Dust and Pollution:
A Recipe for Enhanced Ocean Fertilization?
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Abstract: For Fe contained in aeolian dust to act as a micronutrient for oceanic phytoplankton, some fraction of it must first be transformed (mobilized) into a form soluble in ocean water. Fe solubilization in deliquesced mineral dust aerosols emanating from East Asia during the springtime outflow conditions is investigated here with a Lagrangian box model of the gas and aqueous-phase chemistry. The model simulates the scavenging of soluble and reactive gaseous species by mineral dust aerosols, chemical reactions of these species and mineral dust ions in deliquesced solution, and dissolution of Fe-III oxides that occurs as a result of the acid mobilization. The calculations indicate that mineral calcite (CaCO₃) strongly buffers deliquesced dust aerosols with a pH that remains close to 8 until the amount of acid added to the aerosol solution exceeds CaCO₃ alkalinity. SO₂ pollutant emissions are a potential source of acidity to advecting dust from East Asia. The model is used to simulate the chemical evolution of dust plumes formed from two contrasting documented Gobi-desert storms that advected dust to Fe-limited regions of the North Pacific Ocean (NPO). These calculations indicate that only plumes with relatively high initial SO₂-to-dust ratios are capable of delivering significant amounts of bioavailable Fe to the NPO. The estimated change in phytoplankton
population inferred from the model-calculated inputs of bioavailable Fe for these two episodes are consistent with the satellite measured chlorophyll \( a \) concentrations in the NPO. Model simulations indicate that (1) large dust advection episodes, that can export vast amounts of mineral dust to the open ocean, should have insignificant DIF as the amount of SO\(_2\) required to acidify such dust plumes is about an order of magnitude higher than what can typically be entrained in the plume during its advection; (2) smaller dust plumes will generally have higher DIF’s because they require lower amounts of SO\(_2\) and, even if such small plumes may not cause algae blooms, they could still be important sources of dissolved Fe to the NPO. The calculations suggest that future changes in SO\(_2\)-pollutant emissions from East Asia, either up or down, may affect the productivity of the NPO.
1. Introduction

There is compelling evidence that net primary productivity in high-nitrate low-chlorophyll (HNLC) regions of the ocean is limited by the availability of iron (Fe) [Martin and Fitzwater, 1998; Tsuda et al., 2003]. Together, these Fe-limited HNLC waters comprise ~30% of the world ocean [de Baar and Boyd, 2000]. In one of the HNLC regions, the subarctic Pacific, transport and deposition of mineral dust from Asia appears to be the major source of Fe [Duce et al., 1991; Duce and Tindale, 1991]. Although phytoplankton growth in this region has been shown to be stimulated by Fe-enrichment of the surface waters [Tsuda et al., 2003], the establishment of a causal relationship between Asian dust passages and phytoplankton bloom events in the region has been difficult [Young et al., 1991; Boyd et al., 1998; Boyd and Harrison, 1999; Harrison et al., 1999; Bishop et al., 2002]. One complication in establishing such a relationship is quantifying the amount of bioavailable Fe in dust plumes. While only dissolved Fe can be used by phytoplankton, virtually all Fe in Asian desert soils is in a crystalline Fe-III form [Hseung and Jackson, 1952; Claquin et al., 1999], which is insoluble at the pH typical of seawater [Stumm and Morgan, 1981; Zhu et al., 1997]. Thus phytoplankton can only utilize the fraction of the Fe in the deposited dust that has been dissolved during transport in the atmosphere. Processes that affect the solubility of Fe-III oxides in dust and alter fluxes of bioavailable Fe to the ocean may substantially affect ocean ecosystem productivity and, by changing the rate at which atmospheric CO₂ is fixed by oceanic biota, may even exert a global-scale influence on climate [Zhuang et al., 1992; Cooper et al., 1996; Turner et al., 1996].
Estimates of the dissolved iron fraction (DIF) of mineral dust plumes vary significantly [Duce et al., 1991; Zhu et al., 1997; Fung et al., 2000; Jickells and Spokes, 2001; Gao et al., 2003]. In order to establish whether a causal relationship exists between Asian dust and algal blooms in the North Pacific Ocean (NPO), it is first necessary to quantify the processes controlling the DIF in the dust plumes that pass over the region.

Since Fe-III oxides can be dissolved in acidic solutions, it has been proposed that non-negligible DIF can only occur if dust is sufficiently acidified by the incorporation of sulfuric acid from oxidation of SO$_2$ [Colin et al., 1990; Duce and Tindale, 1991; Zhu et al., 1992; 1993; Zhuang et al., 1992; Spokes and Jickells, 1996; Desboeufs et al., 2001; Meskhidze et al., 2003]. Sulfate deposited/formed on the aerosol surface can change dust particle surface properties from hydrophobic to hydrophilic [Dentener et al., 1996]. When such aerosols are advected in the atmosphere they will deliquesce [e.g., Dentener et al., 1996] and makes it possible for aqueous-phase chemistry to proceed.

Both natural and anthropogenic emissions of SO$_2$ have been proposed as sources of acidity in dust that can eventually lead to the production of bioavailable Fe and stimulate phytoplankton growth. Natural sources include volcanic emissions and the production of SO$_2$ from the oxidation of biogenic dimethyl sulfide (DMS) from the ocean [e.g., Duce and Tindale, 1991; Zhuang et al., 1992; Sarmiento, 1993; Spokes and Jickells, 1996; Watson, 1997; Bay et al., 2004]. By comparison, anthropogenic emissions represent a much larger source of SO$_2$; in a normal year without major volcanic perturbations about 80% of the global source of SO$_2$ is estimated to be anthropogenic [e.g., Koch et al., 1999; Chin et al., 2000]. Moreover, anthropogenic SO$_2$ emission sites may be closer to dust sources and therefore have stronger influence on it than natural
SO2. For example, a significant fraction of dust particles downwind of Beijing and Qingdao (China) can be coated by and enriched in sulfate [Parungo et al., 1995; Nishikawa et al., 1991]. Analysis of dust aerosols collected at Barbados suggests that nss-
SO4^{2-} (about 50% of which appeared to be derived from sources in Europe) and NO3^{-} associated with deliquesced dust particles can lower pH values typically in a range between 0 and 1, mobilizing significant fraction of Fe in mineral dust plumes during their long range transport across the North Pacific Ocean [Zhu et al., 1997]. Elliot et al. [1997] proposed that economic development of China could increase SO2 emissions enough to alter fluxes of bioavailable Fe to the ocean. Recently, Meskhidze et al. [2003] examined the production of bioavailable Fe in dust plumes using the ‘acid mobilization’ mechanism. Based on the diagnostic analysis of a specific dust plume that had originated from the Gobi desert and advected over the Yellow Sea, Meskhidze et al. [2003] suggested a possible link between ocean productivity and solubilization of Fe in aeolian dust from anthropogenic SO2 emissions.

However, there does not yet appear to have been an investigation that attempts to assess how much bioavailable Fe can be produced from the concentrations of SO2 typically found in both the unpolluted and the polluted atmosphere. Nor has it been studied how variations in the amount of mineral dust and/or sulfur oxides contained in an advecting plume might influence DIF of the plume.

In this work we use a Lagrangian box model of the gas- and aqueous-phase chemistry to examine how the DIF within a dust-laden plume from East Asia is affected by amount of SO2 that is mixed into the plume as it is advected from the continent. Our results are based on simulations of the evolution of DIF in dust plumes generated from
two contrasting historical episodes that advected mineral dust from East Asia to the remote western NPO: one that had relatively large amounts of SO$_2$-pollution mixed into the plume and the other with relatively little SO$_2$. The estimated inputs of bioavailable Fe to the surface waters of the North Pacific are then used to calculate changes in phytoplankton population and these changes are then compared to the increases in chlorophyll $a$ concentrations [Chl $a$] inferred from space-borne Moderate Resolution Imaging Spectroradiometer (MODIS).

The Asian outflow was chosen because i) it represents one of the largest sources of mineral dust to the remote ocean [Duce and Tindale, 1991; Tegen and Fung, 1994; Prospero, 1996; Ginoux et al., 2001]; ii) analyses of dust-storm tracks indicates that these storms often pass through the highly populated and industrialized regions of Beijing, Qingdao, and Shanghai before leaving the coast and therefore have ample opportunity to entrain pollutants from urban and industrial activities [Hoell et al., 1996; 1997]; iii) during the springtime, prevailing westerly winds can transport this dust far into the HNLC region of the subarctic North Pacific Ocean; and iv) it is expected that the economic development of East Asia will lead to changes in the rates at which pollutants are emitted from the region [Nakicenovic et al., 2001; Streets et al, 2001] and, assuming that anthropogenic emission of SO$_2$ has non-negligible effect on Fe mobilization from mineral dust, such changes could alter the flux of bioavailable Fe to the NPO.

2. Model Formulation

The evolution of DIF in two different cases of mineral dust advection from East Asia to the NPO is investigated using a Lagrangian box model of gas- and aqueous-phase chemistry of reactive compounds within an air mass containing dust.
2.1. Plume Trajectory and Conditions Adopted for Simulations

The Gobi Desert of northern China and Mongolia is the primary source of mineral aerosols emanating from East Asia [Parungo et al., 1994; Tegen and Fung, 1994; Sun et al., 2001; Liu et al., 2003]. Based on 40-years of dust-storm reports, Sun et al. [2001] estimated that the major fraction of Gobi dust entrains at low elevations and moves southeastward (passing near the Beijing metropolitan area) before departing the continent and advecting over the Yellow Sea and the Pacific Ocean. Beijing (39°55’N, 116°25’E) was therefore chosen as the nominal starting point for the plumes in our simulations. The initial concentrations of dust and pollutants for the simulated plumes are specified based on observations of dust plume compositions over the Beijing area (see below). Plumes are then assumed to advect from the Beijing area to the Pacific Ocean.

Two dust plumes simulated here originated over the Gobi desert of China on April 6, 2001 and on March 12, 2001 (hereafter referred to as A6 and M12, respectively). A6 was a part of an exceptionally strong multi-day dust storm, while M12 was more modest in intensity [Liu et al., 2003; Navy Aerosol Analysis and Prediction System (NAAPS) modeling results, available at http://www.nrlmry.navy.mil/aerosol/Docs/globaer_model.html]. The plume trajectories (see Figure 1) and ambient conditions (e.g., temperature, humidity) were obtained from the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler and Rolph, 2003]. The initial location of the A6 plume (40.5°N, 103°E) was chosen on the basis of Total Ozone Mapping Spectrometer Aerosol Index (TOMS AI) data. An initial altitude of 3.3 km was chosen so that the HYSPLIT predicted trajectory overlapped with the time and location where
mineral-dust laden air masses were sampled by the NCAR C-130 aircraft (Figure 1) operating over the Sea of Japan during the Aerosol Characterization Experiment (ACE-Asia) [Huebert et al., 2003]. After passing over Beijing, the plume rose to about 5km altitude and moved in an easterly direction toward the HNLC region of subarctic North Pacific. The plume’s predicted arrival in NE subarctic Pacific on April 12-13, 2001 is consistent with the TOMS AI data. Detailed modeling studies and analysis of composite satellite images of the plume indicate that a significant amount of dust contained in the plume was deposited as the plume traversed this Fe-limited region [Bishop et al., 2002; Liu et al., 2003].

The M12 plume was assumed to originate at 40ºN, 112ºE at ~500 m (i.e., a much lower altitude than that of A6). HYSPLIT predicts that the plume ascended and moved north-eastward, crossing over Beijing and, by the early morning of March 13, reaching ~1 km altitude north of Shenyang (Figure 1). TOMS AI data could not be used directly to specify the origin of the plume, since aerosols in the boundary layer are not readily detected [Mahowald and Dufresne, 2004]. Therefore the origin of the plume was selected so that the HYSPLIT-predicted trajectory would bring the low-altitude dust plume over Beijing on March 12th, the time when lidar and ground-level filter-based measurements in Beijing documented the presence of such a plume [Chen et al., 2001; China Environmental Protection Network, State Environmental Protection Administration of China (SEPA), Beijing, 2002, available at http://www.zhb.gov.cn/quality/air.php3, hereafter referred as SEPA, 2001], and then, later on March 13th, to the north of Shenyang where it was detected by TOMS. After leaving the continent, the plume moved in an easterly/northeasterly direction, while ascending to ~ 3 km. The plume then began
moving in a southeasterly direction while slowly subsiding to the marine boundary layer. According to MODIS data and NOAA-CIRES Climate Diagnostics Center modeling results (http://www.cdc.noaa.gov/cdc/reanalysis/reanalysis.shtml), the plume encountered a precipitating low-pressure system on March 19, 2001 over the central North Pacific Transition Zone [Polovina et al., 2001] (see Figure 1) and most of the remaining dust was likely deposited on the ocean surface ~40°N, 155°W. Although the region of the NPO where the plume encountered precipitation and the dust was deposited is somewhat south of the subarctic Pacific HNLC region [Boyd et al., 1998], marine productivity in this transitional zone is still likely to be Fe-limited [Moore et al., 2002].

2.2. Species Simulated in Model

Table 1 lists the species simulated in our model along with information on the various chemical forms the species were allowed to assume. Each species “I” can have more than one chemical form and be partitioned in the gas phase, denoted by the subscript “g;” the aqueous phase within the aerosols, denoted by the subscript “aq;” and the solid phase within aerosols, denoted by the subscript “s.”

Aerosols are assumed to have two size modes: (i) a dust particle mode, dominated by mineral dust; and (ii) an anthropogenic particle mode, dominated by sulfate and ammonium. This separation reflects the contrasting formation mechanisms (and thus chemical compositions) typical of fine and coarse aerosols: fine mode particles tend to arise from air pollution and other combustion processes either through direct emission or gas-to-particle conversion; while coarse particles are generally produced by mechanical processes such as soil erosion and sea-salt formation [e.g., Song and Carmichael, 1999].
Coagulation between the two modes can be neglected in the model [Wexler et al., 1994; Dentener et al., 1996] and thus mass transport between the dust and anthropogenic modes only occurs through the gas phase. For simplicity, each mode is treated as being monodisperse. Based on ACE-Asia and TRACE-P (TRAnsport and Chemical Evolution over the Pacific) field campaign observations [Clarke et al., 2003], the anthropogenic mode diameter, $D_a$, is set at 0.12 $\mu$m, and the dust mode diameter, $D_d$, is set at 1.7 $\mu$m.

