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Aerosol effects on ozone concentrations in Beijing: A model sensitivity study

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Abstract

Most previous O₃ simulations were based only on gaseous phase photochemistry. However, some aerosol-related processes, namely, heterogeneous reactions occurring on the aerosol surface and photolysis rate alternated by aerosol radiative influence, may affect O₃ photochemistry under high aerosol loads. A three-dimensional air quality model, Models-3/Community Multi-scale Air Quality-Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution, was employed to simulate the effects of the above-mentioned processes on O₃ formation under typical high O₃ episodes in Beijing during summer. Five heterogeneous reactions, i.e., NO₂, NO₃, N₂O₅, HO₂, and O₃, were individually investigated to elucidate their effects on O₃ formation. The results showed that the heterogeneous reactions significantly affected O₃ formation in the urban plume. NO₂ heterogeneous reaction increased O₃ to 90 ppb, while HO₂ heterogeneous reaction decreased O₃ to 33 ppb. In addition, O₃ heterogeneous loss decreased O₃ to 31 ppb. The effects of NO₂, NO₃, and N₂O₅ heterogeneous reactions showed opposite O₃ concentration changes between the urban and extra-urban areas because of the response of the reactions to the two types of O₃ formation regimes. When the aerosol radiative influence was included, the photolysis rate decreased and O₃ decreased significantly to 73 ppb O₃. The two aerosol-related processes should be considered in the study of O₃ formation because high aerosol concentration is a ubiquitous phenomenon that affects the urban- and regional air quality in China.

Key words: aerosol; heterogeneous reactions; ozone; radiative influence

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Introduction

China is one of the countries with the most severe air pollution. Even before unsolved problems related to coal-combustion has plagued the country, photochemical smog had already been prevalent in some highly developed regions. Smog is caused primarily by rapid economic development, especially the sharp increase in vehicle population in urban areas. Both high O₃ and fine particulate pollution have caused the most serious problems in urban and regional-scale air quality in China (Xie et al., 2000); the air quality in the country exhibits an “air pollution complex” case (Wehner et al., 2004; Tang et al., 2006; Shao et al., 2006).

High aerosol loading is common in urban China. As reported daily in 47 major cities, PM₁₀ is a constant chief pollutant for almost all the cities year-round (www.sepa.gov.cn/english/air-list.php3). Rapid urbanization has caused a tremendous volume of pollutants to be released into the atmosphere, and emissions are usually concentrated in urban areas, endowing the atmosphere with high oxidation capacity. When high aerosol concentration levels accompany high atmospheric oxidation capacity,

the interaction between O₃ photochemistry and aerosols is activated. Some aerosol-related processes, such as the heterogeneous reactions occurring on the aerosol surface, radiative influence caused by the aerosol optical properties, etc., may not be noticeable in the atmosphere because of low aerosol levels, as observed in Europe and North America; however, these processes may have significant effects on O₃ photochemistry in China. The heterogeneous reactions affect the atmospheric oxidation capacity and formation of aerosol components (Xu et al., 2006; Tang et al., 2003a), playing an important role in pollutant conversion. Aerosol radiative influence may alter photolysis rate coefficients, consequently affecting photochemistry and aerosol formation. The mechanism of aerosol influence on O₃ photochemistry may be characteristic of urban- or regional-scale air pollution photochemistry in China.

Some researchers have endeavored to identify the effect of certain heterogeneous reactions (Calvert et al., 1994; Denterner et al., 1996; Horowitz et al., 1998; Riemer et al., 2003; Tang et al., 2003a; Li and Han, 2010) and aerosol radiative influence (Dickerson et al., 1997; Jacobson, 1998; He and Carmichael, 1999; Tang et al., 2003b;) on O₃ formation or tropospheric chemistry at urban, regional, and global scales using chemical transportation

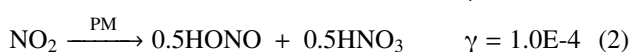
* Corresponding author.

