Impact of dust on tropospheric photochemistry over polluted regions: a case study of the Beijing megacity

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The box model MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) is updated by incorporating detailed heterogeneous chemistry occurring on mineral aerosol surfaces. The model is used to investigate the impact of dust on tropospheric photochemistry, when the dust is transported to a polluted region together with other trace gases. The impacts of dust via heterogeneous removal of gases are analyzed for different hypothetical transport rates which are described by four different exchange rate coefficients $K_t$ in the model. Substantial impacts are found for many gases, including $O_x$ ($O_3+O(3P)$), $NO_x$ ($NO+NO_2$) and OH. The $O_x$ daily average mixing ratio decreases due to heterogeneous reactions on dust. The change ranges from $-2.5$ to $-18.4 \text{ nmol/mol}$, and is larger for faster mixing with upwind air masses (i.e. greater $K_t$). This translates into a large relative change in $O_x$, ranging from $-44\%$ to $-55\%$, which changes slightly with increasing values of $K_t$. By assuming an artificial 50% decrease of all photolysis rates, the impacts of dust via photolysis perturbation are also estimated. Furthermore, the uncertainties in the results due to the uncertainties in the uptake coefficients are evaluated. It is found that for all gases which are heterogeneously removed, the self-removal results in the largest uncertainty (e.g. $-49\%$ for $O_3$, $-76\%$ for $NO_2$, $-47\%$ for $HNO_3$, $-92\%$ for $HCHO$, $-64\%$ for $CH_3OH$ and $-93\%$ for $SO_2$). The heterogeneous removal of $NO_2$ is found to be particularly important, because it results in significant uncertainties not only in itself, but also in OH (340%) and $HO_2$ (365%). Moreover, the heterogeneous removal of $HCHO$ and $O_3$ also has farther-reaching effects on the OH concentration (resulting in changes of $-55\%$ and $45\%$, respectively), and the heterogeneous removal of $HCHO$ results in an uncertainty of $-38\%$ in the $HO_2$ concentration.
1 Introduction

The dust aerosol plays an important role in the physical, chemical, and ecological processes in the earth’s system: it is suspected to play a large role in the earth’s radiation budget (IPCC, 2007; Haywood et al., 2003; Highwood et al., 2003; Kaufman et al., 2002; Reddy et al., 2005; Stier et al., 2007); it influences ocean and terrestrial biogeochemistry by transporting nutrients like iron (Jickells et al., 2005); and it influences atmospheric chemistry by providing large surfaces for heterogeneous reactions and deposition and mixing with other smaller aerosols (e.g., Dentener et al., 1996.)

Chemical box models as well as global and regional chemistry-transport models have been used to calculate the changes in trace gas mixing ratios due to heterogeneous reactions on mineral dust aerosols. Zhang et al. (1994) and Zhang and Carmichael (1999), for example, used a box model to simulate the loss of SO$_2$, NO$_x$, HO$_2$ and O$_3$ due to heterogeneous reactions on mineral dust aerosol. They found that the presence of dust resulted in decreases in the concentrations of SO$_2$ (10–53%), NO$_y$ (16–100%, defined as NO$_3$+N$_2$O$_5$+HNO$_3$), H$_x$O$_y$ (11–59%, defined as OH+HO$_2$+H$_2$O$_2$), and O$_3$ (11–40%) under model conditions representative of spring dust storms in East Asia. Dentener et al. (1996) performed simulations with a global chemistry-transport model and calculated an O$_3$ reduction up to 10% in and nearby dust source areas. De Reus et al. (2000) calculated a 30–40% reduction of O$_3$ in a Saharan dust plume near the coast of Africa, attributed to the direct removal of O$_3$ and HNO$_3$. Bian and Zender (2003) found a very small effect (less than 1%) on the global mean O$_3$ burden while Bauer et al. (2004) predicted a decrease in the O$_3$ burden of 5% due to heterogeneous reactions on mineral dust. Tie et al. (2005) calculated a maximum reduction of HO$_x$ and O$_3$ concentrations of 30% and 20%, respectively, over the Sahara desert. In general the effect on surface O$_3$ concentrations is found to be globally small, but can be significant in dust aerosol source regions such as eastern Asia, the western United States and central Africa.

Mineral dust can affect the tropospheric ozone concentration directly by adsorption
of ozone and indirectly by the heterogeneous reactions of ozone precursors (e.g., NO₂ and RO₂). The relationships between tropospheric ozone and its precursors are quite non-linear. Consequently, when dust encounters fresh pollutants, these heterogeneous reactions can lead to a series of complex responses of the photochemical system (Tang et al., 2004). Moreover, mineral dust aerosols can influence tropospheric ozone by changing the photolysis rates of O₃, NO₂, etc.

Although all studies indicate a strong regional influence of mineral dust aerosols on tropospheric chemistry, the results vary greatly. This is mainly due to the large uncertainty in the uptake coefficients for the different trace gases on mineral dust aerosols (e.g., De Reus et al. (2000) calculated that the O₃ mixing ratio ranged from 29–45 nmol/mol using an accommodation coefficient of 10⁻⁴ and 10⁻⁵, respectively) and the representation of aerosols (e.g., bulk approach versus size resolved and internally mixed aerosols). Moreover, for box model calculations it is difficult to provide realistic initial and boundary conditions, while for 3-D models the resolution is a challenge, and for all models the comparison with observations is a major challenge.

In this paper we further explore the potential impact of mineral aerosol on tropospheric chemistry, under conditions characteristic of a polluted region. We focus on the example of Beijing city (39.92° N, 116.46° E), the capital city of China. In addition to high anthropogenic emissions, Beijing is also frequently affected by dust storms in spring, which originate from dry regions like the Taklimakan Desert, the Gobi Desert and the Loess areas (Gong et al., 2006) (Fig. 1). For this study, the chemistry box model MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) is extended by combining dust surface uptake processes with detailed gas-phase chemistry. We assume that the upwind air masses including dust and gases are transported into the polluted region at various mean velocities. The influences of dust via heterogeneous removal of gases and perturbations of the photolysis rates are investigated. In particular, considering the above-mentioned complex responses of the photochemical system, we focus on determining the contributions of the various effects, using chemical budget equations together with the box model outputs, and on qualifying the
uncertainty due to the lack of exact knowledge of uptake coefficients.

Section 2 describes the heterogeneous removal processes considered in this study and our modeling setup. In Sect. 3 the results of our model runs are discussed and the uncertainties in the uptake coefficients are analyzed. Section 4 provides a summary of the main results with conclusions.

2 Model description

To investigate the influence of dust aerosol on the mixing ratios of ozone and other reactive gases, model calculations are performed with the chemistry box model MECCA. The chemical reaction scheme has been described by Sander et al. (2005) and includes detailed chemistry of organic species with up to four C-atoms and isoprene (von Kuhlmann et al., 2003). The reaction rates have generally been adopted from the Jet Propulsion Laboratory (JPL) 2003 database (Sander et al., 2003) and the Master Chemical Mechanism (MCM) (http://mcm.leeds.ac.uk/MCM/).

For this study 12 heterogeneous removal reactions on mineral dust have been added to the chemical scheme. In order to describe the transport of dust and gases over polluted regions, three physical processes have been incorporated, including: 1) inflow of upwind dust-rich air masses, 2) deposition and 3) emissions. Sensitivity simulations have been performed with four different exchange coefficients which are used to represent a range of transport velocities. These aspects of the model setup are described in detail in the following subsections.

