{-1}, derived from the surface momentum flux) as follows [*Shao et al.*, 1993]:

$$E = C\, S(x, y)\, u^* \left(u^{*2} - u_t^{*2}\right) \qquad (1)$$

where C is a scaling factor (= 0.008 kg m^{-5} s^2), S(x, y) is a function of longitude (x) and latitude (y) that specifies the spatial distribution of dust sources taken from *Ginoux et al.* [2001], and u_t^* is a threshold of u* below which there is no entrainment. The S(x, y) function has implicitly incorporated factors such as vegetation cover, soil texture, and erosion surface area, and was guided by topography and multi-year satellite observations of dust aerosols [*Prospero et al.*, 2002]. The original S(x, y) is doubled in Taklimakan and Gobi deserts to increase model dust concentrations at the Asian sites. The magnitude of u_t^* depends on soil moisture [*Fecan et al.*, 1999] and surface roughness [*Raupach et al.*, 1993; *Marticorena and Bergametti*, 1995]. However, we choose to use $u_t^* = 0.35$ m s^{-1} everywhere based on a lack of spatial data on surface roughness. We neglect the influence of soil moisture on the desert sources [*Tegen et al.*, 2002], where annual rainfall is low (<0.2 m) and surface soils are dry.

[6]   The size distribution of the dust source is specified based on average observations made over the Sahara during dust-carrying wind events [*D'Almeida*, 1987]. Transport of dust is simulated separately for 8 size bins (0.2–0.36, 0.36–0.6, 0.6–1.2, 1.2–2.0, 2.0–3.6, 3.6–6, 6–12, and 12–20 μm in diameter). Larger particles (>20 μm) settle out of the atmosphere quickly, with a lifetime less than half a day. The model size distribution is compared to measurements in Asia, North Pacific, and North Atlantic in another paper.
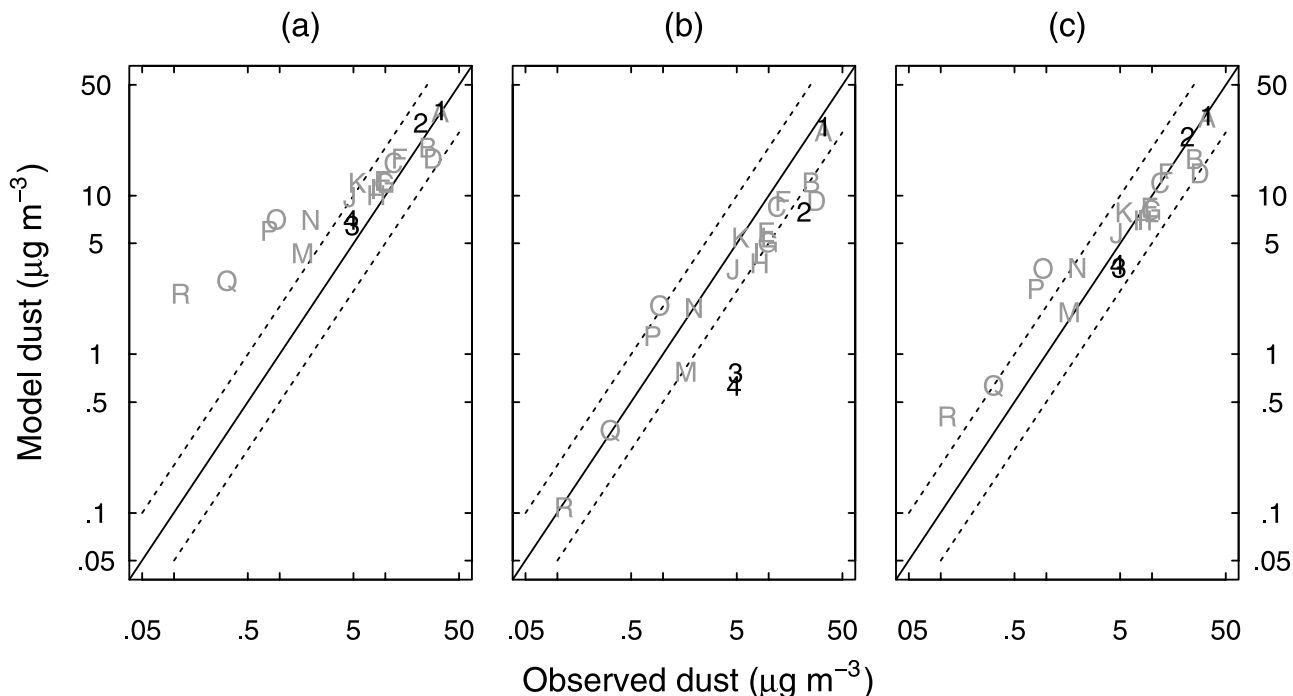
Figure 1. Model vs. observed annual average dust concentrations for (a) hydrophobic, (b) hydrophilic, and (c) chemical aging simulations. Numerical symbols indicate North Atlantic sites, and alphabetical symbols indicate North Pacific sites. They are (1) Izaña (28°N, 17°W), (2) Barbados (13°N, 60°W), (3) Bermuda (32°N, 65°W), (4) Miami (26°N, 80°W), (A) Qingdao (36°N, 121°E), (B) Jeju (33°N, 126°E), (C) East China Sea (31°N, 130°E), (D) Mallipo (27°N, 130°E), (E) Xiamen (24°N, 119°E), (F) Izumo (35°N, 131°E), (G) Wajima (37°N, 136°E), (H) Okushiri (42°N, 138°E), (I) Hachijojima (33°N, 139°E), (J) Chichijima (33°N, 142°E), (K) Okinawa (27°N, 128°E), (L) Onna (26°N, 128°E), (M) Shemya (53°N, 174°E), (N) Northwest Pacific (35°N, 171°E), (O) Midway (28°N, 177°W), (P) Oahu (21°N, 158°W), (Q) Enewetak (11°N, 162°E), (R) Fanning (4°N, 159°W). The solid line indicates a 1:1 relation; the dotted lines indicate 1:2 and 2:1 relations.