2.3. Initial Plume Composition

Recall that time $t = 0$ in our model simulations corresponds to the point in the plume trajectory when, after the plume has already entrained an initial loading of air pollutants as well as dust, it leaves the Beijing area and begins its long-range transport over the NPO.

2.3.1 The amounts of dust and pollutants assumed to be in the plumes

The initial concentrations of dust, $SO_2$, $NO_x (=NO+NO_2)$, and $O_3$ are constrained (Table 2) by observation (see below). The initial $NH_3$ concentration was based on model-calculations for Beijing during a March, 1994 dust storm [Song and Carmichael, 2001]. The plumes are then allowed to advect over the NPO according to the HYSPLIT trajectories while the model simulates their gas-phase and particulate-phase chemical evolution. Dust and pollutants in the model are removed from the plumes by depositional and mixing processes.

Since the A6 plume was already at high altitudes when over Beijing (Figure 1), direct measurements of plume composition could not be used to initialize the model.
Instead, the initial A6 dust concentration was assigned from the NAAPS modeling results for Beijing at ~06 UTC on April 7, 2001. Note that large initial dust concentration of 1500 \( \mu g/m^3 \) for this simulation indicates that the A6 plume was formed from an exceptionally strong storm [Kurosaki and Mikami, 2003; Liu et al., 2003].

Initial concentrations of SO\(_2\), NO\(_x\) and O\(_3\) for A6 were adjusted so that model-calculated concentrations over the Sea of Japan matched values measured by the NCAR C-130 (ACE-Asia Flight 5) when it intercepted a dust-laden air-mass between 8 and 9 UTC over this same area on April 8, 2001 [Huebert et al., 2003; Lee et al., 2003]. The initial dust and pollutant concentrations thus obtained (Table 2) are characteristic of a large mineral dust plume mixed with concentrations of pollutants that are typical of the Beijing area during spring [Song and Carmichael, 2001; Tan et al., 2002].

The M12 plume crossed over the Beijing area while in the boundary layer, so ground-based measurements [SEPA, 2002; Chen et al., 2001] can be used to initialize the model. It should be noted, that while the initial dust concentration for M12 is lower than that for A6, the initial SO\(_2\) is considerably higher. The lower dust concentration is typical of the more frequent and more modest dust storms that pass through the region [Shao et al., 2003]. However, the elevated SO\(_2\) is not at all typical of springtime Beijing and is indicative of an intense pollution episode [SEPA, 2002].

2.3.2. Initial Composition of Mineral Dust Transported in the Plumes

The initial mineral content of the dust particle mode is designed to be representative of the transportable fraction of Gobi-desert soils in Mongolia and northern China (i.e., the fraction of the soil particles that can be uplifted and transported over large distances by wind). It should be borne in mind, however, given that the Gobi Desert
covers about 1,050,000 sq km of north central China and Mongolia [Parungo et al., 1994] it is expected and the mineralogical composition of the soils changes considerably over this expanse [Claquin et al., 1999; Gong et al., 2003]. Calculations documenting the sensitivity of our results to reasonable variations in the most critical aspect of the assumed dust composition, namely the weight percent of Ca, are presented in Section 4.

Measurements of mineral dust composition and mass-size distribution over the Yellow Sea and western North Pacific Ocean during ACE-Asia and TRACE-P suggest that the composition of mineral dust from East Asia is relatively invariant to the mineral dust loadings in the atmosphere [Clarke et al., 2003]. We therefore assume the same initial mineralogical composition for A6 and M12 dust events.

The U.S. Department of Agriculture (USDA) classification system classifies soil particles according to their size into three major texture classes: sand (2.0-0.05 mm), silt (0.05-0.002 mm), and clays (<0.002 mm) [Soil Survey Staff, 1998]. In general, both the mineral composition and transportable fraction of each class can vary significantly from the others [Leinen et al., 1994]. The mineralogical composition of the mineral dust produced from a given soil can be obtained using the following formula:

\[
X_{i}^{\text{air}} = \frac{X_{i}^{\text{sand}} \beta_{\text{sand}} F_{\text{sand}} + X_{i}^{\text{silt}} \beta_{\text{silt}} F_{\text{silt}} + X_{i}^{\text{clay}} \beta_{\text{clay}} F_{\text{clay}}}{\beta_{\text{sand}} F_{\text{sand}} + \beta_{\text{silt}} F_{\text{silt}} + \beta_{\text{clay}} F_{\text{clay}}}
\]  

where \(X_{i}^{\text{air}}\) is the weight percent of mineral “i” in the mineral dust transported in the atmosphere, \(X_{i}^{\text{sand}}\), \(X_{i}^{\text{silt}}\) and \(X_{i}^{\text{clay}}\) are the weight percents of mineral “i” in sand, silt and clay fractions of the soil, respectively, \(\beta_{\text{sand}}\), \(\beta_{\text{silt}}\) and \(\beta_{\text{clay}}\) are the transportable fractions of sand, silt, and clay in the surface soil, respectively, and \(F_{\text{sand}}, F_{\text{silt}}, F_{\text{clay}}\) are the weight percent of sand, silt, and clay in the surface soil, respectively. It can be easily seen from
equation (1) that for the soils containing only one type of textural-classes, the mineralogical composition of the transportable fraction is exactly equal to the mineralogical composition of the soil. However, if more than one textural class is present, than mineralogical composition of the transportable fraction of the soil is determined by the magnitudes of $\beta$ and $F$.

The surface soils of the Gobi Desert have been found to be about 50% sand, 30% silt, and 20% clay [Webb et al., 2000] (i.e., $F_{\text{sand}} = 0.5$, $F_{\text{silt}} = 0.3$ and $F_{\text{clay}} = 0.2$). However, sand particles are relatively large, are difficult to uplift and tend to be rapidly removed from the atmosphere by gravitational settling, and thus, $\beta_{\text{sand}} \sim 0$ and the transportable fraction is generally limited to the clay and silt fractions (Tegen and Fung, 1994; Ginoux et al., 2001). Moreover, measurements of the size spectra of mineral dust aerosols show that during a dust storm, the mass of clay-containing particles (with diameter, $D_p$ between 0.2-2 $\mu$m) is generally 1-2 orders of magnitude smaller than mass of silt-containing particles ($D_p$ between 2 to 50 $\mu$m) [Prospero and Bonatti, 1969; Clarke et al., 2003]. We therefore assume $\beta_{\text{clay}} = 0.1$ and $\beta_{\text{silt}} = 1$.

Table 3 lists our estimates of the weight percent concentrations of the key minerals in the silt and clay fractions of Gobi-desert soils obtained from a synthesis and analysis of data on Gobi-desert soils and dust in the literature. Also shown are the resulting mineral abundances in mineral dust, derived from equation (1). Table 4 presents the percent weight abundances of various key elements in mineral dust that result from the mineral abundances listed in Table 3.

2.4. Mass Balance Equations for Determining Species’ Concentrations
The concentrations of gas- and particulate-phase species in the advecting plume are determined by solving a system of coupled continuity equations. In its most general form, this equation is:

$$\frac{d[I]}{dt} = P_i - D_i - \alpha_{\text{dep}} [I] F_{\text{frac}} - \alpha_{\text{dil}} ([I] - [I_{\text{amb}}])$$

(2)

where $[I]$ is the concentration of species “I” within the plume (in units of mole m$^{-3}$), $P_i$ and $D_i$ are in-plume production and destruction rates for “I” species (in units of mole m$^{-3}$ s$^{-1}$), $\alpha_{\text{dil}}$ is a first-order rate constant for dilution of the plume due to mixing with ambient air, and $I_{\text{amb}}$ is the assumed ambient concentration of species “I,” $\alpha_{\text{dep}}$ is a first-order rate constant for loss from the plume of species contained within dust mode aerosols due to deposition (wet and dry), $F_{\text{frac}}$ is the fraction of species “I” contained within dust mode aerosols. (Note that anthropogenic particles are assumed to not have a significant deposition velocity and thus the components of this mode are not lost via an $\alpha_{\text{dep}}$-like parameterization.)

Tables 5, 6, 7, 8 and 9 list the constants for all the relevant gas-phase, heterogeneous and aqueous-phase reactions and thermodynamic equilibria that form the basis for calculating the $P_i$ and $D_i$ terms in equation (2). A more detailed discussion of the specific mass balance equation used for each of the species listed in Table 1 follows below.

2.4.1 Mass Balance for Dust and Estimation of Alpha Terms

Dust has no in-plume production and destruction terms and a negligible ambient concentration, and thus applying equation (2) to Dust we obtain:

$$\frac{d[Dust]}{dt} = -\alpha_{\text{dep}} [Dust] - \alpha_{\text{dil}} [Dust]$$

(3)
As described below, we can use this equation in combination with observations of dust concentrations during the dust storm of April 9, 2001 to estimate the values for $\alpha_{dep}$ and $\alpha_{dil}$.

**Parameterization for Deposition:** Deposition in the model is treated as combined process of dry and wet removal, i.e., $\alpha_{dep} = \alpha_{dep}(dry) + \alpha_{dep}(wet)$. Measurements and modeling results of dust transport show that the size composition of dust particles close to the source is non-uniform and dominated by the relatively large particles with $2 < D_p \leq 20$ $\mu$m [Tegen and Fung, 1994; Zender et al., 2003]. (Particles with $D_p > 20$ $\mu$m rapidly fall out of the plume [e.g., Tegen and Fung, 1994] and therefore are not considered in the model as part of the transportable dust fraction.) As the mineral dust advects, however, the larger particles settle out (i.e., they are deposited), leaving behind the smaller sized particles in the plume [Arimoto et al., 1997]. Thus we would expect $\alpha_{dep}(dry)$ to decrease as a function of transport time. To account for this variation, we assume that $\alpha_{dep}(dry)$ has the following form:

$$\alpha_{dep}(dry) = C_{dep1} \cdot \xi(t)$$

(4A)

where $C_{dep1}$ is a constant determined from the observations (see discussion below) and $\xi(t)$ is a time-dependent unitless parameter that varies inversely with the average settling velocity of the dust particles that remain in the plume at time $t$. (The formula used in the model for $\xi(t)$ is derived in Appendix A.)

Wet deposition is the dominant removal process for small dust particles with $D_p < 2\mu$m [e.g., Seinfeld and Pandis, 1997]. Zender et al. [2003] show, while dry and wet deposition have roughly equal annual mean values over the continents (downwind from the source regions), wet deposition is the principal removal mechanism for the dust over
the oceans. Recent modeling studies further suggest that wet removal could be particularly significant for the Asian dust since increased air pollution can produce high levels of readily soluble materials on the dust surface, making mineral dust aerosols effective cloud condensation nuclei (CCN) [Fan et al., 2004]. In the model the rate of wet removal is given as:

\[ \alpha_{\text{dep}}(\text{wet}) = C_{\text{dep2}} \]

where \( C_{\text{dep2}} \) is a constant determined from the observations (see discussion below).

Parameterization for Dilution: In general as dust plumes are advected, they tend to disperse from the action of turbulent velocity fluctuations. The rate at which a plume will expand depends on its size relative to the length scales of turbulent motion [e.g., Seinfeld and Pandis, 1998; Blackadar, 1998]. Composite satellite images of the dust cloud passage show, that by the time dust plumes get advected to the Beijing area (the initial location for the model simulations), they have already reached the size, when further dilution becomes inversely proportional to the square root of the plume transport time [Csanady, 1973; Blackadar, 1998]. So, in the model, plume dilution is treated using the following equation:

\[ \alpha_{\text{dil}} = \frac{C_{\text{dil}}}{\sqrt{t}} \]

where \( C_{\text{dil}} \) is a constant determined from the observation (see discussion below) and \( t \) is the plume transport time.

Derivation of Constant for Deposition and Dilution: Considering that over the continents, downwind from the source regions, dry and wet depositions are roughly equal [Zender et
al., 2003], we can write $C_{\text{dep}1} = C_{\text{dep}2} = C_{\text{dep}}$. Integration of equation (3) and substitution of (4A), (4B) and (5) yields:

$$\text{Dust}(t) = \text{Dust}(0) \cdot \exp\left\{-\int (C_{\text{dep}} (1 + \xi(t)) + C_{\text{dil}}/\sqrt{t})\,dt\right\} \quad (6)$$

Values for $C_{\text{dep}}$ and $C_{\text{dil}}$ are derived from observations of a mineral dust plume that passed over Beijing on April 10, 2001. Filter-based and lidar measurements in Beijing on that day indicated that the average boundary layer dust concentrations was about 700 $\mu g/m^3$ [Chen et al., 2001; SEPA, 2002]. Back trajectory analysis shows, that on April 11, 2001, this same plume was encountered the NCAR C-130 aircraft operating over the Yellow Sea as part of the ACE-Asia project [Huebert et al., 2003]. Instruments on board the aircraft measured an average $Ca^{2+}$ concentration within the plume of 18.7 $\mu g/m^3$. If we assume that all of the $Ca^{2+}$ measured on board of the C-130 was associated with the dust from the Gobi Desert and a weight percent concentration of Ca in dust of 6.2% (see Table 4, as well as Song and Carmichael [2001] and Zhang et al. [2003]), then the total concentration of dust at the time of the C-130 sampling was about 300 $\mu g/m^3$. In other words, deposition and dilution processes caused roughly 60% reduction in the concentration of mineral dust within the plume during the first 20 hrs of its transport.

To estimate the relative contribution of the two processes, we consider the measurements of Tsunogai et al. [1985]. By analyzing weekly aerosol samples collected for two years at six stations located in the western NPO, these investigators observed that within dust plumes advecting from East Asia, dust concentrations generally decreased at about twice the rate of $^{210}$Pb concentrations. If we assume that $^{210}$Pb (being a proxy for
anthropogenic aerosols) is carried in the anthropogenic particle mode and thus behaves similar to that of gaseous species [Thornton et al., 1997], then it follows that decrease in \(^{210}\text{Pb}\) concentration is caused by dilution alone while the loss of dust is caused by dilution and deposition.