2.1 Heterogeneous removal reactions

Heterogeneous reactions can deplete gas-phase species by condensation or deposition on aerosol particles. The removal rate of gas-phase species \( i \) by aerosol particles can be described by a pseudo first-order rate coefficient \( (s^{-1}) \), given by Heikes and
Thompson (1983):

\[ k_i = \int_{r_{\text{min}}}^{r_{\text{max}}} k_{mt,i}(r)n(r)d(r), \]  

(1)

where \( n(r)dr \) (cm\(^{-3}\)) represents the number concentration of particles with a radius between \( r \) and \( r + dr \) and \( k_{mt,i}(r) \) is the size-dependent mass transfer coefficient (m\(^3\) s\(^{-1}\)), which can be calculated using the formulation given by Fuchs and Sutugin (1970):

\[ k_{mt,i} = \frac{4\pi D_i V}{1 + K_n \chi + 4(1 - \alpha)/3\alpha}, \]  

(2)

where \( D_i \) (cm\(^2\) s\(^{-1}\)) is the gas phase molecular diffusion coefficient of species \( i \), \( V \) is the ventilation coefficient, which is close to unity, and \( K_n \) is the dimensionless Knudsen number, which is defined as the ratio of the effective mean free path of a gas molecule in air, \( \lambda \), to the particle radius \( r \), and \( \chi \) represents a correction factor for anisotropic movement and is dependent on the Knudsen number. The parameter \( \alpha \) is the mass accommodation coefficient (or sticking coefficient), which is a dimensionless number defined as the number of molecules adsorbed by the surface of an aerosol divided by the number of collisions with the aerosol. An alternate parameterization by Schwartz (1986) was used by Dentener et al. (1996), Zhang and Carmichael (1999), de Reus et al. (2000) and de Reus et al. (2005). We have tested using this instead, and find that all results differ by less than 5% compared to using Eq. (2).

There are two important parameters for interactions of gases with dust surfaces: the mass accommodation coefficient, \( \alpha \), and the reactive uptake coefficient, \( \gamma \). \( \gamma \) represents the fraction of collisions with a particle that leads to irreversible loss of the gas, whereas \( \alpha \) only indicates the reversible adsorption. The value of \( \alpha \) usually represents an upper limit of \( \gamma \). For the calculation of the gas removal rate in the model, we use values of \( \gamma \) based on laboratory studies.

In recent years, numerous measurements of the accommodation or uptake coefficient on mineral aerosol have been performed and have been used in model studies.
A discussion of the available measurements for the species of interest and the values used in model studies are given in Appendix A. The 12 heterogeneous removal pathways, along with the “best guess” values and the lower and upper limits for the reactive uptake coefficient of the different gases on dust aerosol mentioned above are listed in Table 1.

2.2 Inflow, deposition and emission

In this work, three physical processes are included in the box model MECCA: 1) inflow of upwind dust-rich air masses, 2) deposition and 3) emissions, as described below.

We consider the transport of dust and gases in a highly simplified way, by replacing a fraction of the air mass in the box directly by the incoming air mass, so that the tendency is calculated as:

\[
\frac{\partial C_i}{\partial t} = (C_i' - C_i) \cdot f, \tag{3}
\]

where \(C_i'\) is the concentration of component \(i\) (dust and gases) in the upwind air masses, \(t\) is the modeling time step and \(f\) is the exchange rate coefficient, which is defined as the fraction of air mass in the box replaced per unit time by the incoming air mass (note that \(f\) is the same for all components \(i\)).

We assume a homogeneous vertical distribution of all the simulated species in the boundary layer. For the emitted species, the increase in concentration \(C_i\) can be calculated from the emission flux \(J_e\) and the height of the boundary layer \(Z_{pbl}\):

\[
\frac{\partial C_i}{\partial t} = \frac{J_e}{Z_{pbl}}. \tag{4}
\]

The deposition flux \(J_d\) for the dry deposition can be parameterized as the product of the concentration \(C_i\) and the deposition velocity \(v_d\):

\[
J_d = -v_d C_i. \tag{5}
\]
To obtain the concentration change, the deposition flux is divided by the height of the boundary layer $Z_{pbl}$:

$$\frac{\partial C_i}{\partial t} = -\frac{v_d C_i}{Z_{pbl}}.$$  

Note that the parameters $J_e$ and $v_d$ (and thus $J_d$) differ for each species $i$; these are discussed further in the following sections, and information on their values is given in Table 2. Wet deposition is not included in this study, considering that dust storm events only occur when it is not raining.

### 2.3 Input parameters

The air parcel encompasses the boundary layer which is assumed to be uniformly mixed up to 756 meters. Temperature, air pressure, and relative humidity as input parameters are kept constant during the simulations at 284.35 K, 943.17 hPa, and 44%, respectively. These physical parameters, the initial gas-phase species concentrations $C_i$ and the upwind gas-phase species concentrations $C'_i$ are derived from the global atmospheric chemistry general circulation model ECHAM5/MESSy Atmospheric Chemistry (EMAC) (Jöckel et al., 2006). The EMAC simulation from which these parameters were obtained (B. Steil, personal communication) was performed with a horizontal resolution of T106 on a Gaussian grid (approximately $1.1° \times 1.1°$ in longitude and latitude, respectively) and 31 levels on a hybrid-pressure grid in the vertical. The output was archived every 5 h. The monthly average values for April 2006 for the boundary layer of the grid covering Beijing are used for the initial concentration. And the values of the neighboring grid to the west are used for the upwind concentrations. The initial ($C_i$) and upwind ($C'_i$) mixing ratios of key gases, along with their deposition velocities, are listed in Table 2. The dust size distribution measured over Northern China coastal areas during a dust storm episode in April 2006 is assumed to be representative for North China suffering the dust storm during the same period (Wang et al., 2008).
this assumption, the upwind dust size distribution is set to be same as the measured as shown in Fig. 2.

The emission fluxes of CO, NO\textsubscript{x}, NMVOC and SO\textsubscript{2} for the Beijing urban area are derived from the regional emission inventory of North China for the year 2006 (Zhao, 2007). The calculated emission rates of key gases are listed in Table 2.

The dry deposition velocities of dust in different size classes are taken from Lee et al. (2005). They estimated the dry deposition velocity of Asian dust in spring of 2002 for 11 particle size bins with diameter ranging from 0.2 to 74 µm. The deposition velocities of gases are derived from the archived output of the EMAC simulation.

2.4 Sensitivity simulations

The wind speed and direction at 10 m above ground observed hourly at one meteorological station located in the Beijing urban area (39.48° N, 116.28° E) show that in April 2006 the wind originating from the west has a average velocity of 2.2 m s\textsuperscript{-1} and a maximum velocity of 5.0 m s\textsuperscript{-1}, while the wind from the northwest has an average velocity of 5.1 m s\textsuperscript{-1} and a maximum velocity of about 10.5 m s\textsuperscript{-1} (Fig. 3). To investigate the impact of dust which is imported to the Beijing region with different transport velocities, four cases are considered with different mixing time lengths. From slow to fast mixing, they are the “T16” case (1/f = 16 h), “T08” case (1/f = 8 h), “T04” case (1/f = 4 h) and “T02” case (1/f = 2 h), in which the exchange rate coefficients \( f \) are 1.7×10\textsuperscript{-5}, 3.5×10\textsuperscript{-5}, 7.0×10\textsuperscript{-5} and 1.4×10\textsuperscript{-4} pers, respectively. According to Gurjar et al. (2008), the surface area of Beijing megacity is about 20 000 km\textsuperscript{2}, which would correspond to \( \sim 150 \) km per side. However, this applies to the entire Beijing district; only considering the highly populated central district would be about 10% of this area, or about 50 km per side. If we take a length scale of 100 km as intermediate between these extremes, then we estimate corresponding mean horizontal wind speeds ranging from 1.7 m s\textsuperscript{-1} to 14 m s\textsuperscript{-1}. Thus the T16 case is at the low end of the mean winds originating from the west or northwest, while the T02 case represents an extreme case of very strong inflow from upwind regions. Since larger dust particles have greater deposition velocities (Lee
et al., 2005), and the effect of deposition becomes more important when the advection is weaker (i.e. smaller $f$), we obtain decreasing dust surface areas from the T02 case to the T16 case, especially for the dust in the larger size bins, as shown in Fig. 2.