[7] Dry deposition of dust aerosols is parameterized according to *Giorgi* [1986]. The dry deposition velocity is expressed in terms of u* and particle size and density. In-cloud wet-deposition for highly soluble aerosols is described in *Kasibhatla et al.* [1991]. In-cloud scavenging is assumed to be 100 percent for hydrophilic aerosols. The wet-deposition parameterization is modified in this study for hydrophobic dust aerosols. Scavenging of hydrophobic aerosols is set to zero by droplet nucleation, and is 100 percent when ice nucleation occurs (ambient temperature below 258 K) in stable clouds or in a convective column. The model uses precipitation from the NCEP reanalysis, which tends to under-estimate annual precipitation by up to 20 percent in wet areas of the tropical oceans and over the storm tracks of the mid-latitudes of both hemispheres [*Janowiak et al.*, 1998]. The wet deposition has been evaluated by comparing modeled ^{7}Be and ^{210}Pb to observations.

[8] We show results from three separate simulations: (S1) dust aerosols are prescribed to be hydrophobic, (S2) dust aerosols are hydrophilic, and (S3) dust aerosols are transformed from hydrophobic to hydrophilic by reaction with SO$_2$. We use this reaction to represent the combined effect of dust reactions with SO$_2$, N$_2$O$_5$, H$_2$SO$_4$, HNO$_3$, and organic acids (referred to as "chemical aging"). The rate of chemical aging is given by