Using the two sets of observations in concert with equation (6), the values for \(C_{\text{dep}}\) and \(C_{\text{dil}}\) can be derived using a simple iterative scheme:

\[
C_{\text{dep}} = 4.6 \times 10^{-6} \text{ sec}^{-1} \quad \text{and} \quad C_{\text{dil}} = 3.9 \times 10^{-4} \text{ sec}^{-1/2}
\]  

An independent check on the validity of these values can be obtained from observations of A6 plume. Trajectory analysis suggests that the plume had been over Beijing some 30 hours earlier before it was intercepted by NCAR C-130 over the Sea of Japan. Using this transport time, an initial dust concentration of 1500 \(\mu\text{g m}^{-3}\) (see Table 2) and the \(C_{\text{dep}}\) and \(C_{\text{dil}}\) values given in equation (7), the model predicts a dust concentration at the time and location of the C-130 observations of 510 \(\mu\text{g m}^{-3}\). This value is reasonably consistent with 550\(\mu\text{g m}^{-3}\) average dust concentration derived from Ca content measured on board of the C-130 [Huebert et al., 2003] and Ca-to-mineral dust ratio used above.

Unless noted otherwise, our model simulations use the values for \(C_{\text{dep}}\) and \(C_{\text{dil}}\) listed in equation (7). However, we recognize that the derivation of these two parameters involves a number of assumptions and simplifications. For this reason, in Section 4, we present sensitivity calculations to assess how reasonable variations in the deposition and dilution parameterization affect the model calculations; suffices to say, reasonable variations in these parameters do not alter the essential results of the model calculations.
2.4.2 SO₂ Mass Balance

In addition to dilution, in the model SO₂ is assumed to be removed from the plume via a homogeneous, gas-phase reaction with the free radical OH as well as via a heterogeneous reaction with mineral dust (RG1) and (RG2), respectively (Table 5). Thus, for SO₂ equation (2) becomes:

\[
\frac{d[SO₂]}{dt} = -k_{G1} \cdot [OH][SO₂] - k_{G2} \cdot [Dust][SO₂] - \alpha_{dil} ([SO₂] - [SO₂]_{amb})
\]

(8)

where [Dust] is the dust concentration in µg m⁻³, [SO₂] and [OH] are the SO₂ and OH concentrations in molecules cm⁻³, kᵢ are the rate constants for reactions “i” (see Table 5), and [SO₂]_{amb}, the background concentration of SO₂ over the remote Pacific is assumed to 50 pptv [Thornton et al., 1997; Andronache et al., 1997]. Note that inclusion of a non-zero value for [SO₂]_{amb} allows for the entrainment into the plume of SO₂ from the remote atmosphere. Since [SO₂]_{amb} presumably reflects the SO₂ present in the remote atmosphere as a result of natural processes (e.g., the oxidation of oceanic DMS [Davis et al., 1999]), its inclusion provides a mechanism for the production of bioavailable Fe from natural as opposed to anthropogenic SO₂.

Presence of mineral dust in the atmosphere can alter UV radiative fluxes and perturb the photochemistry of the atmosphere. Potentially most critical for our model is the fact that large dust loadings can reduce [OH] thereby affecting gas phase oxidation rates of SO₂ [e.g., Bian and Zender, 2003]. However, sensitivity studies indicate that our model results for episodes with mineral dust concentrations larger than 100 µg m⁻³ are not affected considerably by the likely variations in [OH] caused by dust-induced perturbations to J-values. During the intensive dust episodes (i.e., M12 and A6) the surface area available for the gas-particle interaction increases several orders of
magnitude and heterogeneous oxidation becomes the major removal mechanism for acidic trace gases [e.g., Dentener, 1996; Zhang and Carmichael, 1999; Phadnis and Carmichael, 2000]. For M12 case, the heterogeneous removal rate of SO2 is more than an order of magnitude higher than SO2 gas phase oxidation at local noon. Although two oxidation rates may become comparable after several days of transport time (when the plume gets depleted of dust), at that point the dust has only a minor impact on J-values. Therefore, [OH] in our simulations is specified as a function of time of day following Liu et al. [2001] without considering dust-induced perturbations.

The mechanism for SO2 oxidation on dust particles is uncertain [Goodman et al., 2001; Usher et al., 2003]. In our model simulations, we assume that (RG2) is controlled by a quasi-second order kinetic relationship with the rate constant derived from an analysis of SO2 oxidation by mineral dust in the plumed from Kuwaiti oil fires [Herring, et al., 1996]. Since mean concentrations of air pollutants and desert dust in these plumes were similar to ones observed during the springtime Asian outflow, we believe that this approach should produce reasonable results. Moreover, Garrett et al. [2003] showed that the SO2 uptake coefficient calculated from Herring et al. [1996] parameterization is within the range reported by Ullerstam et al. [2002] for SO2 uptake by mineral dust. In Section 4, sensitivity calculations are presented to assess how reasonable variations in kG2 affect the model simulations.

2.4.3 S(VI) Mass Balance and Speciation

Sulfate or S(VI) is treated in the model as a nonvolatile species (see Table 1) that can either reside in anthropogenic or dust mode particles. It is produced from the
oxidation of SO₂ via reactions (RG1) and (RG2). Production via (RG1) can lead to S(VI) in either anthropogenic or dust mode particles, while production via (RG2) only results in S(VI) production in dust mode particles. The fraction of S(VI) produced via (RG2) that is deposited into the anthropogenic and dust modes is in turn determined by the relative surface areas contained in the two modes.

Assuming a negligibly small concentration for S(VI) in the background atmosphere, the mass balance equations for S(VI) in each of the modes become:

\[
\frac{d[S(VI)]_a}{dt} = k_{G1} \cdot [\text{OH}][\text{SO}_2] \left[ \frac{S_d}{S_a + S_d} \right] + k_{G2} \cdot [\text{Dust}][\text{SO}_2] - (\alpha_{\text{dil}} + \alpha_{\text{dep}}) [S(VI)]_d \quad (9A)
\]

and

\[
\frac{d[S(VI)]_d}{dt} = k_{G1} \cdot [\text{OH}][\text{SO}_2] \left[ \frac{S_a}{S_a + S_d} \right] - \alpha_{\text{dil}} [S(VI)]_a \quad (9B)
\]

where the “a” and “d” subscripts are used to denote the anthropogenic and dust modes, respectively, and \( S_{\text{mode}} \) is the surface area of the relevant particle mode (in units of \( \mu \text{m}^2/\text{m}^3 \)). Since, as discussed above, we assume each mode to be monodisperse, \( S_{\text{mode}} \) is given by

\[
S_{\text{mode}} = \frac{6 \cdot \text{PM}_{\text{mode}}}{\rho_{\text{mode}} \cdot D_{\text{mode}}} \quad (10)
\]

where \( \text{PM}_{\text{mode}} \) is the concentration (in \( \mu \text{g} \text{ m}^{-3} \)) of the relevant mode, \( \rho_{\text{mode}} \) is the mode’s density, and \( D_{\text{mode}} \) is the mode’s nominal diameter (i.e., 0.12 and 1.7 \( \mu \text{m} \) for the anthropogenic and dust modes, respectively). If we assume that \( \rho_a = \rho_d \), then,

\[
\left[ \frac{S_a}{S_a + S_d} \right] = \frac{1.7 \text{PM}_a}{1.7 \text{PM}_a + 0.12 \text{PM}_d} \quad (11A)
\]

and
\[
\frac{S_d}{S_a + S_d} = \frac{0.12 \text{ PM}_d}{1.7 \text{ PM}_a + 0.12 \text{ PM}_d}
\]

\text{(11B)}

\textit{S(VI) speciation:} As indicated in Table 1, S(VI) within the anthropogenic and dust modes is distributed among 10 possible different solid or aqueous-phase species. The relative amounts of each of these species are determined somewhat differently in the two modes. Within the anthropogenic particle mode, the speciation of S(VI) is determined by the thermodynamic module discussed in Section 2.6. Within the dust particle mode, on the other hand, where Ca\(^{+2}\) from the dissolution of calcite can be present, the solution is first tested for supersaturation with respect to gypsum. If the solution is supersaturated, an appropriate amount of S(VI), along with Ca\(^{+2}\) is removed from the solution. The remaining S(VI) is then speciated using the thermodynamic module described in Section 2.6.

2.4.4 NO\(_x\) Mass Balance and Speciation

As in the case of SO\(_2\), NO\(_x\) is removed in the model via gas- and heterogeneous phase reactions (RG3) and (RG4), respectively (Table 5). In addition, it is assumed that the reaction between NO\(_2\) and O\(_3\) (RG5) ultimately leads to the production of N(V) at night [Munger et al., 1998].

The mass balance equation for NO\(_x\) is thus given by

\[
\frac{d\text{NO}_x}{dt} = -k_{g3}[\text{OH}][\text{NO}_2] - k_{g4}[\text{Dust}][\text{NO}_2] - 2 \cdot k_{g5}[\text{NO}_2][O_3]_{\text{night}} -
\]

\[-a_{\text{dil}}([\text{NO}_x] - [\text{NO}_x]_{\text{amb}})
\]

\text{(12)}
where \([O_3]\) and \([NO_x]_{amb}\) are set at 40 ppbv and 50 ppt \([\text{Talbot et al., 1997; Kondo et al., 1997]}\), respectively. As in the case of \(SO_2\), the rate of loss of \(NO_2\) on dust using a second order kinetic relationship with a rate constant from Herring et al. \([1996]\).

\(NO_x\) speciation: \(NO_x\) is comprised of two gas-phase species: NO and \(NO_2\). The relative concentration of NO and \(NO_2\) in the remote troposphere is determined by a photostationary state between NO reaction with ozone and \(NO_2\) photolysis. Modeling results of Crawford et al. \([1997]\) indicate that NO oxidation rate by peroxyl radicals in the springtime over the western North Pacific is considerably smaller than its oxidation by ozone and therefore this reaction is not considered in the model. \(NO_2\) photolysis rates are derived from Crawford et al. \([1997]\).

2.4.5 N(V) Mass Balance and Speciation

Unlike \(S(VI)\) which is nonvolatile, \(N(V)\) can exist in the gas-phase as \(HNO_3\) and as a result, \(N(V)\) that is initially in one particulate mode can volatize and re-condense on the other mode. This makes it necessary to use one single mass balance equation for \(N(V)\):

\[
\frac{d[N(V)]}{dt} = k_{G3}[OH][NO_2] + k_{G4}[\text{Dust}][NO_2] + 2 \cdot k_{G5}[NO_2][O_3]\big|_{\text{night}} - \alpha_{\text{dep}}[N(V)] \cdot F_{\text{frac}} - \alpha_{\text{dil}}[N(V)]
\]

\[(13)\]

where \(F_{\text{frac}}\) is calculated using the following equation:

\[
F_{\text{frac}} = \frac{[N(V)]_{\text{dust}}}{[N(V)]_{\text{anthropogenic}} + [N(V)]_{\text{dust}} + [HNO_3]_g}
\]

\[(14)\]

and it is assumed that the ambient \(N(V)\) concentration is negligible.
**N(V) speciation:** The partitioning of N(V) between the gas-phase and the two particulate matter modes, and speciation of N(V) within each of the modes are determined in the model using the thermodynamic module, as described in Section 2.6.

### 2.4.6 N(-III) Mass Balance and Speciation

N(-III) consists of gas-phase NH₃ and the various dissolved and solid forms of ammonium that can exist in the anthropogenic and dust particle modes. While NH₃ can be oxidized by OH, the reaction is relatively slow; the tropospheric lifetime of NH₃ due to its reaction with OH is estimated at about 3 months [Warneck, 1998], considerably longer than the plume transport time of several days considered here. So this reaction can be neglected in our calculation. The mass balance equation for N(-III) then becomes, in-plume production or destruction terms for N(-III) (concentration of all species with nitrogen in -3 oxidation state) were not included in the model. For the mass balance of N(-III) we have:

\[
\frac{d[N(III)]}{dt} = -\alpha_{dep}[N(III)] \cdot F_{frac} - \alpha_{dil} ([N(III)] - [N(III)]_{amb})
\]  \hspace{1cm} (15)

where \( F_{frac} \) shows relative abundance of particulate phase \( \text{NH}_4^+ \) in the dust mode and \([N(-III)]_{amb}=50 \text{ ppt}\) is background concentration of ammonia over the remote Pacific [Dentener and Crutzen, 1994].

**N(-III) speciation:** The partitioning of N(-III) between the gas-phase and the two particulate matter modes, and speciation of N(-III) within each of the modes are determined in the model using the thermodynamic module, as described in Section 2.6.

### 2.4.7 Mass Balance and Speciation For Dissolved, Dust Mode Fe
Two possible sources of Fe in advecting plume are mineral dust and anthropogenic emissions. In polluted atmospheres of the various urban/industrial sites in Asia anthropogenic activities (and most significantly coal combustion) can cause considerable enrichments in the atmospheric concentrations of elements typically associated with mineral dust (i.e., Fe, Al, Ca, Fe, K, Mg) [e.g., Arimoto et al., 1997]. During intensive dust storms enrichment of crustal elements relative to their concentration in the soil are negligible [Zhou et al., 1996; Zhuang et al., 2001; Xiao et al., 2002; Arimoto et al., 2004]; however, as M12 episode had unusually high concentration of anthropogenic pollutants (i.e., SO$_2$) below we estimate the possible contribution of anthropogenic Fe (Fe$_{ant}$). Assuming coal combustion is the major emitter of SO$_2$ in China [e.g., Carmichael et al., 2002] and the emissions of fugitive fly ash from power plants are the main contributors of Fe$_{ant}$, we write:

$$\frac{Fe_{ant}}{Fe_{dust}} = \frac{C_s \cdot X_{Fe}}{X_s \cdot C_d \cdot X_{dust}}$$  \hspace{1cm} (16)

where $Fe_{dust}$ is atmospheric concentration of Fe from mineral dust, $X_{dust}$ is the fraction of Fe in mineral dust (3.5 wt.%, Table 4), $X_{Fe}$ and $X_s$ are the transportable fractions of Fe$_{ant}$ and sulfur (S) emitted in the atmosphere per unit mass of raw coal (RC) burned, $C_d$ and $C_s$ are concentrations of dust and sulfur (both in units of $\mu$g m$^{-3}$) for the M12 episode (Table 2). Considering that S discharged to the atmosphere is ~1 wt.% of RC burned in China [e.g., Xu et al., 2000; Carmichael et al., 2002] and expressing $X_{Fe}$ in terms of AC-ash content of RC (10 - 15 wt.%, [McElroy et al., 1982; Ninomiya et al., 2004]), FA-fraction of AC in the form of fly ash (45 - 70 wt.%, [e.g., Liu et al., 2004]), FA$_{Fe}$- fraction of Fe$_{ant}$ in fly ash particles (~3.5 wt.%, [e.g., Ausset et al., 1999]), FA$_{tr}$- transportable
fraction of FA mass (~20 wt.%, [McElroy et al., 1982; Meij and Winkel, 2001]) and FA\textsubscript{esc} average escaping efficiency for FA in China (~5 wt.%, [Streets et al., 2001]) we get:

$$\frac{\text{Fe}_{\text{ant}}}{\text{Fe}_{\text{dust}}} = \frac{C_S \cdot AC \cdot \text{FA} \cdot \text{FA}_{\text{Fe}} \cdot \text{FA}_{\text{dil}} \cdot \text{FA}_{\text{esc}}}{C_d \cdot X_{\text{dust}} \cdot X_S}$$  \hspace{1cm} (17)

Equation 17 shows that Fe\textsubscript{ant} is minor contributor to the total Fe in the plume (about two orders of magnitude lower than Fe\textsubscript{dust}) and therefore in our model, we assume that Fe within the dust mode is produced primarily through the dissolution of hematite. The mass balance equation for this species is therefore

$$\frac{d[\text{Fe}]_d}{dt} = W_{\text{hem}} \cdot R_{\text{hem}}^{\text{net}} \cdot [\text{Dust}] - (\alpha_{\text{dil}} + \alpha_{\text{dep}})[\text{Fe}]_d$$ \hspace{1cm} (18)

where [Fe]_d is the concentration of dissolved, dust mode Fe, W_{\text{hem}} is the number of moles of Fe in a mole of hematite (i.e., 2); and R_{\text{hem}}^{\text{net}} is the hematite dissolution rate (moles of hematite dissolved/g of dust/s).