The settings of these four cases are listed in Table 3. In each case, three simulations are performed: a simulation without dust (NO_DUST), a simulation with dust but only considering the heterogeneous reactions (DUST_H), and a simulation considering the heterogeneous reactions and a decrease of photolysis rates (DUST_H+J). Jeong et al. (2007) calculated a 47.3% decrease in the reactions having photolytic wavelengths in the UV (210–380 nm) at surface, for dust assumed to have a size distribution like that measured during ACE-Asia, and to mix with high levels of pollution. In this study, an artificial 50% decrease of all photolysis rates is used for the DUST_H+J simulation, to examine the basic sensitivity in the context of dust over Beijing.

For the simulations, we allow a spinup time of 96 h. This is sufficient to establish equilibrium with the upwind air mass for the long-lived tracers (e.g. CO and dust), even for the T16 case. In the following sections, analyses are based on the fifth simulation day, after equilibrium has been established.

The difference between the DUST_H and NO_DUST simulations isolates the influence of dust via heterogeneous reactions. The additional dust influence through photolysis rates perturbation is represented by the difference between the DUST_H+J and DUST_H simulations. These differences are discussed separately in the following section.

3 Results

3.1 Influence of the exchange rate coefficient

In this section, we will first discuss the influence due to mixing with upwind air mass (without the additional influence of dust), then in Sects. 3.2 and 3.3, we will consider the influence of dust via heterogeneous reactions and photolysis perturbation, respectively.
The time series of the mixing ratios of O$_3$, NO, NO$_2$ and the concentration of OH for 24 h (beginning at 00:00 LT of the fifth simulation day) are shown in Fig. 4 (black curves). A positive correlation with the exchange rate coefficient $f$ is found for the O$_3$ mixing ratio and the OH concentration for the NO$_x$DUST simulation, and a negative correlation is found for the NO and NO$_2$ mixing ratios. We can understand the main factors contributing to these changes by examining the budget equations for each of these gases.

Considering the existence of the null cycle, Reactions (R1) and (R2) in Table 4, the Reaction (R3) is a dominant loss term for O$_3$, from which the corresponding loss frequency will be much larger than the loss frequency due to dust heterogeneous removals. In order to better display the influence of dust heterogeneous removals on the tropospheric photochemistry in the following sections, only the family budget of O$_x$ (defined as O$_3$+O($^3$P)) will be analyzed. O($^1$D) is not included in O$_x$ due to its negligible effect (only $\sim$1%). Similarly, the rapid photochemical equilibrium between NO and NO$_2$, established by the Reactions (R3), (R4) and (R2), tends to dominate the individual budgets of NO and NO$_2$, so that it is more enlightening to examine the budget of the family NO$_x$ (defined as NO+NO$_2$).

Considering that steady state has been reached, we have the equation:

$$K_t \cdot (C'_i - C_i) + B_e - K_d \cdot C_i + B_{cp} - K_{cl} \cdot C_i = 0,$$

where $C'_i$ is the mixing ratio of component $i$ in the upwind air masses, $C_i$ is the daily average mixing ratio of component $i$, $K_t$ represents the exchange rate coefficient (i.e. “$f$” in Eq. 3), $B_e$ is the source term due to direct emission into the box, $K_d$ is the deposition coefficient (i.e. “$\nu_d/Z_{pbl}$” in Eq. 6), $B_{cp}$ is the daily average gross chemical production rate, and $K_{cl}$ is the daily average gross chemical loss frequency (so that $K_{cl} \cdot C_i$ is the daily average gross chemical loss term in the budget). Based on Eq. (7), we can solve for $C_i$:

$$C_i = \frac{K_t \cdot C'_i + B_e + B_{cp}}{K_t + K_{cl} + K_d},$$
where $C_i'$, $B_e$ and $K_d$ are fixed, while $B_{cp}$ and $K_{cl}$ change with $K_t$ because the tracer concentrations in the box are influenced by the inflowing upwind air mass.

For O$_x$, no emission is considered, so in Eq. (8), $B_e=0$. $C_i'$ and $K_d$ are fixed for O$_3$ as listed in Table 2, and no physical process effects on O($^3$P), while $B_{cp}$ and $K_{cl}$ change with the increasing $K_t$, as shown in Fig. 5a. From the T16 case to the T02 case, $K_t$ doubles each step from $1.7 \times 10^{-5}$ s$^{-1}$ to $1.4 \times 10^{-4}$ s$^{-1}$, while $B_{cp}$ and $K_{cl}$ decrease in magnitude. Since no heterogeneous reactions on dust are included yet, the changes in $B_{cp}$ and $K_{cl}$ are due only to the changes in NO$_x$ and other gases. Although $K_t$ doubles each step, $B_{cp}$ and $K_{cl}$ are the dominating factors of the numerator and denominator of Eq. (8), respectively. As a result, both the numerator and the denominator decrease with the doubling $K_t$. However, for each step from the T16 case to the T02 case, the relative decrease of the denominator is about 2 times larger than the relative decrease of the numerator. Consequently, the O$_x$ daily average mixing ratio increases with the doubling $K_t$, but not exactly doubles each step as seen in Fig. 5a.

For NO$_x$, both the chemical production rate $B_{cp}$ and the chemical loss frequency $K_{cl}$ increase with the doubling $K_t$, as shown in Fig. 5c. Different from O$_x$, the local emission rate $B_e$ is the largest production term, and $K_t$ is the largest loss frequency, especially when the mixing is slow (i.e. smaller $K_t$). Both the numerator and the denominator of Eq. (8) increase with the doubling $K_t$. However, for each step from the T16 case to the T02 case, the relative increase of the denominator is larger than the relative increase of the numerator. Consequently, both the NO and NO$_2$ daily average mixing ratios decrease with the doubling $K_t$, as seen in Fig. 5b.

As a short-lived radical, the OH concentration is determined only by its chemical budget. As shown in Fig. 6, the major source terms of OH are Reactions (R5), (R6) and (R7). As already discussed, when the exchange rate coefficient increases, the NO and NO$_2$ mixing ratios decrease. Thus, the rates of Reactions (R5) and (R6) decrease with the increasing exchange rate coefficient $K_t$. This causes the decrease of the OH gross production rate with the increasing $K_t$, as seen in Fig. 5d. On the other hand, the major loss terms of OH are Reactions (R8), (R9), (R10) and (R11), due to the high
mixing ratios of NO, NO₂, CO, and SO₂ from local emissions. The “Miscellaneous” loss term, which represents the loss of OH due to all other reactions, mostly with various hydrocarbons, is also important. It is worth noting that the Reaction (R11) plays an unusually large role over Beijing, due to the high SO₂ mixing ratios originating largely from local emissions. Since the mixing ratios of NO, NO₂, CO, SO₂ and hydrocarbons decrease with the increasing $K_t$, the gross loss reaction frequency decreases in magnitude, as seen in Fig. 5d. We find that the relative decrease in the gross loss frequency is larger than the relative decrease in the gross production rate. As a result, the daily average OH concentration increases with increasing $K_t$, as seen in Fig. 5d.

### 3.2 Influence of heterogeneous uptake on dust

The influence of dust via heterogeneous reactions is discussed in this section. First, following up on the discussion in the previous section, as shown in Fig. 7, for the DUST_H simulations, when $K_t$ increases, the tendencies of $O_x$, NOₓ mixing ratios are qualitatively similar to those for the NO_DUST simulations discussed in Sect. 3.1. However, the tendency of the OH concentration is different: it stays nearly constant, decreasing slightly from the T16 case to the T04 case, then increasing again to the T02 case. The OH concentration results from a delicate balance between loss and production terms as discussed above. Introducing losses of several gases on dust, especially NO₂ and SO₂, shifts this balance so that OH responds differently to $K_t$ in the DUST_H case than in the NO_DUST case.