$$r_i = k[SO_2][m_i]/(\Sigma[m_i]) \qquad (2)$$

where k is a constant, [SO$_2$] is monthly mean volume mixing ratio predicted by MOZART2 [*Horowitz et al.*, 2003], [m$_i$] is mass mixing ratio of hydrophobic dust in the ith size bin, and $\Sigma[m_i]$ is the sum over all size bins. We chose k = 0 for RH < 50%, increasing linearly with RH up to k = 0.001 s^{-1} for RH > 60% [*Dentener et al.*, 1996]. The neutralizing capacity of calcite (forming gypsum by reaction with sulfuric acid) is related to $\Sigma[m_i]$. It should be noted that chemical aging of dust is a complex process, involving calcite reactions with nitric and sulfuric acids, deliquescence, absorption and oxidation of SO$_2$ and hydrolysis of N$_2$O$_5$ [*Usher et al.*, 2002; *Krueger et al.*, 2003]. The simplified aging model is admittedly a crude representation of the processes.

[9] Figures 1a, 1b, and 1c show average dust concentrations simulated using NCEP winds from 1994–1998, in comparison with observations at sites where annual cycles were measured. The measurements were made with filter samples collected in the 1980s and early 1990s [*Gao et al.*, 2003; and references therein]. It is noted that the modeled seasonal variations of dust concentration are in phase with surface observations and the total dust deposition fluxes are in agreement with oceanic measurements, which will be presented elsewhere. The observations range over 2 orders of magnitude, while uncertainties of the data are usually less than a factor of 2. The distances of transport from dust sources to measurement sites are ordered numerically (1–4)
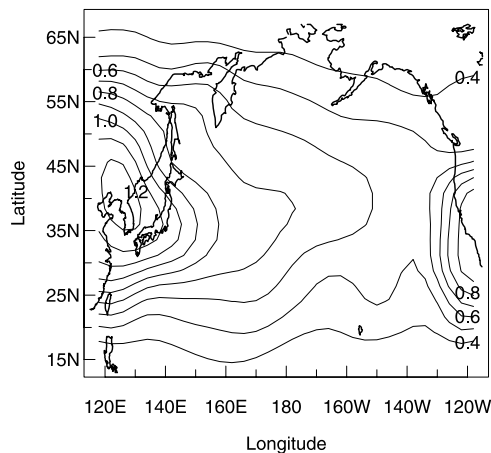
Figure 2. Ratio of dust deposition (dry + wet) predicted for hydrophilic aerosol to that for hydrophobic aerosol in the North Pacific. Contour lines are super-imposed on the coastlines.

in the North Atlantic and alphabetically (A–R) in the North Pacific (Figures 1a, 1b, and 1c). The spatial gradient from Izaña to Barbados to Bermuda and Miami in the North Atlantic is well simulated by S1, but that from coastal China to Japan to remote sites in the North Pacific is not, as indicated by increasing error with distance (Figure 1a). By contrast, the agreement between observations and S2 results is good (within a factor of 2) in the North Pacific, but that in the North Atlantic is degraded (Figure 1b). It is noted that previous models tend to over-predict the spatial gradient in the North Atlantic (as in S2) and/or under-predict that in the North Pacific (as in S1), depending on the parameterization for wet deposition of dust aerosols [e.g., *Ginoux et al.*, 2001; *Tegen et al.*, 2002; *Gao et al.*, 2003; *Mahowald et al.*, 2003; *Zender et al.*, 2003].

[10] The observed depletion of dust with distance from source regions provides a constraint on the rate of wet deposition. Results shown in Figures 1a and 1b together suggest that dust aerosols originating from the Saharan desert remain largely hydrophobic in the Atlantic region and that those from Asia have become hydrophilic in the Pacific region. It has been observed that dust aerosols reaching Korea and Japan are coated with ammonium, sulfate, and nitrate ions [*Carmichael et al.*, 1996; *Zhang et al.*, 2000]. These ions would make the dust aerosols hydrophilic [*Rosenfeld et al.*, 2001]. Sulfate is also observed in Saharan dust aerosols [*Li-Jones and Prospero*, 1998]. However, sulfate may be present in solid anhydrite or gypsum [*Andreae et al.*, 1986; *Falkovich et al.*, 2001], which are not readily soluble.