**Fe speciation:** The acid dissolution of Fe from hematite will initially give rise to dissolved iron in the +3 oxidation state; i.e. Fe(III). In principle, subsequent reactions (e.g., triggered by photons and/or catalysts) can give rise to Fe(II) and both Fe(III) and Fe(II) can coexist in solution [Behra and Sigg, 1990; Sedlak and Hoigné, 1993; Blesa et al., 1994; Cornell and Schwertmann, 1996]. Because of the high concentration of oxidants in the atmosphere, Fe(II) tends to be thermodynamically unstable in atmospheric particles and thus maintenance of Fe(II) in dust-containing aerosols requires continual cycling of Fe between the two oxidation states [Behra and Sigg, 1990; Zhu et al., 1993; Siefert et al., 1996]. The possible reaction scheme for the Fe(II)/Fe(III) cycling in ambient aerosols should perhaps include photochemistry, aqueous sulfite ions (SO$_3^{2-}$),
aldehydes, radicals (\(\text{HO}_2/O_2\), \(\text{RO}_2\)), Cu(I), hydrogen peroxide (\(\text{H}_2\text{O}_2\)) and some organic reductants (oxalate, ascorbate) [Behra and Sigg, 1990; Sedlak and Hoigné, 1993; Hislop and Bolton, 1999; Balmer and Sulzberger, 1999]. Photochemical/chemical cycling between Fe(III) and Fe(II) are not included in our model calculations, and thus \([\text{Fe}]_d\) is given by the total concentration of Fe(III) species in the aerosol dust mode not associated with hematite. (Although Fe(II) has much higher solubility [e.g., Cornell and Schwertmann 1996], consideration of only ferric complexes should not affect considerably Fe dissolution in mineral dust when solution remains under-saturated with respect to Fe(III). It is shown below that for most of the simulated cases deliquesced mineral dust solution remained under-saturated with respect to Fe(III) and formation of \(\text{Fe(OH)}_3(s)\) was not observed.)

Iron hydrolysis (even when restricted to Fe(III)) is rather complex [e.g., Blesa et al., 1994; Cornell and Schwertmann 1996] and some simplifications have been made to keep the calculations tractable. In our model, we assume that \([\text{Fe}]_d\) can take assume six different aqueous-phase forms, as well as one amorphous precipitate; i.e.,

\[
[\text{Fe}]_d = (\text{Fe}^{3+})_{(aq)}^+ (\text{FeOH}^{2+})_{(aq)}^+ (\text{Fe(OH)}_2^+)_{(aq)}^+ (\text{Fe(OH)}_3^+)_{(aq)}^+ (\text{Fe(OH)}_4^+)_{(aq)}^+ + (\text{FeSO}_4^+)_{(aq)}^+ (\text{Fe(OH)}_3)_{(s)}
\]

(Note that, the Fe\(^{3+}\) ion in solution actually contains six water molecules in its coordination spheres (i.e., \([\text{Fe(H}_2\text{O})_6]^{3+}\)) [Stumm and Morgan, 1981], however, for simplicity, we simply refer to it here as Fe\(^{3+}\).) The higher, polymeric iron hydroxide complexes, such as \(\text{Fe}_2(\text{OH})_2^{4+}, \text{Fe}_{12}(\text{OH})_{22}^{3+}\), are not considered in the model, as their concentrations only become significant at much higher concentrations of Fe(III) then those encountered in our calculations [Blesa et al., 1994; Millero et al., 1995]. Out of the
several possible inorganic complexes that Fe(III) can form (i.e., \(\text{FeSO}_4^+\), \(\text{FeHSO}_4^{2+}\), \(\text{Fe(SO}_4)_2\), \(\text{FeCl}^{2+}\), \(\text{FeF}^{2+}\)), we only include \(\text{FeSO}_4^+\), as other inorganic form of Fe(III) appear to be less important under our model conditions [Millero et al., 1995].

Using the assumption about the absence of metastable supersaturation with respect to \(\text{Fe(OH)}_3(s)\), at every time step the total Fe(III) concentration allowed to be present in a solution is calculated based on equilibrium constant of RAQ6 (Table 6), and pH and ionic strength of the solution. Since the establishment of hydrolysis equilibria between all Fe(III) species in Table 6 is usually very fast [Stumm and Morgan, 1981], the relative concentrations of each of the species appearing in equation (19) is determined by using appropriate equilibrium constants, pH and ionic strength of the solution.

### 2.4.8 Mass Balance for Dissolved, Dust Mode Na

The concentration of dissolved Na in the dust mode aerosol is of interest because it can influence the pH of the dust mode, and thus the dissolution of Fe, which, because it arises from dust, is only in the dust mode. Dissolved Na in the dust mode can arise from the dissolution of the Na-containing minerals in dust; as described in Section 2.3.2 these minerals are albite and smectite. Thus, if we neglect the coagulation of dust particles with sea-salt, and assume a negligible ambient dust mode Na concentration, the mass balance for dissolved, dust mode Na can be written as:

\[
\frac{d[\text{Na}]_d}{dt} = W_{\text{Na}_{\text{alb}}} \cdot R_{\text{alb}}^{\text{net}} \cdot [\text{Dust}] + W_{\text{Na}_{\text{smt}}} \cdot R_{\text{smt}}^{\text{net}} [\text{Dust}] - (\alpha_{\text{dil}} + \alpha_{\text{dep}})[\text{Na}]_d
\]  

(20)

where \([\text{Na}]_d\) is total concentration (in units of mole m\(^{-3}\)) of dissolved dust mode Na (and excludes Na that is bound in albite and smectite minerals); \(W_{\text{Na}_{\text{alb}}}\) and \(W_{\text{Na}_{\text{smt}}}\) are the number of moles of Na contained in a mole of albite and smectite (i.e., 1 and 0.6,
respectively); and $R_{\text{alb}}^{\text{net}}$ and $R_{\text{smt}}^{\text{net}}$ are the dissolution rates (in units of moles/g of dust/s) of albite and smectite, respectively. The formulation and methodology used to calculate mineral dissolution rates are discussed in Section 2.5. The speciation of dissolved dust mode Na is determined using the thermodynamic module discussed in Section 2.6.

Mass balance equations for dust mode, dissolved K and Mg are similar to Na and are not specifically discussed. K and Mg are speciated in the model by first converting them to equivalent concentrations of Na and then speciating the Na.

2.4.9 Mass Balance and Speciation for Dissolved, Dust Mode Ca

In principle, Ca can be mobilizes in the dust mode from the dissolution of two dust-containing minerals: calcite and anhydrite [Hseung and Jackson, 1952; Claquin et al., 1999]. However, in view of the evidence of gypsum precipitation in mineral aerosols during their long-range transport [Zhou and Tazaki, 1996; Mori et al., 1998; Böke et al., 1999; Kim and Park, 2001], we only consider calcite dissolution as a potential source of dissolved Ca. The mass balance for dissolved, dust mode Ca then takes the following form:

$$\frac{d[\text{Ca}]_d}{dt} = W\text{Ca}_\text{cal} \cdot R_{\text{cal}}^{\text{net}} \cdot [\text{Dust}] - (\alpha_{\text{dil}} + \alpha_{\text{dep}})[\text{Ca}]_d$$  \hspace{1cm} (21)

where $[\text{Ca}]_d$ is total concentration of dissolved, dust mode Ca (and excludes Ca bound in calcite and gypsum); $W\text{Ca}_\text{cal}$ is the number of moles of Ca contained in a mole of calcite (i.e., 1); and $R_{\text{cal}}^{\text{net}}$ is calcite dissolution rate (expressed in units of moles of calcite dissolved/g of dust/s).
Ca speciation: The speciation of dissolved, dust mode Ca is determined in a two-step process. First, if the solution is supersaturated with respect to gypsum, Ca$^{+2}$ along with an appropriate amount of S(VI) is removed (i.e., precipitate out) from solution, and then the remaining Ca is converted to an equivalent concentration of Na and speciated using the thermodynamic module (see Section 2.6).

2.4.10 Mass Balance and Speciation For Dissolved, Dust Mode Al

In acidic solutions, elevated concentrations of dissolved Al can increase the acid neutralizing capacity (ANC) and act as pH buffer [Sullivan, et al., 1989; Bi, 1995; Bi et al., 2001]. Al-buffering effect in the model is calculated by determining total concentration of dissolved Al in the dust mode and its subsequent speciation in hydroxo and inorganic complexes. Mass balance for dissolved Al is calculated using the following equation:

$$\frac{d[Al]_d}{dt} = \sum_i W_{Al_i} \cdot R_{i,net} \cdot [Dust] - (\alpha_{dil} + \alpha_{dep})[Al]_d$$  \hspace{1cm} (22)

where $[Al]_d$ is the concentration of dissolved, dust mode Al, $i$ represents each of the Al-containing minerals from dust include in our model (i.e., albite, microcline, illite, smectite, and kaolinite), W$_{Al_i}$ is the number of moles of Al in a mole of each of the aluminum-containing minerals (1, 1, 2.3, 1.4, and 2, respectively), and $R_{i,net}$ is dissolution rate of each of mineral “$i$” (moles of mineral dissolved/g of dust/s).

Al speciation: Speciation of dissolved Al is determined by invoking equilibrium between all monomeric Al-hydroxo and Al-sulfate (i.e., AlSO$_4^-$) complexes [Bi, 1995]:

$$[Al]_d = Al^{3+} + \sum_n (Al(OH)_n)^{3-n} + (AlSO_4^+)_{(aq)} + (Al(OH)_3)_{(s)}$$, where $n=1,2,3,4$  \hspace{1cm} (23)
For model simplicity, polynuclear Al-hydoxides (i.e., $\text{Al}_2(\text{OH})_2^{2+}$, $\text{Al}_3(\text{OH})_4^{3+}$) and other Al-inorganic complexes [Bi, 1995] were not taken into account.

The relative concentrations of $[\text{Al}]_d$-species is determined at each time step by assuming a steady state between the reactions in Table 6 involving Al species while assuring the absence of supersaturation with respect to $(\text{Al(OH)}_3)^{(s)}$. The impact of these various Al-species on pH and liquid water content is then simulated by converting each species to an equivalent concentration of Na (i.e., all Al-containing species with a charge of +1 is equivalent to one Na ion, species with a charge of +2 correspond to two Na ions, etc), and then calculating the subsequent speciation of Na using the thermodynamic module (see Section 2.6).

2.5. Mineral Dissolution Kinetics

In this work we consider the dissolution of 7 minerals contained in dust: calcite, albite, microcline, illite, smectite, kaolinite and hematite. The stoichiometry and equilibrium constants for the dissolution/precipitation of each of these minerals are provided in Table 7.

To calculate $R_{i}^{\text{net}}$, the rate of dissolution of mineral “i,” we adopt the formulation of Lasaga et al. [1994]:

$$R_{i}^{\text{net}} = K_r(T) a(H^+)^m f(\Delta G_r) A_i W_i$$

(24)

where $R_{i}^{\text{net}}$ has units of moles of mineral dissolved per gram of dust per s and is positive when the mineral is dissolving and negative when precipitating, $K_r$ has units of mole dissolved/m$^2$ of mineral/s and is a function of temperature, $T$, $a(H^+)$ is the $H^+$ activity, $m$ is an empirical parameter, $f$ is a function of Gibbs free energy, $\Delta G_r$, and accounts for the
variation of the rate with deviation from equilibrium [Cama et al., 1999], \( A_i \) is the specific surface area of mineral in units of \( m^2/g \) of mineral, and \( W_i \) is the weight fraction of the mineral in dust in units of \( g \) of mineral/g of dust. Values for \( K_r, m, A_i, \) and \( W_i \) for each of the mineral-dissolution reactions considered here are listed in Table 8.

The function \( f \) is in turn given by:

\[
f(\Delta G_r) = [1 - \exp(n\Delta G_r/RT)]
\]

where

\[
\Delta G_r = RT \ln(Q/K_{eq})
\]

and \( Q \) is the reaction activity quotient (i.e., the ratio of the product of the reactants over and the product of the species produced), \( K_{eq} \) is the equilibrium constant (given in Table 6), and \( n \) is an empirical parameter that in mineral-fluid reaction kinetics is most commonly set to 1 [e.g., Burch et al., 1993]. Such choice reduces equation (26) to the form for a single rate-limiting elementary reaction. Note that \( Q/K_{eq} \) describes the state of saturation of the solution with respect to a solid, so that when \( Q/K_{eq} > 1 \) the solution is oversaturated with respect to solid and \( R_{i,\text{net}} < 0 \), and when \( Q/K_{eq} < 1 \) the solution is undersaturated and \( R_{i,\text{net}} > 0 \) [Stumm and Morgan, 1981].