The overall effect of introducing the heterogeneous dust reactions is to decrease the $O_x$ mixing ratio, as seen in Fig. 8a. The change ranges from $-2.5$ to $-18.4$ nmol/mol, and is larger for faster mixing in of upwind air masses (i.e. greater $K_t$). This translates into a large relative change in $O_x$, ranging from $-44\%$ to $-55\%$, which changes slightly with increasing values of $K_t$. In order to understand how the various changes due to the inclusion of heterogeneous dust reactions contribute to this decrease in $O_x$, as well as for other gases (discussed below), we can analyze the budget equations for the DUST_H and NO_DUST cases more closely. Based on Eq. (8), the heterogeneous
influence on the tracer daily average mixing ratio is represented as (for any species $i$, leaving out the subscript here for readability):

$$\Delta C = \frac{\Delta B_{cp} - \Delta K_{cl} \cdot C_{\text{NO\_DUST}}}{(K_t + K_{cl\text{\_DUST\_H}} + K_d)}.$$  \hspace{1cm} (9)

The derivation of Eq. (9) is explained in Appendix B. Since the denominator in Eq. (9) is always positive, this indicates that the balance between the changes in the gross chemical production rate $B_{cp}$ and the gross chemical loss frequency $K_{cl}$, determine whether the heterogeneous reactions will cause an increase or decrease in the daily average mixing ratio. Since the direct influence of dust due to heterogeneous uptake of $C$ is included in the chemical loss frequency, $K_{cl}$, and its change, $\Delta K_{cl}$, one would expect this to result in a tendency for the mixing ratios of most gases to decrease, as seen to be the case for O$_x$, though this is not always the case, as shown below. Eq. (9) also shows that, all else being equal, the relative change in $C$ becomes smaller as the rate of mixing ($K_t$) becomes larger (in comparison to $K_{cl\text{\_DUST\_H}}$).

As shown in Fig. 8a, for each of the four exchange rate coefficient cases, the gross chemical production rate ($B_{cp}$) decreases when the dust reactions are included. This is mainly due to the decrease in the NO$_2$ mixing ratio (Fig. 8b). The relative change (in percentage, calculated as (DUST\_H−NO\_DUST)/NO\_DUST) in $B_{cp}$ is substantial, ranging from about $-37\%$ (T16) to $-21\%$ (T02). On the other hand, as $K_t$ increases from the T16 case to the T02 case, the dust surface area concentration also increases as shown in Fig. 2. Consequently, the O$_x$ loss frequency due to the heterogeneous removal (HR1) also increases, as shown in Fig. 8a. This, however, is small compared to the change in $K_{cl}$, also shown in Fig. 8a. The relative change in $K_{cl}$ is substantial, ranging from $13\%$ (T16) to $61\%$ (T04), as shown in Fig. 9a, and is mostly governed by the change in NO via the Reaction (R3) which increases substantially as shown in Fig. 8b. This is part of another null cycle (R3, R4 and R2), which can principally be removed by extending the definition of O$_x$ to include NO$_2$ (Crutzen and Schmailzl, 1983). When the budget of O$_x$ with this broader definition as $O_3$+$O(3P)$+NO$_2$+$O(1D)$ is ana-
lyzed, the strong direct effect of the heterogeneous reaction becomes apparent. For example, in the T08 case, the loss frequency of the heterogeneous uptake (HR1 + HR3) is $1.6 \times 10^{-5} \text{s}^{-1}$ and the $\Delta c_l$ is $1.2 \times 10^{-5} \text{s}^{-1}$, which corresponds to a relative increase of 125% (the value of $K_{c/l}$ in the NO_DUST run is $0.96 \times 10^{-5} \text{s}^{-1}$). $\Delta K_{c/l}$ is a bit smaller than the loss frequency of the heterogeneous uptake, due to the negative response of some gas phase reactions (e.g. the loss frequency of the reaction $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ (R12) decreases by $3.3 \times 10^{-6} \text{s}^{-1}$). Since, however, $\text{O}_3$ and $\text{NO}_x$ more closely correspond to the quantities that are normally reported in observations and other modeling studies, we will mostly employ these standard definitions here, rather than the extended $\text{O}_x$ definition.

The overall effect of introducing the heterogeneous dust reactions is to decrease the $\text{NO}_x$ mixing ratio, as seen in Fig. 8c. The decrease ranges from $-18$ to $-2.7 \text{ nmol/mol}$, and is smaller for faster mixing in of upwind air masses (i.e. greater $K_t$). This translates into a relative decrease ranging from $-8$% to $-9$% (Fig. 9b), which changes slightly with increasing values of $K_t$. For each of the four exchange rate coefficient cases, the gross chemical production rate ($B_{cp}$) decreases when the dust reactions are included. This is mainly due to the decrease in other gases, e.g. $\text{NO}_3$ and $\text{N}_2\text{O}_5$. The relative decrease in $B_{cp}$ is substantial, increasing in magnitude from about $-42$% (T16) to $-93$% (T02). From the T16 case to the T02 case, the $\text{NO}_x$ loss frequency due to the heterogeneous removal (HR3) increases due to the increasing dust surface area concentration, as shown in Fig. 8c. This translates into a substantial relative change in the gross chemical loss frequency $K_{c/l}$, which is positive for T16 and T08 and negative for the other two cases, as shown in Fig. 9b. This is because the change in $K_{c/l}$ is also influenced by the decrease in $\text{NO}_3$ via the reaction $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$, which changes from $-2.7 \times 10^{-8} \text{s}^{-1}$ in the T16 case to $-9.0 \times 10^{-5} \text{s}^{-1}$ in the T02 case, and is larger in magnitude than the increase in the loss frequency of the heterogeneous removal HR3 in the T04 and T02 cases.

As shown in Figs. 8d and 9c, the overall influence of the heterogeneous dust reactions is to increase the OH concentration in the T16 case, and reduce OH in the other
three cases. The corresponding relative change ranges from 4% in the T16 case to 
−33% in the T02 case. On the whole, this is due to the balance in the production and 
loss terms in the chemical budget (see Eq. 11), especially given the short lifetime of 
OH. For all four cases, both the gross production rate $B_{cp}$ and the gross loss frequency 
$K_{cl}$ decrease. However, as $K_t$ increases from the T16 case to the T02 case, the 
relative change in $B_{cp}$ increases in magnitude and the relative change in $K_{cl}$ decreases 
in magnitude. In the T16 case, the relative change in $B_{cp}$ is smaller in magnitude than 
in $K_{cl}$, leading to the increase in OH concentration. In the other three cases the relative change in $B_{cp}$ is larger in magnitude than in $K_{cl}$, leading to the decrease in OH 
concentration. For the T08, T04 and T02 cases, the relative change in OH concentra-
tion increases in magnitude as $K_t$ increases. The main reactions responsible for 
these changes are depicted in Fig. 8d. The change in the gross production rate $B_{cp}$ 
is mainly due to the Reaction (R5), because of the strong local buildup of NO$_x$ (up to 
about 150 nmol/mol of NO in the T16 case) caused by the strong urban emissions. 
The change in the gross loss frequency $K_{cl}$ is primarily due to the Reactions (R9) 
and (R11), especially strongly in the T16 case, again due to the buildup of high local pollution levels, in this case NO$_2$ and SO$_2$, where the latter can be expected to be particularly applicable to Chinese megacities (Tang et al., 2004). On the whole, this 
shows that the OH response to dust reactions is complex and will be difficult to pre-
dict for other cities without model simulations (box or 3-D) applicable to their specific conditions.

### 3.3 Photolysis influence

In order to investigate the influence of dust via photolysis rate perturbations, the sim-
ulation DUST$_H$+J is performed for the T04 case with the heterogeneous reactions 
(using the same uptake coefficients in the DUST$_H$ simulation) and an artificial 50% 
decrease of all photolysis rate coefficients. The differences in the daily (24 h) mean 
mixing ratios and the gross chemical production budgets and loss frequencies of O$_x$, 
NO$_x$ and OH between the DUST$_H$+J and DUST$_H$ simulations are shown in Fig. 10,
and the relative differences are listed in Table 5. This artificial photolysis rate perturbation causes a large relative decrease in OH (−54%) and $O_x$ (−19%), respectively, while only a small relative decrease (−0.6%) is computed for NO$_x$.