[11] In simulation S3, the rate of dust aging is rapid over East Asia due to high concentrations of SO_2, and slow over West Africa due to lower concentrations of SO_2. Nitrogen oxides and SO_2 are oxidized, forming acidic aerosols, during transport from Europe to Africa and the tropical North Atlantic. Nitrate and sulfate transported from Europe may be found in Saharan dust plumes, but they are more likely present in sub-micron particles separate from dust particles [*Garrett et al.*, 2003]. At stations near the sources (e.g., Izaña and Qingdao), the results from all three simulations are similar, reflecting the short time of transport for

chemical aging and occurrence of wet deposition. At stations farther away, the S3 results are in agreement with observations at the Atlantic sites and at Pacific sites near the Asian coast. The S3 results are more than twice as high as the observations at the remote Pacific sites (Figure 1c), implying perhaps more rapid chemical aging (e.g., by reactions with N_2O_5 and HNO_3) than calculated in the model. The model biases at Midway and Oahu could have resulted in part from the under-estimation of annual precipitation over the storm track in the North Pacific [*Janowiak et al.*, 1998].

[12] Based on the model-data comparisons shown in Figures 1a–1c, we hypothesize that desert dust is transformed by air pollution from hydrophobic to hydrophilic particles, becoming CCN for droplet as well as ice nucleation. Hydrophilic dust aerosols are more rapidly removed from the atmosphere. The observed scavenging ratio of mineral dust (concentration in rain water to concentration in surface air) is higher in the North Pacific than in the tropical North Atlantic by a factor of 5 [*Duce et al.*, 1991]. The modeled scavenging ratio in simulation S3 is indeed 5 times higher for hydrophilic dust in the North Pacific than for hydrophobic dust in the tropical North Atlantic. This is consistent with our hypothesis that Asian dust is aged chemically in air pollution plumes and is more readily removed by droplet nucleation.

[13] Aeolian dust supplies iron to the oceans and may be the main source of iron in the northeast North Pacific Ocean (NPO) [*Fung et al.*, 2000; *Moore et al.*, 2002]. It has been observed that phytoplankton growth can be limited by iron supply in high nitrate low chlorophyll regions including the Northeast Pacific [*Martin and Gordon*, 1988]. Dust storm enhancement of carbon biomass was observed in the NPO, suggesting a biotic response to natural iron fertilization by the dust [*Bishop et al.*, 2002]. Figure 2 shows the ratios (S2/S1) of dust deposition to the NPO. The ratios are calculated from dust depositions averaged over five years. Dust deposition to the coastal oceans off of East Asia is increased, but that to the northeast NPO is decreased by as much as 50% from S1 to S2. Such a decrease of dust deposition to the NPO could have occurred from pre-industrial time to the present due to the rise of air pollution in East Asia. On the other hand, soluble iron may be increased when mineral dust is coated with acidic aqueous solution of sulfate [*Meskhidze et al.*, 2003], which would increase aeolian iron supply to the surface ocean.

[14] In conclusion, chemical reactions of air pollutants on the surface of mineral dust are hypothesized to change the lifetime of dust aerosols in the atmosphere and its deposition to the oceans. Modeling of mineral dust may be improved in the future by including heterogeneous reactions, the chemical and mineralogical compositions of soils, concurrent gas phase chemistry, and more advanced physical parameterizations. This study suggests that the CCN activity of dust aerosols needs to be investigated under varying levels of air pollution. Air pollution may influence iron supply to the remote oceans, affecting diatom biomass and causing potential ecological changes in marine ecosystems.

References

Andreae, M. O., R. J. Charlson, F. Bruynseels, H. Storms, R. Van Grieken, and W. Maenhaut (1986), Internal mixtures of sea salt, silicates and excess sulfate in marine aerosols, *Science*, 232, 1620–1623.

Bishop, J. K., R. E. Davis, and J. T. Sherman (2002), Robotic observations of dust storm enhancement of carbon biomass in the North Pacific, *Science*, 298, 817–821.