2.5.1 Hematite Dissolution Kinetics

Because of the complexity of hematite dissolution, as well as its importance to our modeling study, some further discussion of this process is in order. The formulation for hematite dissolution adopted here was derived from the data illustrated in Figure 1 of Azuma and Kametani [1964]. As indicated in Table 8, rates are calculated for three stages of hematite dissolution: the first stage, which is characterized by relatively slow
dissolution, is applicable to the dissolution of the first 0.8% of the oxide’s mass; the second stage, with an accelerated dissolution rate likely associated with the digestion of the oxide phase [Gorichev et al., 1976] is applied when the mass of oxide dissolution ranges from 0.8 to 40%; and the third stage is applied when the dissolved mass is > 40%, as dissolution approaches completion [Azuma and Kametani, 1964].

Additional Mechanisms for Fe Mobilization: There are several processes that have been shown to enhance Fe dissolution rates in laboratory studies but have not been included in the model. For example, it has been suggested that sunlight can significantly accelerate hematite dissolution rates in sulfuric acid solutions, making photoinduced reductive dissolution an important mechanism for mobilizing Fe in acidic ambient aerosols [Simnad and Smoluchowski, 1955; Faust and Hoffman, 1986; Behra and Sigg, 1990; Zhuang et al., 1992; Jickells and Spokes, 2001]. The presence of organic photosensitizers (i.e., oxalate, formate, acetate and continentally derived humic-like organic species) frequently measured in aerosols collected over the polluted areas [Zuo and Holgnè, 1992; Siefert et al., 1994; Havers et al., 1998] can further increase Fe mobilization rates in the presence of sunlight by factors ranging from 5 to 50 [Chang and Matijević, 1983; Zinder et al., 1986; Banwart et al., 1989; Siffert and Sulzberger, 1991; Pehkonen et al., 1993; Faust and Zepp, 1993; Siefert et al., 1994; Blesa et al., 1994; Sulzberger and Laubscher, 1995; Voelker et al., 1997].

In addition, it has been suggested that saltation bombardment (sand blasting) process, the main mechanism for dust uplift into the atmosphere [Gomes, 1990; Prospero, 1999; Ginoux et al., 2001], and the impact of wind-driven particles during their long-range transport can cause dislodgement of the dust particles [Prospero, 1999], increasing
reactive surface area of dust and making Fe-III oxides more susceptible for acid dissolution.

To account for these processes in our simulations, we assume that the net daytime rate of hematite dissolution is 5-10 times greater than that calculated using the standard kinetics described above. (No change is made to the nighttime rate.) In Section 4 sensitivity calculations are presented to assess how these additional mechanisms for Fe mobilization can affect the model simulations.

In the model we do not consider the effect of in-cloud processing of mineral dust on Fe solubilization rates. The acid mobilization mechanism we use in the model would not yield considerable amount of bioavailable Fe in cloud water, as the dilution that takes place in the cloud droplets raises dust particle pH and slows down hematite dissolution process significantly. Therefore, if pH of the aqueous phase is not modified considerably between the cycles (i.e., due to scavenging of water-soluble atmospheric trace gases by cloud droplets that remain in particles after cloud dissipation), according to the chemical mechanism we use here DIF should not be affected considerably by multiple cloud cycling. This result is in agreement with studies of Desboeufs et al. [2001] who did not observe increase in solubility of crustal aerosol after multiple condensation/evaporation cycles with constant pH. Finally it has also been suggested that Fe solubility could be enhanced significantly by precipitation [Gao et al., 2003], although no explicit mechanism that could explain such enhancement has been offered.

2.6. Thermodynamic Module
Once the concentrations of the major species listed in Table 1 have been determined at a given time step using the equations described in Section 2.4, these species must be speciated into their various possible chemical forms. This is accomplished in the model by invoking thermodynamic equilibrium between the gas-phase and the two aerosol modes using a modified form of ISORROPIA [Nenes et al., 1998].

ISORROPIA is an aerosol thermodynamics module which calculates the equilibrium solid-, aqueous- and gas-phase concentrations of relevant species along with the liquid-water content of an internally mixed aerosol as a function of ambient relative humidity and temperature, while considering solution non-idealities. In our model we have two independent aerosol modes (e.g., anthropogenic and dust). To calculate the equilibrium state between the gas-phase and these two aerosol modes, we iteratively run ISORROPIA for each mode separately until a self-consistent set of gas-phase concentrations is obtained for both modes.

ISORROPIA provides options to treat the particles as being in a thermodynamically stable state, where particles can be solid, liquid or both, or in a metastable state, where particles are always an aqueous solution. Unless otherwise specified, the metastable-state option has been adopted in our simulations.

The standard version of ISORROPIA (http://nenes.eas.gatech.edu/ISORROPIA) treats the sodium-ammonium-chloride-sulfate-nitrate-water gas/aerosol system. To simulate the chemistry of mineral dust and dissolution of Fe additional species and reactions must be considered. We have therefore modified ISORROPIA to explicitly include reactions involving gas-phase CO₂ and aqueous-phase carbonates and Fe-species.
The additional reactions and equilibrium constants used for these processes are listed in Table 6. The effects of other crustal elements (i.e., Ca, Mg, K and Al) on chemical properties of the dust mode aerosols are modeled by converting them to the equivalent concentration of sodium. Moya et al. [2001] showed under relatively low concentration of particulate matter ISORROPIA performs well when crustal element concentrations, expressed as equivalent sodium, are used as an input. Such approach might encounter some difficulties when crustal material (particularly Ca) comprises a significant portion of total particulate matter. However, even under such conditions no significant errors in the amount of the dissolved Fe are expected, as the dissolution of hematite only takes place in highly acidic deliquesced mineral dust particles when most of the Ca$^{2+}$ in the solution is bounded in the insoluble mineral, gypsum and has no direct effect on the properties of dust particles.

In order to include these additional reactions in ISORROPIA it was also necessary to calculate activity coefficients for the additional species involved in these reactions. We calculated binary activity coefficients for each new ion pair using the formulation of Kusik and Meissner [1978] and the q-parameters for each relevant salt listed in Table 9. Activity coefficients for Fe(OH)$_3$ and Fe(OH)$_4^-$ have been neglected; the former is assumed to be equal to 1 [Millero et al., 1995] and latter is only important for high pH values (pH> 8) not relevant to our problem. Activity coefficients for weak electrolytes (i.e., H-HCO$_3$ and H$_2$CO$_3$) and uncharged species (i.e., CO$_2$ (aq)) were also omitted in this study, as such corrections are generally only for alkaline and neutral solutions. The multicomponent activity coefficients for the aerosol solutions were determined using the method of Bromley [1973].
3. Results

We focus here on two major aspects of our model calculations: (1) to evaluate if the nominal springtime amounts of anthropogenic air pollutants (particularly SO\(_2\)) found in the urban/industrial centers of East China are sufficient to acidify dust-containing plume and produce considerable DIF during plume transport time; (2) to study how variations in the amount of mineral dust and/or SO\(_2\) contained in the advecting plumes can affect the DIF.

*Model-Calculated DIF:* As illustrated in Figure 2, the model-calculated DIF remains insignificant for the A6 case, while it reaches 4% for M12. Interestingly, even though M12 had less total Fe (Fe content in dust is assumed to be proportional to the dust concentration) than A6, the amount of the dissolved Fe in M12 ends up being significantly higher than in A6; i.e. 0.4 nmole m\(^{-3}\) versus 1x10\(^{-10}\) nmole m\(^{-3}\). The reason for this perhaps counterintuitive result lies in the amount of acidifying pollutants in the plume relative to the buffering capacity of the mineral dust. In A6, the initial ratio of dust to SO\(_2\) is very high, and the sulfuric acid produced from the oxidation of SO\(_2\) is not sufficient to overcome the buffering capacity of the CaCO\(_3\) contained in the dust. As a result, the pH of dust in A6 remains ~8, characteristic of aqueous systems containing undissolved CaCO\(_3\) [Stumm and Morgan, 1981], the rate of Fe mobilization, which requires highly acidic conditions, remains very small, and DIF is effectively zero (see Figure 2).

By contrast, because of the relatively low ratio of dust to SO\(_2\) in M12 simulations, the carbonate buffer in the dust is rapidly overwhelmed and the mineral dust pH falls soon after the plume begins its passage over the North Pacific Ocean (NPO). However,
the pH decrease is not monotonic but involves several distinct regimes in which uptake of gas phase ammonia \((\text{NH}_3)_{(g)}\) and volatilization of particulate-\(\text{NO}_3^-\) [Meskhidze et al., 2003] counter the addition of nss-\(\text{SO}_4^{2-}\) to mineral aerosol. Eventually each of these buffers is overwhelmed by the continuous addition of \(\text{SO}_4^{2-}\) produced from the oxidation of \(\text{SO}_2\) (all \(\text{NH}_4^+\) is neutralized and all \(\text{NO}_3^-\) is driven out of the aerosol and volatized), and the pH reaches ~ 0 – 1. While further decreases in pH are prevented by buffering from the self-neutralization of \(\text{SO}_4^{2-}\), the Fe-mobilization rate in this pH regime (0 < pH < 1) is high enough to yield considerable amount of DIF (Figure 2).

The importance of the dust-to-\(\text{SO}_2\) ratio in determining DIF is further demonstrated by the results of two additional simulations illustrated in Figure 2: A High pollution simulation for A6 (HPA6) with initial \(\text{SO}_2 = 80\ \text{ppbv}\) instead of the 8 ppbv in the standard case; and a low pollution simulation for M12 (LPM12) with initial \(\text{SO}_2 = 8\ \text{ppbv}\) instead of 50 ppbv. The increase in \(\text{SO}_2\) in going from A6 to HPA6 changes the initial dust-to-\(\text{SO}_2\) ratio from ~200 to ~ 20 µg m\(^{-3}\) ppbv\(^{-1}\), and as a result DIF increased from being negligible to almost 1%. The decrease in \(\text{SO}_2\) in going from M12 to LPM12 changes the initial dust-to-\(\text{SO}_2\) ratio from 15 to ~ 100 µg m\(^{-3}\) ppbv\(^{-1}\), and DIF decreased from a few percent to negligible.

*Contribution from the natural sources of \(\text{SO}_2\):* To evaluate the contribution from natural sources of \(\text{SO}_2\) (i.e., from the oxidation of DMS) to the model-calculated DIF’s plotted in Figure 2, we carried out additional A6 and M12 simulations with zero background \(\text{SO}_2\) (i.e., \([\text{SO}_2]_{\text{amb}}\) in equation (8) set to 0 instead 50 pptv). The results with and without background \(\text{SO}_2\) were identical (not shown), indicating that \(\text{SO}_2\) from natural sources played minor role in the model calculated DIFs for A6 and M12 dust transport episodes.
To further assess the role of natural sources, we carried a series of simulations termed here as zero emission (ZE) scenarios: in these scenarios we set $[\text{SO}_2]_{\text{amb}} = 50$ pptv, as in the Standard Model cases, but set the initial in-plume SO$_2$ concentrations equal to 0, Model calculated DIFs for both A6 and M12 were insignificant, suggesting that the amount of SO$_2$ entrained in advecting large dust plumes from the oxidation of DMS is not high enough to acidify large dust plumes and generate considerable DIF using acid mobilization hypothesis.

Due to the importance of dust-to-SO$_2$ ratio reported above, we also carried out ZE simulations for small dust plumes (20-30 $\mu$g m$^{-3}$) advecting over the ocean. Within the relative humidity and temperature conditions typical for marine boundary layer, model calculated mineral aerosol pH after about 2 days of travel time dropped to $3.5 < \text{pH} < 4$, close to pH value suggested for marine background aerosols [e.g., Chameides and Stelson, 1992]. The model estimated range in DIF $\sim0.05\%$ to 0.3$\%$ is somewhat smaller than the global-average DIF of 0.8$\%$ to 2.1$\%$, recently estimated by Jickells and Spokes [2001] on the bases of estimated fluxes of dust to the ocean and data on the abundance and residence time of dissolved Fe in the ocean. While these calculations can not be used to assess the relative roles of natural and anthropogenic SO$_2$ emissions on the production of bioavailable Fe and ocean productivity, the fact that the model-calculated DIF’s for the ZE simulations are so much smaller than the simulations with SO$_2$ pollution suggests that the flux of bioavailable Fe to the ocean was probably lower in pre-industrial times as compared to today.

*Dissolved Fe Input to Ocean:* Let $Dust_F$ and $DIF_F$ denote the model-calculated dust concentration (in $\mu$g m$^{-3}$ air) and DIF when the plume reaches the Fe-stressed regions of
the NPO. If this dust column of vertical height $H$ (m) is deposited onto a patch of the ocean and evenly distributed within the surface mixed layer, then the concentration of the enriched bioavailable Fe (mole/liter of seawater) in the patch should be given as:

$$[\text{Fe}]_{\text{enrich}} = 0.035 \cdot \frac{\text{Dust}_s \cdot \text{DIF}_F}{M_{\text{Fe}} \cdot D / \rho} \quad (27)$$

where 3.5wt.% is the Fe content of the Asian dust [Duce and Tindale, 1991], $\text{Dust}_s = \text{Dust}_F \cdot H$ is the amount of dust deposited per surface area of the ocean surface ($\mu$gm$^{-2}$); $M_{\text{Fe}}$ is gram-molecular weight of Fe, $D$ is the ocean mixed layer depth (m) and $\rho$ is the density of seawater. Equation (27) implicitly assumes that all of the mobilized mineral Fe remains in a bioavailable form after its deposition to the ocean. Such an assumption is supported by the mesoscale in situ Fe enrichment experiment (SEEDS) conducted in subarctic NPO [Tsuda et al., 2003].

Using equation (27) with the model calculated values for $\text{Dust}_s$ and $\text{DIF}_F$ (Table 10), it is estimated that $[\text{Fe}]_{\text{enrich}}$ from M12 ~ 0.01 - 0.1 nMFe, and ~ 0 for A6. As A6 was a part of an exceptionally severe multi day dust outbreak [Liu et al., 2003] and did not reveal any substantial removal over one particular region of the North Pacific Ocean, $[\text{Fe}]_{\text{enrich}}$ was estimated by carrying out back-of-the-envelope calculations for the total amount of dust removed to the ocean from the April 2001 dust storm (see Table 10). The results of our calculations indicate the overwhelming importance of DIF in $[\text{Fe}]_{\text{enrich}}$ estimates. Equation (27) further shows that with the model calculated DIF for A6 case, even several orders of magnitude variations in $\text{Dust}_s$ would have no significant impact on the amounts of enriched bioavailable Fe deposited to the HNLC waters of subarctic NE Pacific.
Change in [Chl a] from the Fe enrichment: Space-borne platforms such as MODIS measure phytoplankton abundance by monitoring ocean color and inferring [Chl a], the concentration of Chlorophyll a in the surface water column [Esaias et al., 1998]. Could the $[Fe]_{enrich}$ from M12 been sufficient to have caused a bloom that could have been sensed by MODIS? To address this question we estimate here the increase in [Chl a] that might have resulted from M12.