When the photolysis rate coefficients are reduced, the rate of the Reaction (R4) decreases, and thus the $B_{cp}$ of $O_x$ decreases. On the other hand, the values of $K_{cl}$ for $O_x$ also decrease due to the change in NO mixing ratio (−3.5 nmol/mol). Since the relative decrease in the $B_{cp}$ is larger than the relative decrease in the $K_{cl}$, and based on Eq. (9), the $O_x$ mixing ratio decreases due to the dust photolysis perturbation.

For NO$_x$, as discussed in Sect. 3.1, the numerator and denominator of Eq. (8) are dominated by the emission rate $B_e$ and the exchange rate coefficient $K_t$, respectively. As a result, although $B_{cp}$ decreases by 12.3% and $K_{cl}$ decreases by 1.17%, the numerator and denominator of Eq. (8) do not change significantly. Consequently, NO$_x$ mixing ratio only decreases slightly.

As shown in Fig. 10, all the production terms of OH decrease due to the decrease in the photolysis rate coefficients, so the $B_{cp}$ of OH decreases. On the other hand, the small increase in the OH loss frequency is due to the balance between large changes in the reactions with NO (R8) and NO$_2$ (R9), with the latter dominating slightly. This combination results in the large decrease in the OH concentration.

### 3.4 Uncertainties

As described in Appendix A, due to the different types of mineral dust and different methodologies used in the laboratory experiments, the measured accommodation or uptake coefficients have large uncertainties, in some cases several orders of magnitude. This can lead to large uncertainties in the calculated heterogeneous removal influence of dust. We can make use of the numerical model to examine the relative significance of the influence of each heterogeneous removal reaction and the uncertainty in the results. For this purpose, simulations in the T08 case have been performed in which one removal reaction is calculated individually with either the “Lower Limit” or “Upper Limit” coefficient from Table 1, and all the other removal reactions are calculated with...
the “Best Guess” coefficients. The differences in the tracer mixing ratios calculated with the “Upper Limit” and “Lower Limit” coefficients are normalized by the tracer mixing ratio calculated without dust considered, i.e. $C_{\text{DUST}}(\gamma_{\text{Upper}}) - C_{\text{NO-DUST}}(\gamma_{\text{Lower}})$, and the results are compared in Fig. 11. The absolute differences, i.e. $C_{\text{DUST}}(\gamma_{\text{Upper}}) - C_{\text{DUST}}(\gamma_{\text{Lower}})$, are shown in Appendix C for reference. The uncertainties are negative for the gases which are reduced due to the heterogeneous removals, and positive for the gases which are increased due to the heterogeneous removal. Although the cumulative effect of all reactions can be different, some insight into the effect of each single reaction is provided by this approach.

For all gases which are heterogeneously removed, the self-removal results in the largest uncertainty (e.g. $-49.2\%$ for O$_3$, $-75.7\%$ for NO$_2$, $-46.6\%$ for HNO$_3$, $-92.2\%$ for HCHO, $-64.3\%$ for CH$_3$OH and $-93.3\%$ for SO$_2$), except for OH and HO$_2$, for which the largest uncertainties come from the heterogeneous removal of NO$_2$. We find that the heterogeneous removal of NO$_2$ is particularly important, because it results in significant uncertainties not only in itself, but also in OH (340.4%) and HO$_2$ (365.6%). Moreover, the heterogeneous removals of HCHO and O$_3$ also have farther-reaching effects, causing uncertainties in the OH concentration of $-54.8\%$ and 45.0%, respectively; furthermore, the heterogeneous removal of HCHO results in an uncertainty of $-38.4\%$ in HO$_2$ concentration.

If we instead normalize by the tracer mixing ratio calculated with the “Best Guess” coefficients, i.e. $C_{\text{DUST}}(\gamma_{\text{Upper}}) - C_{\text{DUST}}(\gamma_{\text{Lower}})$, we compute larger uncertainties (e.g. $-89.8\%$ for O$_3$) and some with extremely large values (e.g. $-558,552\%$ for HNO$_3$). This is because introduction of the heterogeneous removal reactions (i.e., the DUST_H “Best Guess” case) already decreases these tracer mixing ratios as discussed in Sect. 3.2, even to extremely low values for some tracers like HNO$_3$ due to their rapid uptake. The uncertainties computed with this manner are also shown in Appendix D for reference.

On the whole, the results clearly indicate that the uncertainty in the uptake coefficients result in large uncertainties for the influence of dust under polluted conditions.
4 Summary and conclusions

In this study, a box model is used in which detailed gas-phase chemistry is combined with dust surface uptake processes. Based on the output from a global atmospheric chemistry general circulation model and a regional emission inventory of North China, we confine the “box” to represent the typical polluted condition in urban area of Beijing megacity. Dust is assumed to be transported together with other gas-phase species over a polluted region at different speeds. The influences of dust on tropospheric photochemistry via heterogeneous removal under different assumed transport speeds have been investigated and discussed in detail.

The influences due to mixing with upwind air mass have been discussed first, without considering the heterogeneous reactions on dust (i.e. NO\textsubscript{DUST} simulations). It is found that the \(O_x\) (defined as \(O_3+O(^3P)\)) mixing ratio and OH concentration both increase with the increasing exchange rate coefficients \(K_t\). However, the \(NO_x\) (defined as \(NO+NO_2\)) mixing ratio decreases with the increasing \(K_t\). Similar tendencies of the \(O_x\) and \(NO_x\) mixing ratios are found when the heterogeneous reactions are considered (i.e., in the DUST\textsubscript{H} simulations), while the tendency of the OH concentration is different.

The overall effect of introducing the heterogeneous dust reactions is to decrease the \(O_x\) mixing ratio. The change ranges from \(-2.5\) to \(-18.4\) nmol/mol, and is larger for faster mixing in of upwind air masses (i.e. greater \(K_t\)). This translates into a large relative change in \(O_x\), ranging from \(-44\%\) to \(-55\%\), which changes slightly with increasing values of \(K_t\). This is comparable to the global results of Dentener et al. (1996), which found changes in the range of \(-50\%\) to \(-20\%\).

The \(NO_x\) mixing ratio is decreased due to introducing the heterogeneous dust reactions. The decrease ranges from \(-18\) to \(-2.7\) nmol/mol, and is smaller for faster mixing in of upwind air masses (i.e. greater \(K_t\)). This translates into a relative decrease ranging from \(-8\%\) to \(-9\%\), which changes slightly with increasing values of \(K_t\).

The influence on OH due to the heterogeneous dust reactions on dust is complex.
The OH concentration is increased for smaller $K_t$ (4% in the T16 case), but decreased for greater $K_t$ (up to $-33\%$ in the T02 case). It would be difficult to predict the anticipated change in OH for other cities without model simulations (box or 3-D) applicable to their specific conditions.

In the T04 case, by introducing an artificial 50% decrease of all photolysis rate coefficients, we estimate that the relative contributions of the heterogeneous removal on dust and the decrease in photolytic rates are 87% and 13%, respectively. They fit to the values reported by Zhang et al. (1999) which are 79.7–92.9% and 7.1–20.3%, respectively.

It should be noted that in reality there is a dependence of the dust source on the wind speed (normally faster winds cause larger upwind sources), so the approach of assuming a constant upwind dust mixing ratio and size distribution for all four exchange rate coefficient cases will tend to underestimate the spread in the effects from T16 to T02.