Carmichael, G. R., Y. Zhang, L.-L. Chen, M. S. Hong, and H. Ueda (1996), Seasonal variation of aerosol composition at Cheju island, Korea, *Atmos. Environ.*, 30, 2407–2416.

D'Almeida, G. A. (1987), On the variability of desert aerosol radiative characteristics, *J. Geophys. Res.*, 92(D3), 3017–3026.

Dentener, F. J., G. R. Carmichael, Y. Zhang, J. Lelieveld, and P. J. Crutzen (1996), Role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.*, 101(D17), 22,869–22,889.

Duce, R. A., et al. (1991), The atmospheric input of trace species to the world ocean, *Global Biogeochem. Cycles*, 5(3), 193–259.

Falkovich, A. H., E. Ganor, Z. Levin, P. Formenti, and Y. Rudich (2001), Chemical and minerological analysis of individual mineral dust particles, *J. Geophys. Res.*, 106(D16), 18,029–18,036.

Fecan, F., B. Marticorena, and G. Bergametti (1999), Parameterization of the increase of the aeolian erosion threshold wind friction velocity due to soil moisture for arid and semi-arid areas, *Annales Geophysicae*, 17, 149–157.

Fung, I. Y., S. K. Meyn, I. Tegen, S. C. Doney, J. G. John, and J. K. B. Bishop (2000), Iron supply and demand in the upper ocean, *Global Biogeochemical Cycles*, 14(1), 281–295.

Gao, Y., S.-M. Fan, and J. L. Sarmiento (2003), Aeolian iron input to the ocean through precipitation scavenging: A modeling perspective and its implication for natural iron fertilization in the ocean, *J. Geophys. Res.*, 108(D7), 4221, doi:10.1029/2002JD002420.

Garrett, T. J., L. M. Russell, V. Ramaswamy, S. F. Maria, and B. J. Hubert (2003), Microphysical and radiative evolution of aerosol plumes over the tropical North Atlantic Ocean, *J. Geophys. Res.*, 108(D1), 4022, doi:10.1029/2002JD002228.

Ginoux, P., M. Chin, I. Tegen, J. Prospero, B. Holben, O. Dubovik, and S.-J. Lin (2001), Sources and distributions of dust aerosols simulated with the GOCART model, *J. Geophys. Res.*, 106(D7), 20,255–20,273.

Giorgi, F. (1986), A particle dry-deposition parameterization scheme for use in tracer transport models, *J. Geophys. Res.*, 91(D9), 9794–9806.

Horowitz, L. W., et al. (2003), A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res*, 108(D24), 4784, doi:10.1029/2002JD002853.

Janowiak, J., A. Gruber, C. Kondragunta, R. Livezey, and G. Huffman (1998), A comparison of NCEP-NCAR reanalysis precipitation and the GPCP rain gauge-satellite combined data set with observational error considerations, *J. Clim.*, 11, 2960–2979.

Kalnay, E. (1996), The NCEP/NCAR 40-year reanalysis project, *Bull. Am. Meteorol. Soc.*, 77, 437–471.

Kasibhatla, P. S., H. Levy II., W. J. Moxim, and W. L. Chameides (1991), The relative impact of stratospheric photochemical production on tropospheric NO_y levels: A model study, *J. Geophys. Res.*, 96(D10), 18,631–18,646.

Krueger, B. J., V. H. Grassian, A. Laskin, and J. P. Cowin (2003), The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, *Geophys. Res. Lett.*, 30(3), 1148, doi:10.1029/2002GL016563.

Levy, H., II, J. D. Mahlman, and W. J. Moxim (1982), Tropospheric N_2O variability, *J. Geophys. Res.*, 87(C4), 3061–3080.

Li-Jones, X., and J. M. Prospero (1998), Variations in the size distribution of non-sea-salt sulfate aerosol in the marine boundary layer at Barbados: Impact of African dust, *J. Geophys. Res.*, 103(D13), 16,073–16,084.