Experiments in the NPO indicate that the Fe to C molar ratio of the dominant phytoplankton species after Fe-enrichment is $\sim 10 - 40 \, \mu\text{molFe:molC}$ [Sunda and Huntsman, 1995; Boyd and Harrison, 1999; Schmidt and Hutchins, 1999]. The C:Chl a ratio for phytoplankton typically ranges from 30 - 50 mgC (mg Chl a)$^{-1}$ [Boyd and Harrison, 1999; Gallegos and Vant, 1996]. This suggests that the $[Fe]_{enrich}$ from M12 would have caused an algal biomass increase of $\sim 0.25 - 10 \, \text{mmol C m}^{-3}$ (3 - 120 mg C m$^{-3}$), or $0.06 - 4$ mg Chl a m$^{-3}$. This represents roughly an order of magnitude increase in chlorophyll over that typically found in the region of the NPO where the dust was deposited [Polovina et al., 2001; Chai et al., 2003]. Such an increase, if it occurred, qualifies as a bloom, and should be observable by the satellite retrievals. By comparison, the [Chl a] enhancement for A6, with its exceedingly small DIF, is predicted to be <1ng m$^{-3}$, and thus not detectable.

Expected Bloom Time Data: from the SEEDS experiment [Tsuda et al., 2003] indicated that [Chl a] in NPO waters begins to exhibit a significant increase in concentrations $\sim 6$ days after an initial enrichment in dissolved Fe, generally peaks on the 10$^{th}$ day, and remains significantly enhanced for a week or longer depending upon the nutrient level and ocean conditions.
The M12 plume was calculated to have arrived at the Fe-stressed region on March 19, 2001, where it encountered a precipitation event that likely removed much of the Fe-containing dust (Figure 1). Thus we would expect that the [Chl a] increase from the dust deposition and accompanying Fe enrichment would first be observable on ~ March 25, 2001, would approach its maximum ~ March 29, 2001, and remain high at least through the first week of April.

*Satellite Imagery:* [Chl a] in the region of the NPO where the M12 plume encountered precipitation (~40°N, 155°W) typically ranges from 0.2 – 0.4 mg m⁻³ [Polovina et al., 2001, Chai et al., 2003]. MODIS surface [Chl a] images of the NPO during the period from mid-March through mid-April (Figures 3A, 3B, 3C and 3D) clearly indicate the appearance of a phytoplankton bloom in this same region. [Chl a] increases by about an order magnitude over these waters at the beginning of the bloom and persist for a period of about 20 days (i.e., mid-April). The highest 8-day averaged [Chl a] of ~ 3 mg m⁻³ was recorded from March 30 – April 6 (Figure 3B), consistent with our earlier estimates. Our calculations suggest that the fate of phytoplankton bloom was most likely caused by the Fe limitation, although calculations using the Redfield value for C:N molar ratio and measured NO₃⁻ concentrations close to the patch [Martin et al., 1989] suggest that algal growth may have been co-limited by NO₃⁻. It has been noticed previously [Young 1991; Moore et al., 2002], that waters in these transitional zones can shift from being primarily Fe limited to being nitrate limited and then back to Fe limitation as the supply of Fe to the region varies.

There is no evidence suggesting that the bloom in the patch was caused by anything other than Fe-enrichment from the dust. As high winds usually associated with
the arrival of dust-laden air masses [Young et al., 1991] could potentially cause entrainment and upwelling of nutrient-rich waters to the euphotic zone [e.g., Lin et al. 2003], we examined Sea Surface Temperature (SST) data over the NPO. MODIS SST images (not shown) for the period relevant to phytoplankton bloom do not reveal any significant difference between the SSTs of the patch and the surrounding area, indicating that upwelling of nutrient-rich waters did not play a significant role [Lin et al., 2003].

MODIS surface [Chl \( \text{a} \)] images for the HNLC waters of subarctic NPO prior and after dust passage of A6 case (Figures 4A, 4B and 4C) do not reveal any noticeable changes in [Chl \( \text{a} \)]. This result is also in accord with model predicted negligible DIF-values for this plume. It is relevant to note, that small increase (between 0.45 and 0.55 mg m\(^{-3}\)) of chlorophyll concentration in subarctic North Pacific near station PAPA reported by Bishop et al. [2002] falls within natural variability of the background concentration for the western Subarctic Gyre [e.g., Boyd and Harrison, 1999] and, therefore, is not visible on MODIS image (Figures 4A, 4B and 4C).

4. Model Sensitivity Analysis

In this section, sensitivity calculations are presented to illustrate how reasonable variations in the key model parameters affect the final DIF calculated for the A6 and M12 plumes. Specifically, model sensitivities to the transport parameterization (i.e., \( C_{\text{dep}} \) and \( C_{\text{dil}} \)), the heterogeneous oxidation rates for SO\(_2\) (RG2) and NO\(_x\) (RG4), the initial amount of Ca assumed to be present in dust and the possible effect of photochemistry on hematite dissolution rate are examined. The sensitivity test results, summarized in Table 11, reveal that within the range examined, variations in the key model parameters do not
significantly affect calculated DIF-values; i.e., in all cases DIF is negligibly small for the A6 plume and of the order of 3 - 4% for the M12 plume (except for the variations in hematite dissolution rate when DIF for M12 plume ranges between ~1-10%).

5. Summary and Conclusions

A combination of prognostic model simulations and diagnostic data analysis have been used to examine the evolution of dissolved Fe in dust plumes emanating from the source regions of East Asia and advecting to the remote North Pacific Ocean (NPO). A Lagrangian box model of the gas and aqueous-phase chemistry of reactive compounds within an air mass containing mineral dust was developed and used to test the applicability of ‘acid mobilization’ mechanism and evaluate how varying plume conditions affect the amount of mobilized Fe in dust plumes emanating from East Asia during springtime outflow. Model simulations indicate that although large dust plumes can export vast amounts of mineral dust to the open ocean [Liu et al., 2003], the amount of SO₂ required to acidify such large dust plumes and generate significant DIF by acid mobilization is ~5 - 10 times higher than the average springtime SO₂ concentrations that are typically encountered in most industrial cities of China [Song and Carmichael, 2001; Tan et al., 2002; SEPA, 2002]. Thus, our model predicted negligible DIF’s for a large dust plume leading to negligibly small amounts of enriched bioavailable Fe and [Chl a] in the ocean column. It follows that if acid mobilization is the primary mechanism for dissolving Fe in dust plumes, then fertilization of ocean waters after the passage of large dust storms should be a relatively uncommon phenomenon. That blooms can occasionally occur when unusually high amounts of SO₂ (primarily from anthropogenic sources) are
entrained with dust appears to be confirmed by the bloom observed by MODIS for the M12 case. The unusual occurrence of this bloom is confirmed by the fact that this was the only case where we found evidence of a bloom coincident with a known large dust plume track over the NPO over the 4-years of available MODIS data. While other [Chl a]-enhancements over the NPO (not coincident with large dust plume tracks) are seen in the 4-year MODIS dataset, these enhancements are significantly smaller in both magnitude and spatial and temporal extent.

Our calculations also suggest that smaller dust plumes will generally have higher DIF’s because they require lower amounts of SO₂ to neutralize the carbonate buffer. Since the concentration of dust within a plume decreases quasi-exponentially with the distance from the source (Figure 2), small dust plumes far-removed from their source regions, even with substantial DIF’s, might not deposit sufficient quantities of dissolved Fe to cause visible, large scale phytoplankton blooms. However, even if such small plumes may not cause algae blooms, they may still be important sources of dissolved Fe to the NPO. The majority of dust storms reported in northeastern China are relatively weak, low altitude events [Shao et al., 2003; Sun et al., 2001] that could be easily acidified by the SO₂ concentrations typical of urban and industrial centers of eastern China. Using zero emission simulations we also showed that such small dust plumes can be acidified by SO₂ formed in the marine atmosphere as a major product of DMS oxidation. Mineral Fe mobilized in such small dust plumes could have been the primary source of bioavailable Fe in pre-industrial times, for the years free from volcanic eruptions. Thus, while much of the research on understanding the role of mineral-dust Fe
in ocean productivity has focused on large dust storms, work is also needed to better quantify the role of weak dust events.

Finally, because of the simplified nature of the box model adopted here, the uncertainties in mixing and deposition processes, and the limited set of observations used to evaluate the model’s ability to correctly estimate dissolved iron fraction of advecting mineral dust plumes, the results of our calculations should be viewed as preliminary and our conclusions as speculative. In spite of these limitations, however we believe that modeling results presented in this study demonstrate that the ecosystem productivity in NPO can be appreciably affected by anthropogenic activities in Asia. This once again emphasizes the complex interactions between sulfur, iron and carbon cycles in both the atmosphere and the ocean. The long-term simulations by coupling the iron mobilization algorithm with the global three-dimensional (3D) atmospheric transport models might be necessary to fully explore the significance of this modeling result to the global fluxes of bioavailable Fe deposited to the oceans.
Appendix A

The gravitational settling velocity of particles considered in the transportable fraction of mineral dust (with \( D_p \leq 20 \mu m \)) can be determined using Stokes’ law [Tegen and Fung, 1994; Ginoux et al., 2001; Zender et al., 2003] with

\[
\nu_{stk} = \frac{D_p^2 \rho_p g C_c}{18 \mu}
\]  

(A1)

where \( D_p \) is the particle diameter, \( \rho_p \) is particle density, \( g \) is the acceleration of gravity, \( \mu \) is the dynamic viscosity of the air and \( C_c \) is the slip correction factor [Seinfeld and Pandis, 1998].

As particles of different sizes have different atmospheric lifetimes (see Table A1) the particle dry deposition parameter \( \xi(t) \), is allowed to vary in the following way:

\[
\xi(t) = \frac{\hat{v}(r) - \sum_{i=0}^{4} v_i}{\hat{v}(r)}
\]  

(A2)

where \( \hat{v}(r) = v_1 + v_2 + v_3 + v_4 \) with indices denoting particle classes having different diameters (see Table A1) and the summation is carried out according to lifetime of dust particles. For example, when model time \( 0 < t < 26 \) hr, \( 1 < \xi(t) < 0.3 \); if \( 26 < t < 103 \) hr, \( 0.3 < \xi(t) < 0.1 \) and etc. According to this parameterization scheme, dust dry deposition rate reduces by an order of magnitude after about 4 days of transport time and becomes insignificant thereafter. Table A1 summarizes \( \xi(t) \) values at different \( t \).
Table A1. Dust dry deposition parameter and the lifetimes of mineral dust particles

<table>
<thead>
<tr>
<th>Index</th>
<th>$D_p$, (µm)</th>
<th>Lifetime, (hr)$^{(1)}$</th>
<th>$\xi(t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2-2</td>
<td>336</td>
<td>&gt;0.03</td>
</tr>
<tr>
<td>2</td>
<td>2-4</td>
<td>216</td>
<td>0.1 - 0.03</td>
</tr>
<tr>
<td>3</td>
<td>4-6</td>
<td>103</td>
<td>0.3 – 0.1</td>
</tr>
<tr>
<td>4</td>
<td>6-12</td>
<td>26</td>
<td>1.0 - 0.3</td>
</tr>
</tbody>
</table>

(1) From Ginoux et al. [2001].
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Table 1 Species simulated in model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chemical forms allowed for species(^{(1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_2)(^{(2)})</td>
<td>((SO_2)_g)</td>
</tr>
<tr>
<td>S(VI)(^{(3)})</td>
<td>((SO_4^{2-})<em>{aq}), ((HSO_4^-)</em>{aq}), ((FeSO_4^+)<em>{aq}), ((AlSO_4^+)</em>{aq}), ((CaSO_4)_s), ((Na_2SO_4)_s), ((NaHHSO_4)_s), (((NH_4)_2SO_4)_s), (((NH_4)_2H(SO_4)_2)_s)</td>
</tr>
<tr>
<td>NO(_x)(^{(4)})</td>
<td>((NO)_g), ((NO_2)_g)</td>
</tr>
<tr>
<td>N(V)(^{(5)})</td>
<td>((HNO_3)_g), ((NO_2)_aq), ((NH_4NO_3)_s), ((NaNO_3)_s)</td>
</tr>
<tr>
<td>N(-III)(^{(6)})</td>
<td>((NH_3)<em>g), ((NH_4^+)</em>{aq}), (((NH_4)_2SO_4)_s), ((NH_4HHSO_4)_s), (((NH_4)_3H(SO_4)_2)_s), ((NH_4NO_3)_s)</td>
</tr>
<tr>
<td>Na(^{(7)})</td>
<td>((Na^+)_{aq}), ((NaCl)_s), ((NaNO_3)_s), ((NaHHSO_4)_s), ((Na_2SO_4)_s)</td>
</tr>
<tr>
<td>Ca(^{(7)})</td>
<td>((Ca^{2+})_{aq}), ((CaCO_3)_s), ((CaSO_4)_s)</td>
</tr>
<tr>
<td>Fe(^{(7)})</td>
<td>((Fe^{3+})<em>{aq}), ((Fe(OH)^2+)</em>{aq}), ((Fe(OH)^3+)<em>{aq}), ((Fe(OH)^4+)</em>{aq}), ((FeSO_4^+)_{aq}), ((Fe(OH)_3)_s)</td>
</tr>
<tr>
<td>Al(^{(9)})</td>
<td>((Al^{3+})<em>{aq}), ((Al(OH)^2+)</em>{aq}), ((Al(OH)^3+)<em>{aq}), ((Al(OH)^4+)</em>{aq}), ((AlSO_4^+)_{aq})</td>
</tr>
<tr>
<td>Dust(^{(10)})</td>
<td>See section 2.3.2</td>
</tr>
<tr>
<td>Anthropogenic Aerosol Mode(^{(6)})</td>
<td>([PM]_a), the mass concentration (µg m(^{-3})) of anthropogenic aerosols calculated as the sum of the concentrations of anthropogenic mode S(VI), N(-III), and N(V)</td>
</tr>
<tr>
<td>Dust Aerosol Mode</td>
<td>([PM]_a), the mass concentration (µg m(^{-3})) of dust aerosols calculated as the sum of the concentrations of dust mode S(VI), N(-III), and N(V), as well as dissolved, dust mode Na, Ca, Fe, and Al</td>
</tr>
</tbody>
</table>