The potential uncertainties due to different uptake coefficients are investigated in the T08 case. It is found that for all gases which are heterogeneously removed, the self-removal results in the largest uncertainty (e.g. $-49.2\%$ for O$_3$, $-75.7\%$ for NO$_2$, $-46.6\%$ for HNO$_3$, $-92.2\%$ for HCHO, $-64.3\%$ for CH$_3$OH and $-93.3\%$ for SO$_2$), except for OH and HO$_2$, for which the largest uncertainties come from the heterogeneous removal of NO$_2$. We find that the heterogeneous removal of NO$_2$ is particularly important, because it results in significant uncertainties not only in itself, but also in OH (340.4%) and HO$_2$ (365.6%). Moreover, the heterogeneous removal of HCHO and O$_3$ also has farther-reaching effects, causing uncertainties in the OH concentration of $-54.8\%$ and $45.0\%$, respectively; furthermore, the heterogeneous removal of HCHO could cause an uncertainty of $-38.4\%$ in the HO$_2$ concentration. The results clearly indicate that the uncertainty in the uptake coefficients result in large uncertainties for the influence of dust under polluted conditions, and suggest that further laboratory work, especially on the uptake of NO$_2$, HCHO and O$_3$, will be valuable for reducing the uncertainties in future modeling studies.
This paper provides an analysis of potential influences of dust under the conditions of a typical highly polluted region. This study will provide guidance for the incorporation and analysis of heterogeneous dust reactions in a regional 3-D chemistry-transport model, which is being developed to study the impacts of dust on tropospheric photochemistry in different polluted areas of North China. Considering the large uncertainties estimated in this study, we will try to evaluate the uptake coefficients fitting for North China by sensitivity studies in the next step.

Appendix A

Review of the heterogeneous uptake coefficient values measured and adopted in former laboratory and model studies

O₃

Many direct measurements of O₃ uptake on mineral dust were recently performed with contradictory results (Michel et al., 2002, 2003; Hanisch and Crowley, 2003; Usher et al., 2003). Values of γ in the range of approximately 10⁻⁶ to 10⁻⁴ were reported. In recent model studies, 1×10⁻⁵ was used by Liao et al. (2004); Liao and Seinfeld (2005); Tie et al. (2005); Bauer et al. (2004); Pozzoli et al. (2008). In this study, the value 2.7×10⁻⁵ recommended by The International Union of Pure and Applied Chemistry (IUPAC) for China loess is used (http://www.iupac-kinetic.ch.cam.ac.uk).

HNO₃, N₂O₅, NO₃ and NO₂

The reaction of nitric acid with mineral dust aerosols has been recently addressed by several laboratory studies (Hanisch and Crowley, 2001; Goodman et al., 2000; Underwood et al., 2001; Grassian, 2002). This reaction irreversibly removes HNO₃ from the gas phase. The reported γ for HNO₃ varies from approximately 10⁻⁵ to 0.2. In model
studies, $10^{-3}$ was used by Bian and Zender (2003), while 0.1 was used by Liao et al. (2004), Liao and Seinfeld (2005), Tie et al. (2005), Pozzoli et al. (2008), Dentener et al. (1996), and Bauer et al. (2004). A larger value of 0.17 recommended by IUPAC for Chinese dust is adopted for this study.

In recent laboratory work, the uptake of $\text{N}_2\text{O}_5$ on mineral dust was investigated by Seisel et al. (2005), Karagulian et al. (2006) and Wagner et al. (2008). Seisel et al. (2005) and Wagner et al. (2008) reported similar values of about $10^{-2}$, while Karagulian et al. (2006) reported significantly larger values (about $10^{-1}$). In model studies, Dentener et al. (1996), Bian and Zender (2003) used the value 0.1, while values between 0.003 and 0.02 depending on the relative humidity were used by Bauer et al. (2004), Liao et al. (2004), Liao and Seinfeld (2005), and Pozzoli et al. (2008). The value 0.03 is chosen as a compromise for this study.

Some experiments focusing directly on the uptake of $\text{NO}_3$ on mineral dust surfaces have been performed by Karagulian and Rossi (2005). The measured uptake coefficient ranged from roughly 0.01 to 0.23 for different mineral dusts. These values are significantly larger than the $\gamma$ value of $3.0 \times 10^{-3}$ for $\text{NO}_3$ used by Bauer et al. (2004). An intermediate $\gamma$ value of 0.1 for $\text{NO}_3$ was used for the modeling studies performed by Bian and Zender (2003) and Pozzoli et al. (2008), and is also used in this study.

The initial uptake coefficients for $\text{NO}_2$ on the surface of different mineral particles were measured by Underwood et al. (2001). The $\gamma$ value ranges from $<4 \times 10^{-10}$ to $2 \times 10^{-5}$, with most values in the $10^{-6}$ range. Ullerstam et al. (2003) measured the uptake coefficient of $\text{NO}_2$ for Saharan dust. They reported the uptake coefficient as $(2.0 \pm 0.4) \times 10^{-4}$ for geometric area. The modeling study performed by Bian and Zender (2003) used a $\gamma$ value of $4.4 \times 10^{-5}$ for $\text{NO}_2$. In this study, we employ a lower value of $2.1 \times 10^{-6}$ recommended by IUPAC for China loess.
HO₂, OH and H₂O₂

Laboratory experiments on the uptake of OH and HO₂ on sulfuric acid and water surfaces show reactive uptake coefficients which range from 0.004 to 1 for OH, and from 0.01 to 1 for HO₂ (Hanson et al., 1992). Unfortunately no laboratory studies of the uptake of the HO₂ radical on mineral dust aerosol are documented; however, in a review, Jacob (2000) recommends including the uptake of HO₂ by aerosols with γ=0.2 in atmospheric chemistry models, and also concludes that although the mechanism for HO₂ uptake is uncertain, H₂O₂ is the likely product. Here we adopt this recommendation for γ, as well as the assumption that H₂O₂ is the only reaction product with a 100% yield. For the uptake coefficient of OH, we adopt the value of 0.1, based on DeMore et al. (1997). This value was also used by Bian and Zender (2003) and Zhang and Carmichael (1999) in their modeling studies of the heterogeneous chemistry on mineral dust.

Measured mass accommodation coefficients of H₂O₂ on sulfuric acid and water surfaces, within a range from 8×10⁻⁴ to 0.18, are reported by DeMore et al. (1997). In the modeling studies of Dentener et al. (1996), Bian and Zender (2003) and Zhang and Carmichael (1999), γ=1.0×10⁻⁴ was used for mineral dust surfaces. However, de Reus et al. (2005), employing the assumption that H₂O₂ is formed when HO₂ is taken up in the Saharan dust aerosol, concluded that the heterogeneous removal of HO₂ and H₂O₂, with accommodation coefficients of 0.2 and 2×10⁻³, respectively, had to be included in order to obtain agreement between calculated and observed values. In this study, we use the values from de Reus et al. (2005).

Acetic acid, formaldehyde and methanol

The heterogeneous uptake of VOC (volatile organic compound) has rarely been included in modeling studies. In this study, in order to explore the potential sensitivity to these reactions, we use uptake coefficients for acetic acid (CH₃COOH), formaldehyde (HCHO), and methanol (CH₃OH) of 10⁻³, 10⁻⁵ and 10⁻⁵, respectively, based on the
laboratory measurements performed by Carlos-Cuellar et al. (2003).

SO₂

Recently, the heterogeneous reactivity of SO₂ has been studied on metal oxides (Goodman et al., 2001; Usher et al., 2002), China Loess dust (Usher et al., 2002) and Saharan mineral dust (Ullerstam et al., 2002, 2003; Adams et al., 2005). The reported γ values range from roughly $5 \times 10^{-7}$ to $2.6 \times 10^{-4}$. Pozzoli et al. (2008) used a value of $1 \times 10^{-4}$ in their modeling study. The value of $3 \times 10^{-5}$ recommended by IUPAC for Chinese dust has been used in this study.