Mahlman, J. D., and W. J. Moxim (1978), Tracer simulation in a global general circulation model: Results from a mid-latitude instaneous source experiment, *J. Atmos. Sci.*, 35, 1340–1374.

Mahowald, N., C. Luo, J. del Corral, and C. S. Zender (2003), Interannual variability in atmospheric mineral aerosols from a 22-year model simulation and observational data, *J. Geophys. Res.*, 108(D12), 4352, doi:10.1029/2002JD002811.

Marticorena, B., and G. Bergametti (1995), Modeling the atmospheric dust cycle: 1. Design of a soil-derived dust emission scheme, *J. Geophys. Res.*, 100(D8), 16,415–16,430.

Martin, J. H., and R. M. Gordon (1988), Northeast Pacific iron distributions in relation to phytoplankton productivity, *Deep Sea Res. I*, 35, 177–196.

Meskhidze, N., W. L. Chameides, A. Nenes, and G. Chen (2003), Iron mobilization in mineral dust: Can anthropogenic SO_2 emissions affect ocean productivity, *Geophys. Res. Lett.*, 30(21), 2085, doi:10. 1029/2003GL018035.

Moore, J. K., S. C. Doney, D. M. Glover, and I. Y. Fung (2002), Iron cycling and nutrient-limitation patterns in surface waters of the World Ocean, *Deep-Sea Research II*, 49, 463–507.

Prospero, J. M., P. Ginoux, O. Torres, and S. Nicholson (2002), Environmental characterization of global sources of atmospheric soil dust derived from the NIMBUS7 TOMS absorbing aerosol product, *Rev. Geophys.*, 40, 2-1–2-31.

Pruppacher, H. R., and J. D. Klett (1978), *Microphysics of Clouds and Precipitation*, 714 pp., D. Reidel, Hingham, Mass.

Raupach, M. R., D. A. Gillette, and J. F. Leys (1993), The effect of roughness elements on wind erosion threshold, *J. Geophys. Res.*, 98(D2), 3023–3029.

Rosenfeld, D., Y. Rudich, and R. Lahav (2001), Desert dust suppressing precipitation: A possible desertification feedback loop, *Proceedings of the National Academy of Sciences*, 98, 5975–5980.

Shao, Y., M. R. Raupach, and P. A. Findlater (1993), Effect of saltation bombardment on the entrainment of dust by wind, *J. Geophys. Res.*, 98(D7), 12,719–12,726.

Tegen, I., S. P. Harrison, K. Kohfeld, I. C. Prentice, M. Coe, and M. Heimann (2002), Impact of vegetation and preferential source areas on global dust aerosol: Results from a model study, *J. Geophys. Res.*, 107(D21), 4576, doi:10.1029/2001JD000963.

Usher, C. R., A. Al-Hosney, S. Carlos-Cuellar, and V. H. Grassian (2002), A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles, *J. Geophys. Res.*, 107(D23), 4713, doi:10.1029/2002JD002051.

Zender, C. S., H. Bian, and D. Newman (2003), The mineral dust entrainment and deposition (DEAD) model: Description and 1990's dust climatology, *J. Geophys. Res.*, 108(D14), 4416, doi:10.1029/2002JD002775.

Zhang, D., and R. A. Anthes (1982), A high-resolution model of the planetary boundary layer - Sensitivity tests and comparisons with SESAME-79 data, *J. Appl. Meteorol.*, 21, 1594–1609.

Zhang, D., G.-Y. Shi, Y. Iwasaka, and M. Hu (2000), Mixture of sulfate and nitrate in coastal atmospheric aerosols: Individual particle studies in Qingdao (36°04′N, 120°21′E), China, *Atmos. Environ.*, 34, 2669–2679.

————————————————

S.-M. Fan, L. W. Horowitz, H. Levy II, and W. J. Moxim, NOAA Geophysical Fluid Dynamics Laboratory, Princeton University, Princeton, New Jersey, USA. (Songmiao.Fan@noaa.gov)