(1) Subscript “g” denotes a gas-phase species, etc;

(2) Non-oxidative dissolution and condensation of SO\(_2\) and NO\(_x\) (=NO+NO\(_2\)) on anthropogenic and dust mode particles are neglected here;

(3) S(VI) is assumed to be nonvolatile;

(4) All species containing nitrogen in +5 oxidation state;

(5) All species containing nitrogen in -3 oxidation state;

(6) Concentration of K and Mg are expressed as equivalent Na (see text);
(7) Species are assumed to only arise from the dissolution of minerals from dust and therefore are only treated as being in the dust aerosol mode;

(8) For all other Ca-containing compound (i.e., Ca(NO₃)₂), Ca is expressed as equivalent Na (see text);

(9) Under highly acidic conditions concentration of Al₅₃ diss is expressed as equivalent Na;

(10) Dust assumed to only be present in the dust mode aerosol.
Table 2. Initial concentrations of chemical species adopted in model calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A6 simulation</th>
<th>M12 simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dust mode aerosol composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dust(1), (µ g/m³)</td>
<td>1500</td>
<td>750</td>
</tr>
<tr>
<td>SO$_{4}^{2-}$, (µ g/m³)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>NO$_{3}^{-}$, (µ g/m³)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Anthropogenic mode aerosol composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_{4}^{2-}$, (µ g/m³)</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>NO$_{3}^{-}$, (µ g/m³)</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>NH$_{4}^{+}$, (µ g/m³)</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Gas phase mixing ratios</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$ (2), (ppbv)</td>
<td>8.0</td>
<td>50</td>
</tr>
<tr>
<td>NO$_x$, (ppbv)</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>NH$_3$, (ppbv)</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>O$_3$, (ppbv)</td>
<td>55</td>
<td>65</td>
</tr>
</tbody>
</table>

(1) The initial chemical composition of dust is specified to grossly mimic that of the transportable fraction of Gobi-desert soils in Mongolia and northern China (see text for more details).

(2) A ‘Zero Emissions’ (ZE) scenario is also considered with initial SO$_2$ assumed to be 0.
Table 3. Concentration of major minerals in the soil and clay fractions of surface soils in the Gobi Desert and in mineral dust originating from these soils (% wt)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>In soil (1)</th>
<th>In mineral dust and used as initial condition for model simulation (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in silt</td>
<td>in clay</td>
</tr>
<tr>
<td>Anhydrite CaSO₄</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Calcite CaCO₃</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>Albite NaAlSi₃O₈</td>
<td>18</td>
<td>8</td>
</tr>
<tr>
<td>Microcline KAlSi₃O₈</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Illite K₀.₆M₀.₂₅Al₂.₃Si₃.₅O₁₀(OH)₂</td>
<td>18</td>
<td>42</td>
</tr>
<tr>
<td>Smectite/ Montmorillonite (3) Naₐ.₆Al₁.₄M₀.₆Si₄O₁₀(OH)₂·₄H₂O</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>Hematite Fe₂O₃</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Quartz SiO₂</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>Kaolinite Al₂Si₂O₅(OH)₄</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

(1) The mineralogical composition of silt and clay in Gobi-desert soils listed here is largely based on the data from Hseung and Jackson [1952], Leinen et al. [1994], and Claquin et al. [1999], except as noted below;

(2) Calculated using equation (1) assuming F_silt = 0.3, F_clay = 0.2, β_silt = 1, and β_clay = 0.1;

(3) The chemical composition of illite and montmorillonite depends on the extent to which Si and Al are replaced by other cations such as Na, K, and Mg [Wonik, 2001; Deer et al., 1998]. The compositional formulas for illite and montmorillonite used here were determined by keeping the fundamental unit of the structure (so-called 2:1 layered structure) and adding in Na, K, and Mg to the minerals so that the average overall concentration of Na, K, and Mg in Gobi-desert soils was equal to 2.1%, 1.9%,
and 0.9%, respectively [Nishikawa et al., 1999]. It should be noted that the resulting compositions used here for illite and montmorillonite fall within the range of compositions typically observed for these minerals [Wonik, 2001; Deer et al., 1998]; (4) The weight percents for hematite in silt and clay was obtained by assuming that hematite is the only mineral containing significant amounts of Fe, and requiring that the weight percent of Fe in mineral dust was 3.5% in accordance with the observations of mass [Taylor and McLennan, 1985; Duce and Tindale, 1991]. Since Fe (II) can substitute for Mg and Fe(III) for Al in some clay silicates [Coey, 1988], the assumption that hematite is the only Fe-containing mineral in soils is not strictly valid. Nevertheless, the Fe content in clay minerals is usually small [Murad and Fischer, 1988] and thus for the purposes of this study can be neglected.
Table 4. Composition of key elements in mineral dust assumed for model simulations
(wt.%)
Table 5. Heterogeneous and gas phase reactions included in model

<table>
<thead>
<tr>
<th>№</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>RG1</td>
<td>SO$_2$+OH(g)$\rightarrow$M$\rightarrow$H$_2$SO$_4$ +…$^{(1)}$</td>
<td>$k_0=3.0x10^{-31}x(300/T)^{1.3}$</td>
<td>cm$^6$ molecule$^{-2}$ s$^{-1}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_\infty=1.5x10^{-12}$</td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>RG2</td>
<td>SO$_2$ dust$\rightarrow$SO$_4^{2-}$(aq)</td>
<td>$(9 \pm 4)x10^{-8}$</td>
<td>m$^3$ µg$^{-1}$ s$^{-1}$</td>
<td>Herring et al. [1996]</td>
</tr>
<tr>
<td>RG3</td>
<td>NO$_2$ + OH$\rightarrow$M$\rightarrow$HNO$_3$(g)$^{(1)}$</td>
<td>$k_0 = 2.5x10^{-30}x(300/T)^{4.4}$</td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_\infty = 1.6x10^{-11}x(300/T)^{1.7}$</td>
<td></td>
<td>/See text</td>
</tr>
<tr>
<td>RG4</td>
<td>NO$_2$ dust$\rightarrow$NO$_3^-$ (aq)</td>
<td>$(10 \pm 10)x10^{-8}$</td>
<td>m$^3$ µg$^{-1}$ s$^{-1}$</td>
<td>Herring et al. [1996]</td>
</tr>
<tr>
<td>RG5</td>
<td>NO$_2$+O$_3$ night$\rightarrow$2HNO$_3$(aq)</td>
<td>$1.2x10^{-11}x\exp(-2450/T)$</td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/See text</td>
</tr>
<tr>
<td>RG6</td>
<td>NO + O$_3$ $\rightarrow$ NO$_2$ + O$_2$</td>
<td>$2.0x10^{-12}x\exp(-1400/T)$</td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>Sander et al. [2003]</td>
</tr>
</tbody>
</table>

(1) The rate coefficient for this reaction is obtained as follows:

$$k(T) = \left\{ \frac{k_0(T)[M]}{1 + k_0(T)[M]/k_\infty(T)} \right\}^{0.6\left[\frac{1}{2} - \frac{1}{2}\log_{10}(k_0(T)[M]/k_\infty(T))^2 \right]}^{-1}$$
Table 6. Additional aqueous-phase reactions added to modified version of ISORROPIA

and their equilibrium constants

<table>
<thead>
<tr>
<th>№</th>
<th>Equilibrium reaction</th>
<th>K&lt;sup&gt;e&lt;/sup&gt; (298.15K)</th>
<th>a</th>
<th>b</th>
<th>units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAQ1</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;(aq) ≡ CO&lt;sub&gt;2&lt;/sub&gt;(g)</td>
<td>3.404x10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>8.185</td>
<td>-28.9307</td>
<td>mol/kg/atm</td>
<td>Meng et al. [1995]</td>
</tr>
<tr>
<td>RAQ2</td>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;⁻ + H&lt;sup&gt;+&lt;/sup&gt; ≡ CO&lt;sub&gt;2&lt;/sub&gt;(aq)</td>
<td>4.299x10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>3.082</td>
<td>31.8139</td>
<td>mol/kg</td>
<td>Meng et al. [1995]</td>
</tr>
<tr>
<td>RAQ3</td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;²⁻ + H&lt;sup&gt;+&lt;/sup&gt; ≡ HCO&lt;sub&gt;3&lt;/sub&gt;⁻</td>
<td>4.678x10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>5.990</td>
<td>38.8440</td>
<td>mol/kg</td>
<td>Meng et al. [1995]</td>
</tr>
<tr>
<td>RAQ4</td>
<td>CaSO&lt;sub&gt;4&lt;/sub&gt; ⋅ 2H&lt;sub&gt;2&lt;/sub&gt;O(s) = Ca&lt;sup&gt;2+&lt;/sup&gt;(aq) + SO&lt;sub&gt;4&lt;/sub&gt;²⁻(aq) + 2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4.319x10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol²/kg&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Meng et al. [1995]</td>
</tr>
<tr>
<td>RAQ5</td>
<td>Fe(OH)&lt;sub&gt;3&lt;/sub&gt;(s) + 3H&lt;sup&gt;+&lt;/sup&gt; ≡ Fe&lt;sup&gt;3+&lt;/sup&gt; + 3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>9.1x10&lt;sup&gt;7&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Stumm and Morgan [1981]</td>
</tr>
<tr>
<td>RAQ6</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; + SO&lt;sub&gt;4&lt;/sub&gt;²⁻ ≡ FeSO&lt;sub&gt;4&lt;/sub&gt;⁻</td>
<td>1.9x10&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Millero et al. [1995]</td>
</tr>
<tr>
<td>RAQ7</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;⁺⁺ ≡ Fe&lt;sup&gt;3+&lt;/sup&gt; + Cl⁻</td>
<td>1.9x10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Millero et al. [1995]</td>
</tr>
<tr>
<td>RAQ8</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O ≡ FeOH&lt;sup&gt;3+&lt;/sup&gt; + H⁺</td>
<td>6.46x10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Stumm and Morgan [1981]</td>
</tr>
<tr>
<td>RAQ9</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; + 2H&lt;sub&gt;2&lt;/sub&gt;O ≡ Fe(OH)&lt;sub&gt;2&lt;/sub&gt;⁺⁺ + 2H⁺</td>
<td>2.14x10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Stumm and Morgan [1981]</td>
</tr>
<tr>
<td>RAQ10</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; + 3H&lt;sub&gt;2&lt;/sub&gt;O ≡ Fe(OH)&lt;sub&gt;3&lt;/sub&gt;⁺⁺ + 3H⁺</td>
<td>1.59x10&lt;sup&gt;-12&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Millero et al. [1995]</td>
</tr>
<tr>
<td>RAQ11</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; + 4H&lt;sub&gt;2&lt;/sub&gt;O ≡ Fe(OH)&lt;sub&gt;4&lt;/sub&gt;⁺⁺ + 4H⁺</td>
<td>2.51x10&lt;sup&gt;-22&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Stumm and Morgan [1981]</td>
</tr>
<tr>
<td>RAQ12</td>
<td>Al(OH)&lt;sub&gt;3&lt;/sub&gt;(s) + 3H&lt;sup&gt;+&lt;/sup&gt; ≡ Al&lt;sup&gt;3+&lt;/sup&gt; + 3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.7x10&lt;sup&gt;10&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Lindsay [1979]; Bi et al. [2001]</td>
</tr>
<tr>
<td>RAQ13</td>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; + SO&lt;sub&gt;4&lt;/sub&gt;²⁻ ≡ AlSO&lt;sub&gt;4&lt;/sub&gt;⁻</td>
<td>1.0x10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Bi et al. [2001]</td>
</tr>
<tr>
<td>RAQ14</td>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O ≡ AlOH&lt;sub&gt;2&lt;/sub&gt;⁺⁺ + H⁺</td>
<td>1.0x10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Bi et al. [2001]</td>
</tr>
<tr>
<td>RAQ15</td>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; + 2H&lt;sub&gt;2&lt;/sub&gt;O ≡ Al(OH)&lt;sub&gt;2&lt;/sub&gt;⁺⁺ + 2H⁺</td>
<td>1.0x10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Bi et al. [2001]</td>
</tr>
<tr>
<td>RAQ16</td>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; + 3H&lt;sub&gt;2&lt;/sub&gt;O ≡ Al(OH)&lt;sub&gt;3&lt;/sub&gt;⁺⁺ + 3H⁺</td>
<td>1.0x10&lt;sup&gt;-15&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Lindsay [1979]; Stumm and Morgan [1981]</td>
</tr>
<tr>
<td>RAQ17</td>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; + 4H&lt;sub&gt;2&lt;/sub&gt;O ≡ Al(OH)&lt;sub&gt;4&lt;/sub&gt;⁺⁺ + 4H⁺</td>
<td>1.0x10&lt;sup&gt;-23&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>mol/kg</td>
<td>Bi et al. [2001]</td>
</tr>
</tbody>
</table>

(1) For RAQ1, RAQ2, and RAQ3

\[ K_{eq} = K^e \exp \left[ a \left( \frac{T}{T_0} - 1 \right) + b \left( 1 + \ln \left( \frac{T}{T_0} \right) - \frac{T_0}{T} \right) \right], \] where \( T_0 = 298.15K \).