Appendix B

Formula derivation for Eq. (9)

Based on Eq. (8):

$$C_i = \frac{K_t \cdot C_i' + B_e + B_{cp}}{K_t + K_{cl} + K_d}, \quad (B1)$$

the heterogeneous influence on the tracer daily average mixing ratio is represented as (for any species $i$, leaving out the subscript here for readability):

$$\Delta C = C_{(DUST,H)} - C_{(NO\_DUST)} = \frac{K_t \cdot C_i' + B_e + B_{cp(NO\_DUST)}}{K_t + K_{cl(NO\_DUST)} + K_d} \cdot \left(\frac{K_t + K_{cl(NO\_DUST)} + K_d}{K_t + K_{cl(DUST,H)} + K_d}\right)$$

$$+ \frac{(B_{cp(DUST,H)} - B_{cp(NO\_DUST)})}{(K_t + K_{cl(NO\_DUST)} + K_d)} \cdot \left(\frac{(K_t + K_{cl(NO\_DUST)} + K_d)}{(K_t + K_{cl(DUST,H)} + K_d)}\right), \quad (B2)$$
where \( \Delta C \) is the difference in the tracer daily average mixing ratio between the NO DUST and DUST H simulations (DUST H – O DUST). Recognizing that

\[
\frac{(K_t \cdot C' + B_e + B_{cp(NO_DUST)})}{(K_t + K_{cl(NO_DUST)} + K_d)} = C_{(NO_DUST)},
\]

and defining \( K_{cl(NO_DUST)} - K_{cl(DUST_H)} = -\Delta K_{cl} \) and \( B_{cp(DUST_H)} - B_{cp(NO_DUST)} = \Delta B_{cp} \), we can simplify the formula to:

\[
\Delta C = \frac{\Delta B_{cp} - \Delta K_{cl} \cdot C_{(NO_DUST)}}{(K_t + K_{cl(DUST_H)} + K_d)}.
\]

**Appendix C**

The absolute differences in the tracer mixing ratios calculated with the “Upper Limit” and “Lower Limit” coefficients (\( C_{DUST_H(\gamma_{Upper})} - C_{DUST_H(\gamma_{Lower})} \)). Columns are different heterogeneous removal reactions (HR) and rows are absolute differences in ppbv (AD(nmol/mol)). For more details, please note Table C1.

**Appendix D**

The uncertainties computed by normalizing the absolute differences by the tracer mixing ratios calculated with the “Best Guess” coefficients. Columns are different heterogeneous removal reactions (HR) and rows are uncertainties in percent (Un(%)). For more details, please note Table D1.

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References


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Impact of dust on tropospheric photochemistry over polluted regions

S. Zhu et al.


Table 1. Heterogeneous removal reactions and reactive uptake coefficients.

<table>
<thead>
<tr>
<th>No.</th>
<th>Heterogeneous reactions</th>
<th>“Best guess”</th>
<th>Lower limit</th>
<th>Upper limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR1</td>
<td>O₃ → Dummy</td>
<td>2.7 × 10⁻⁵</td>
<td>1 × 10⁻⁶</td>
<td>1 × 10⁻⁴</td>
</tr>
<tr>
<td>HR2</td>
<td>HNO₃ → Dummy</td>
<td>0.17</td>
<td>1 × 10⁻⁵</td>
<td>0.2</td>
</tr>
<tr>
<td>HR3</td>
<td>NO₂ → Dummy</td>
<td>2.1 × 10⁻⁶</td>
<td>4 × 10⁻¹⁰</td>
<td>2 × 10⁻⁴</td>
</tr>
<tr>
<td>HR4</td>
<td>NO₃ → Dummy</td>
<td>0.1</td>
<td>0.01</td>
<td>0.23</td>
</tr>
<tr>
<td>HR5</td>
<td>N₂O₅ → Dummy</td>
<td>0.03</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>HR6</td>
<td>OH → Dummy</td>
<td>0.1</td>
<td>0.004</td>
<td>1</td>
</tr>
<tr>
<td>HR7</td>
<td>HO₂ → H₂O₂</td>
<td>0.2</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>HR8</td>
<td>H₂O₂ → Dummy</td>
<td>2 × 10⁻³</td>
<td>8 × 10⁻⁴</td>
<td>0.18</td>
</tr>
<tr>
<td>HR9</td>
<td>SO₂ → Dummy</td>
<td>3 × 10⁻⁵</td>
<td>5 × 10⁻⁷</td>
<td>2.6 × 10⁻⁴</td>
</tr>
<tr>
<td>HR10</td>
<td>CH₃COOH → Dummy</td>
<td>1 × 10⁻³</td>
<td>2.4 × 10⁻⁴</td>
<td>2 × 10⁻³</td>
</tr>
<tr>
<td>HR11</td>
<td>CH₃OH → Dummy</td>
<td>1 × 10⁻⁵</td>
<td>4 × 10⁻⁶</td>
<td>1.9 × 10⁻⁴</td>
</tr>
<tr>
<td>HR12</td>
<td>HCHO → Dummy</td>
<td>1 × 10⁻⁵</td>
<td>2.6 × 10⁻⁷</td>
<td>1.1 × 10⁻⁴</td>
</tr>
</tbody>
</table>
Table 2. The initial ($C_i$) and upwind ($C'_i$) mixing ratios, deposition velocities ($\nu_d$), emission rates ($B_e$) and deposition coefficients ($K_d$) of key gases.

<table>
<thead>
<tr>
<th>Gases</th>
<th>$C_i$ (ppbv)</th>
<th>$C'_i$ (ppbv)</th>
<th>$\nu_d$ (cm s$^{-1}$)</th>
<th>$B_e$ (ppbv s$^{-1}$)</th>
<th>$K_d$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>55.5</td>
<td>59.2</td>
<td>0.18</td>
<td>0</td>
<td>2.38×10$^{-6}$</td>
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<tr>
<td>NO$_2$</td>
<td>8.6</td>
<td>5.7</td>
<td>0.13</td>
<td>4.3×10$^{-4}$</td>
<td>1.72×10$^{-6}$</td>
</tr>
<tr>
<td>NO</td>
<td>1.3</td>
<td>0.9</td>
<td>6.3×10$^{-3}$</td>
<td>3.8×10$^{-3}$</td>
<td>8.33×10$^{-8}$</td>
</tr>
<tr>
<td>CO</td>
<td>245.4</td>
<td>222.1</td>
<td>0</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>19.8</td>
<td>13.8</td>
<td>0.19</td>
<td>1.3×10$^{-3}$</td>
<td>2.51×10$^{-6}$</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>0.23</td>
<td>0.19</td>
<td>0.29</td>
<td>0</td>
<td>3.84×10$^{-6}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1789.6</td>
<td>1787.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCHO</td>
<td>0.91</td>
<td>0.83</td>
<td>0.07</td>
<td>7.3×10$^{-5}$</td>
<td>9.26×10$^{-7}$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>2.13</td>
<td>1.97</td>
<td>0.06</td>
<td>1.4×10$^{-4}$</td>
<td>7.94×10$^{-7}$</td>
</tr>
</tbody>
</table>
**Table 3.** The settings used for the sensitivity simulations. The equivalent mean transport speed is estimated based on the assumption of a characteristic spatial scale for a megacity of the order of 100 km.