All other \( K_{eq} \)'s assumed to be temperature independent and are based on experimental data at 298 K.
Table 7. Equilibria describing the dissolution/precipitation of minerals contained in dust

<table>
<thead>
<tr>
<th>№</th>
<th>Equilibrium reaction</th>
<th>Equilibrium constants(^{(1)})</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>REQ1</td>
<td>Calcite $\rightleftharpoons$ Ca(^{2+}) + CO(_3^{2-})</td>
<td>4.959x10(^{-9})</td>
<td>Meng et al. [1995]</td>
</tr>
<tr>
<td>REQ2</td>
<td>Albite + 4H(^+) + 4H(_2)O $\rightleftharpoons$ Na(^+) + Al(^{3+}) + 3H(_4)SiO(_4^0)</td>
<td>1.6x10(^3)</td>
<td>Lindsay [1979]</td>
</tr>
<tr>
<td>REQ3</td>
<td>Microcline + 4H(^+) + 4H(_2)O $\rightleftharpoons$ K(^+) + Al(^{3+}) + 3H(_4)SiO(_4^0)</td>
<td>1x10(^1)</td>
<td>Lindsay [1979]</td>
</tr>
<tr>
<td>REQ4</td>
<td>Illite + 6H(^+) + 4H(_2)O $\rightleftharpoons$ 0.4K(^+) + 0.25Mg(^{2+}) + 1.7Al(^{3+}) + 4H(_4)SiO(_4^0)</td>
<td>2.24x10(^{10})</td>
<td>Lindsay [1979]</td>
</tr>
<tr>
<td>REQ5</td>
<td>Smectite + 4H(^+) $\rightleftharpoons$ 0.8Na(^+) + 0.4Mg(^{2+}) + 0.8Al(^{3+}) + 4H(_4)SiO(_4^0)</td>
<td>4.79x10(^2)</td>
<td>Lindsay [1979]</td>
</tr>
<tr>
<td>REQ6</td>
<td>Kaolinite + 6H(^+) $\rightleftharpoons$ 2Al(^{3+}) + 2H(_4)SiO(_4^0) + H(_2)O</td>
<td>2.8x10(^5)</td>
<td>Lindsay [1979]</td>
</tr>
<tr>
<td>REQ7</td>
<td>Hematite + 6H(^+) $\rightleftharpoons$ 2Fe(^{3+}) + 3H(_2)O</td>
<td>4.4x10(^{-1})</td>
<td>Blesa et al. [1994]</td>
</tr>
</tbody>
</table>

\(^{(1)}\) All K\(_{eq}\)'s are for 298 K.
<table>
<thead>
<tr>
<th>№</th>
<th>Mineral</th>
<th>Rate constant $K_r$ (mol$_{mineral \ dissolved}$/m$^2$/sec)</th>
<th>m</th>
<th>$A_i$ (m$^2$ g$^{-1}$)</th>
<th>$W_i$ g(mineral)/g(dust)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS1</td>
<td>Calcite</td>
<td>$7.0 \times 10^{-2} \exp[1200(1/298-1/T)]$</td>
<td>1</td>
<td>0.1</td>
<td>11</td>
<td>Morse and Arvidson [2002]; Alkattan et al. [1998]; Chou et al. [1988]; Sjöberg [1976]</td>
</tr>
<tr>
<td>RS2</td>
<td>Albite</td>
<td>$2.4 \times 10^{-10} \exp[7200(1/298-1/T)]$</td>
<td>0.5</td>
<td>1.0</td>
<td>17</td>
<td>Blum and Stillings [1995]; Hodson [1999]</td>
</tr>
<tr>
<td>RS3</td>
<td>Microcline</td>
<td>$2.0 \times 10^{-10} \exp[6600(1/298-1/T)]$</td>
<td>0.5</td>
<td>1.0</td>
<td>8</td>
<td>Blum and Stillings [1995]; Hodson [1999]</td>
</tr>
<tr>
<td>RS4</td>
<td>Illite</td>
<td>$1.3 \times 10^{-11} \exp[6700(1/298-1/T)]^{(1)}$</td>
<td>0.39</td>
<td>90</td>
<td>20</td>
<td>Nagy [1995]; Tessier [1990]; Skopp [2000]</td>
</tr>
<tr>
<td>RS5</td>
<td>Smectite</td>
<td>$8.1 \times 10^{-12} \exp[6700(1/298-1/T)]^{(1)}$</td>
<td>0.3</td>
<td>300</td>
<td>8</td>
<td>Nagy [1995]; Tessier [1990]; Skopp [2000]</td>
</tr>
<tr>
<td>RS6</td>
<td>Kaolinite</td>
<td>$4 \times 10^{-11} \exp[6700(1/298-1/T)]$</td>
<td>0.1</td>
<td>20</td>
<td>5</td>
<td>Carroll and Walther [1990]; Nagy [1995]; Skopp [2000]</td>
</tr>
<tr>
<td>RS7</td>
<td>Hematite</td>
<td>Stage I (0 to 0.8% of total oxide dissolved) $4.4 \times 10^{-12} \exp[9.2 \times 10^{3}(1/298-1/T)]$</td>
<td>0.5</td>
<td>100</td>
<td>5</td>
<td>Azuma and Kametani [1964]; Blesa et al. [1994]; Cornell and Schwertmann [1996]; Zinder et al. [1986]; Skopp [2000]</td>
</tr>
</tbody>
</table>

(1) Average activation energy for kaolinite [Carroll et al., 1990] is used.
Table 9. Average values of q-parameter for the species used in model (apart from those in ISORROPIA)

<table>
<thead>
<tr>
<th>Species</th>
<th>q</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃</td>
<td>0.424</td>
<td>(1)</td>
</tr>
<tr>
<td>Fe(OH)Cl₂</td>
<td>6.04</td>
<td>(1)</td>
</tr>
<tr>
<td>Fe(OH)₂Cl</td>
<td>7.05</td>
<td>(1)</td>
</tr>
<tr>
<td>FeSO₄Cl</td>
<td>7.05</td>
<td>(2)</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>1.92</td>
<td>Kusik and Meissner [1978]</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>2.9</td>
<td>Kusik and Meissner [1978]</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃</td>
<td>0.43</td>
<td>(3)</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>0.369</td>
<td>Kusik and Meissner [1978]</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.15</td>
<td>Kusik and Meissner [1978]</td>
</tr>
<tr>
<td>Fe(NO₃)₃</td>
<td>1.51</td>
<td>(4)</td>
</tr>
<tr>
<td>Al(NO₃)₃</td>
<td>1.51</td>
<td>(4)</td>
</tr>
<tr>
<td>Mg(NO₃)₂</td>
<td>2.32</td>
<td>Kusik and Meissner [1978]</td>
</tr>
</tbody>
</table>

(1) Parameters for Fe(III) chlorides were calculated from Table 4 of Millero et al. [1995] by using definition of mean binary activity coefficient ($\gamma_{ij}$) for a single-salt solution containing an $i$-$j$ ion pair: $\gamma_{ij}^{\nu_i+\nu_j} = \gamma_{i}^{\nu_i} \cdot \gamma_{j}^{\nu_j}$ where $\nu_i$ and $\nu_j$ are stoichiometric coefficients [Robinson and Stokes, 1959]. After the value of activity coefficient for the electrolyte was determined at some temperature and ionic strength the associated parameter q was calculated using Kusik and Meissner [1978] equations;

(2) Following Millero et al. [1995] same activity coefficients for FeSO₄Cl and Fe(OH)₂Cl were used;

(3) Value for Cr₂(SO₄)₃ from Kusik and Meissner [1978] was used;

(4) Value for Cr(NO₃)₃ from Kusik and Meissner [1978] was used.
Table 10. Parameters used and calculated values for \([Fe]_{enrich}\), the surface ocean enrichment in dissolved Fe.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A6 simulation</th>
<th>M12 simulation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dust_F), (µg/m³)</td>
<td>90 (^{(1)})</td>
<td>15 (^{(4)})</td>
<td>Model</td>
</tr>
<tr>
<td>(DIF_F), (%)</td>
<td>2x10⁻¹⁰ (^{(2)})</td>
<td>4 (^{(4)})</td>
<td>Model</td>
</tr>
<tr>
<td>(D), (m)</td>
<td>10-50</td>
<td>10-50</td>
<td>Young et al. [1991]; Boyd et al. [1998]; Harrison et al. [1999]; Tsuda et al. [2003]; Chai et al., [2003]</td>
</tr>
<tr>
<td>(H), (m)</td>
<td>(2-4)x10³</td>
<td>(1-3)x10³</td>
<td>Uno et al. [2001]; Liu et al. [2003]</td>
</tr>
<tr>
<td>([Fe]_{enrich}), (nM)</td>
<td>~1(4)x10⁻¹¹</td>
<td>0.01-0.1</td>
<td>Equation (25)</td>
</tr>
<tr>
<td>(Dust_x10^6), (µg/m²)</td>
<td>~0.7 (^{(3)})</td>
<td>0.02-0.05</td>
<td>Model/see text</td>
</tr>
</tbody>
</table>

1. The model calculated average dust concentration over the HNLC waters of subarctic North Pacific Ocean (NPO) (see Figure 2);
2. The model predicted average DIF over the HNLC waters of subarctic NPO;
3. The average amount of dust deposited per surface area of the ocean by the storm that occurred between 6 to 9 April 2001 was determined using Liu et al. [2003] model calculated total mass of dust particles in PM10 range (PM10 is used here to minimize possible gradient in particle dry deposition) that was removed to the NPO and an the average surface area of the North Pacific between 40°N and 60°N (where according to the satellite images most of the dust advection took place). Using these values we get: 10x10¹² g dust/15x10¹² m² = 0.7 g/m²;
4. Values achieved at the end of M12 simulations (see Figure 2) are used.
Table 11. Model sensitivities to different parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Value</th>
<th>DIF, (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A6 Plume</td>
<td>M12 Plume</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(x10^10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;dep&lt;/sub&gt;</td>
<td>4.6x10^-6 sec^-1 (Standard Model)</td>
<td>1.65</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.9x10^-6 sec^-1</td>
<td>1.64</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.3x10^-6 sec^-1</td>
<td>1.62</td>
<td>4.12</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;dil&lt;/sub&gt;</td>
<td>3.9x10^-3 sec^-1/2 (Standard Model)</td>
<td>1.65</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.9x10^-4 sec^-1/2</td>
<td>1.40</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0x10^-4 sec^-1/2</td>
<td>1.66</td>
<td>3.88</td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;G2&lt;/sub&gt;</td>
<td>9x10^-8 m^3 µg^-1 s^-1 (Standard Model)</td>
<td>1.65</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13x10^-8 m^3 µg^-1 s^-1</td>
<td>1.65</td>
<td>3.94</td>
<td></td>
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<tr>
<td></td>
<td>5x10^-8 m^3 µg^-1 s^-1</td>
<td>1.63</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;G4&lt;/sub&gt;</td>
<td>10x10^-8 m^3 µg^-1 s^-1 (Standard Model)</td>
<td>1.65</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20x10^-8 m^3 µg^-1 s^-1</td>
<td>1.59</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1x10^-8 m^3 µg^-1 s^-1</td>
<td>1.39</td>
<td>3.76</td>
<td></td>
</tr>
<tr>
<td>Wt % Ca</td>
<td>6.2 % (Standard Model)</td>
<td>1.65</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.8 %</td>
<td>1.65</td>
<td>3.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.7 %</td>
<td>1.65</td>
<td>4.11</td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;S7&lt;/sub&gt;</td>
<td>5xK&lt;sub&gt;r&lt;/sub&gt; mol/m^2/sec (Standard model)</td>
<td>1.65</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10xK&lt;sub&gt;r&lt;/sub&gt; mol/m^2/sec</td>
<td>1.65</td>
<td>8.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1xK&lt;sub&gt;r&lt;/sub&gt; mol/m^2/sec</td>
<td>1.65</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>

1) The sensitivity of the modeling results to SO<sub>2</sub> and NO<sub>x</sub> deposition rates are studied for the uncertainties in rate coefficients suggested by Herring et al. [1996];

2) The sensitivity to the dust composition is tested by varying the weight % of Ca contained in the transportable fraction of the Gobi-desert soils. The range examined roughly corresponds to the highest and the lowest values suggested in the literature [Hseung and Jackson, 1952; Claquin et al., 1999; Chang et al., 1996; Song and Carmichael, 2001; Zhang et al., 2003]. Changes in the hematite content of the mineral dust are not considered, as (by the definition of DIF) it has no direct effect on the DIF-values of the advecting dust;
(3) The sensitivity of the modeling results to the hematite dissolution rate is studied for the likely changes caused by photoinduced reductive dissolution and saltation bombardment. 5xKr and 10xKr denote model simulations with daytime dissolution rate increased by 5 and 10 times, respectively, over the values given in Table 8. (No change is made to the nighttime rate.) The 1xKr denotes model simulations using type of kinetics described in text.
Figure Captions

Figure 1. Trajectories and physical conditions predicted by HYSPLIT for the April 6\textsuperscript{th} (blue) and March 12\textsuperscript{th} (red). Plume altitudes are given in meters above ground level (AGL). Stars indicate the assumed location for the origin of the plume and the triangles and squares are used to denote 24 hr intervals. The shaded area at the end of March 12\textsuperscript{th} trajectory indicates the region where dust plume got embedded in precipitating low-pressure system. Oceanography adapted from Harrison et al. [1999]; the location of transition zone is from Polovina et al. [2001].

Figure 2. Model calculated dust (solid line) and DIF (broken line) as a function of plume travel time. Dashed green and blue lines respectively show DIFs for high (HPA6) and low (LPM12) pollution scenarios of A6 and M12 trajectories.

Figure 3. Level-3 8-day averaged MODIS-observed [Chl \textit{a}] over the NPO for the period from (A) 14 to 21 March, (B) 30 March to 6 April, (C) 7 to 14 April and (D) 15 to 22 April, 2001. The black color on the images denotes the missing data due to clouds and the thin white lines indicate the coastal boundary. The arrow indicates the location of a enhanced-[Chl \textit{a}] patch between \( \sim 37^\circ \text{N} -39^\circ \text{N} \), \(151^\circ \text{W} -158^\circ \text{W} \). Because MODIS is not able to monitor ocean surface conditions through clouds, there is a significant amount of patchiness in the data for any given satellite pass over the NPO. More complete spatial coverage can be obtained by compiling the results from multiple passes of the satellite over the same region. In this work we make use of weekly mean values of MODIS ocean color and SST data products (MO04MW), with each weekly mean being composite of
data from 8 satellite passes. The weekly-averaged composites used are level 3 mapped products with 4.63 km special resolution. Ocean color and SST images are prepared using data downloaded from GES Distributed Active Archive Center (on the web: //daac.gsfc.nasa.gov/data/) and plotted using WebWinds interactive science data visualization software (on the web:www.openchannelsoftware.com/projects/WebWinds/).

Figure 4. The 8-day averaged MODIS-observed [Chl \(a\)] over the NPO for the period from (A) 30 March to 6 April, (B) 15 to 22 April and (C) 23 to 30 April, 2001.
Figure 1
Figure 2
Figure 3B
Figure 3C
Phytoplankton bloom got dispersed

Figure 3D
Figure 4C