<table>
<thead>
<tr>
<th></th>
<th>T16</th>
<th>T08</th>
<th>T04</th>
<th>T02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing time length $\lambda$ (h)</td>
<td>16</td>
<td>8</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Exchange rate coefficient $f$ (s$^{-1}$)</td>
<td>$1.7 \times 10^{-5}$</td>
<td>$3.5 \times 10^{-5}$</td>
<td>$7 \times 10^{-5}$</td>
<td>$14 \times 10^{-5}$</td>
</tr>
<tr>
<td>Mean transport speed $\nu$ (m s$^{-1}$)</td>
<td>1.7</td>
<td>3.5</td>
<td>7</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 4. Gas phase reaction index.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>O₃ + hν → O₂ + O(³P)</td>
</tr>
<tr>
<td>R2</td>
<td>O(³P) + O₂ → O₃</td>
</tr>
<tr>
<td>R3</td>
<td>O₃ + NO → NO₂ + O₂</td>
</tr>
<tr>
<td>R4</td>
<td>NO₂ + hν → NO + O(³P)</td>
</tr>
<tr>
<td>R5</td>
<td>NO + HO₂ → NO₂ + OH</td>
</tr>
<tr>
<td>R6</td>
<td>HONO + hν → NO + OH</td>
</tr>
<tr>
<td>R7</td>
<td>H₂O + O(¹D) → 2OH</td>
</tr>
<tr>
<td>R8</td>
<td>NO + OH → HONO</td>
</tr>
<tr>
<td>R9</td>
<td>NO₂ + OH → HNO₃</td>
</tr>
<tr>
<td>R10</td>
<td>CO + OH → H + CO₂</td>
</tr>
<tr>
<td>R11</td>
<td>SO₂ + OH + O₂ + H₂O → H₂SO₄ + HO₂</td>
</tr>
<tr>
<td>R12</td>
<td>NO₂ + O₃ → NO₃ + O₂</td>
</tr>
</tbody>
</table>
Table 5. The differences calculated as DUST_H+J–DUST_H of the daily average mixing ratios $C$ and the gross chemical production rates $B_{cp}$ and the gross chemical loss frequencies $K_{cl}$ of $O_x$, $NO_x$ and $OH$ due to the decrease of photolysis rate coefficients for the T04 case. The relative differences calculated as $(DUST_H+J–DUST_H)/DUST_H$ are shown in parentheses. For $OH$, the units of $C$ and $B_{cp}$ are molecules/cm$^3$ and molecules/cm$^3$/s, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$C$ nmol/mol</th>
<th>$B_{cp}$ nmol/mol/s</th>
<th>$K_{cl}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_x$</td>
<td>$-1.72$ ($-18.6%$)</td>
<td>$-0.034$ ($-39.2%$)</td>
<td>$-2.3\times10^{-3}$ ($-30.3%$)</td>
</tr>
<tr>
<td>$NO_x$</td>
<td>$-0.33$ ($-0.6%$)</td>
<td>$-2.94\times10^{-5}$ ($-12.3%$)</td>
<td>$-1.36\times10^{-7}$ ($-1.17%$)</td>
</tr>
<tr>
<td>$OH$</td>
<td>$-7.13\times10^4$ ($-53.9%$)</td>
<td>$-1.63\times10^6$ ($-52.5%$)</td>
<td>$0.71$ ($3.0%$)</td>
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</table>
Table 6. Values of the uncertainties corresponding to Fig. 11. Columns are different heterogeneous removal reactions (HR) and rows are uncertainties in the tracer mixing ratios in percent (Un(%)).

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<th>NO₃</th>
<th>N₂O₅</th>
<th>HNO₃</th>
<th>OH</th>
<th>HO₂</th>
<th>H₂O₂</th>
<th>HCHO</th>
<th>CH₃OH</th>
<th>CH₃COOH</th>
<th>SO₂</th>
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<tbody>
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Table C1. The absolute differences in the tracer mixing ratios calculated with the “Upper Limit” and “Lower Limit” coefficients ($C_{\text{DUST,H}}(\gamma_{\text{Upper}}) - C_{\text{DUST,H}}(\gamma_{\text{Lower}})$). Columns are different heterogeneous removal reactions (HR) and rows are absolute differences in ppbv (AD(nmol/mol)).

<table>
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<tr>
<th>AD (nmol/mol)</th>
<th>O$_3$</th>
<th>NO$_2$</th>
<th>NO$_3$</th>
<th>N$_2$O$_5$</th>
<th>HNO$_3$</th>
<th>OH</th>
<th>HO$_2$</th>
<th>H$_2$O$_2$</th>
<th>HCHO</th>
<th>CH$_3$OH</th>
<th>CH$_3$COOH</th>
<th>SO$_2$</th>
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</thead>
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</table>
Table D1. The uncertainties computed by normalizing the absolute differences by the tracer mixing ratios calculated with the “Best Guess” coefficients. Columns are different heterogeneous removal reactions (HR) and rows are uncertainties in percent (Un(%)).

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<th>NO₃</th>
<th>N₂O₅</th>
<th>HNO₃</th>
<th>OH</th>
<th>HO₂</th>
<th>H₂O₂</th>
<th>HCHO</th>
<th>CH₃OH</th>
<th>CH₂COOH</th>
<th>SO₂</th>
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<tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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Fig. 1. The distribution map of Chinese Loess Plateau and surrounding potential desert source areas. (http://geology.geoscienceworld.org/content/vol37/issue3/images/large/i0091-7613-37-3-279-f01.jpeg).
Fig. 2. Size distribution of dust surface area concentration in upwind air mass and in the box.
Fig. 3. Wind rose depicting the monthly average, minimum and maximum wind speed and direction during April 2006 at a station in the Beijing urban area (39.48° N, 116.28° E).
Fig. 4. Time series of (a) O₃, (b) NO and (c) NO₂ mixing ratios and (d) OH concentration for 24 h of the fifth simulation day. Different exchange rate coefficient cases are shown from left to right: “T16”, “T08”, “T04” and “T02”. Results of the NO_DUST simulations and the DUST_H simulations are shown in black and red, respectively.
Fig. 5. The daily average mixing ratios of (a) $O_x$, (b) NO and NO$_2$, (c) NO$_x$ and concentration of (d) OH for the NO_DUST simulations, and their gross chemical production rates $B_{cp}$ and gross chemical loss frequency $K_{cl}$. The chemical loss frequencies for $O_x$ and NO$_x$ are multiplied by 10 and 100, respectively, for readability. For each term, the bar sequence from left to right is: “T16”, “T08”, “T04” and “T02”.

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Fig. 6. The daily average chemical production rates (labels in black) and chemical loss frequencies (labels in red) of OH for the NO_DUST simulation. “Miscellaneous” represents the sum of all the other source or loss terms. The bar sequence is same as Fig. 5. The reactions are listed in Table 4.
Fig. 7. The daily average mixing ratios of (a) Ox, (b) NO and NO₂, (c) NOₓ and concentration of (d) OH for the DUST_H simulations, and their gross chemical production rates $B_{cp}$ and gross chemical loss frequencies $K_{cl}$. The loss frequency of NOₓ is multiplied by 10 for readability. The bar sequence is same as Fig. 5.
Fig. 8. Differences of the daily average mixing ratios and the gross chemical production rates $B_{cp}$ and the gross chemical loss frequencies $K_{cl}$ of (a) $O_x$, (b) NO and NO$_2$, (c) NO$_x$, and (d) OH, between the DUST_H and NO_DUST simulations (DUST_H−NO_DUST). For OH, the differences of the chemical producing budgets and chemical loss frequencies are labeled in black and red, respectively. “Miscellaneous” represents the sum of all the other source or loss terms. The reactions are listed in Table 4. The bar sequence is same as Fig. 5.
Fig. 9. Relative differences of the daily average mixing ratios and the gross chemical production rates $B_{cp}$ and the gross chemical loss frequencies $K_{cl}$ of (a) O$_x$, (b) NO$_x$, and (c) OH due to the heterogeneous dust reactions. The bar sequence is same as Fig. 5.
Fig. 10. Differences of the daily average chemical producing budgets (black bars) and chemical loss frequencies (red bars) of OH, between the DUST_H+J and DUST_H simulations (DUST_H+J–DUST_H) in the T04 case. “Miscellaneous” (hollow bars) represents the sum of all the other source or loss terms. The reactions are listed in Table 4.
Fig. 11. Uncertainties of the tracer mixing ratios caused by each heterogeneous removal reaction. The colors red and black represent negative and positive values, respectively. Hollow circle represents the values scaled by 0.1. Corresponding values are shown in Table 6.