model (CTM) simulation. Recently developed fully coupled chemistry-aerosol-meteorology models, such as the Weather Research and Forecasting model coupled with Chemistry (Fast et al., 2006) and Goddard Institute for Space Studies general circulation model (Liao et al., 2009), enable researchers to thoroughly detect the effects of aerosol on tropospheric chemistry. However, the mechanism of the heterogeneous reactions and some coefficients in related processes remain uncertain, rendering such types of simulations tentative. In addition, most studies do not investigate the effects of the above-mentioned aerosol-related processes on O₃ formation under the same simulation framework, and do not detect the separate effects of each heterogeneous reaction. Thus, exploring the potential effect of the aerosol-related processes on O₃ formation under high aerosol loads is highly feasible for China. CTM was used in the current study because meteorology feedback is unable to show and explain the effects in a clear pattern.

Beijing continues to experience nonattainment days even after stringent air pollution mitigation measures have been implemented. An intensive field campaign in the city in the summer of 2000 revealed that high O₃ (hourly concentration above 200 ppb) accompanied by high aerosol loading (hourly concentration above 300 µg/m³) occurred in the urban area and its downwind region (Wang, 2002; Xu et al., 2006), representing a good illustrative case for exploring the mechanism of aerosol influence on O₃ formation. A three-dimensional air quality model, Models-3/Community Multi-scale Air Quality-Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (Models-3/CMAQ-MADRID, Zhang et al., 2004) was employed to simulate the effect of the heterogeneous reactions and aerosol radiative influence on O₃ formation for the typical high O₃ events in Beijing during summer.

1 Description of the simulation

CMAQ-MADRID (Zhang et al., 2004) was employed for the simulation using CMAQ (Byun and Ching, 1999) as a host model. Modules of the transportation processes provided in the original CMAQ (e.g., advection and turbulent diffusion) were adopted, but with improvements on all the modules associated with aerosol processes. In the simulation, a two-section size representation (typically for fine and coarse particles) was selected to reduce computational time. Carbon Bond-IV (Gery et al., 1989) was selected as the gaseous chemical mechanism; the four heterogeneous reactions suggested by Jacob (2000), depicted as Reactions (1)–(4), were also included. Thermodynamic module ISORROPIA (Nenes et al., 1998) was used to treat gas-particle partitioning.



Three-level nesting was used for the simulation. The domain for the first level covered all of East Asia. The second-level domain covered a large part of North China, including Hebei, Beijing, and Tianjin, and parts of the Shanxi, Shandong, Liaoning, and Inner Mongolia areas. The third-level domain focused on the Beijing area (Fig. 1), including both the urban and suburban regions, with a horizontal resolution of 4 km. Fourteen layers were unequally spaced from the ground to an approximately 10 km altitude, with nine layers located under 1 km to resolve the boundary layer problem. The height of the lowest layer is about 20 m. The simulation period was 24 June to 3 July 2000.

The meteorology field was derived from the fifth-generation mesoscale model (Grell et al., 1994) simulation. To nudge the simulated meteorology variables so that they are as close to observed values, four-dimensional assimilation was performed using rawinsonde data and hourly meteorological observations from the ground stations in urban and suburban Beijing.

The 1° × 1° anthropogenic emission inventory (Streets et al., 2003) maintained by the Center for Global and Regional Environmental Research at the University of Iowa was used for the East Asia simulation (first-level domain). Biogenic volatile organic compound (VOC) emissions were obtained from the monthly Global Emissions Inventory Activity (GEIA) (Guenther et al., 1995). The Sparse Matrix Operator Kernel Emissions System (www.cmascenter.org/html/models.html) was used to convert the various types of emission data to files with the format required by CMAQ.

The emission inventory at the second- and third-level nesting domains (Beijing area) was constructed on the basis of the 2000 emission survey in North China (Wang, 2002; Wang and Li, 2003), while the emission inventory for the Beijing urban and suburban areas was prepared

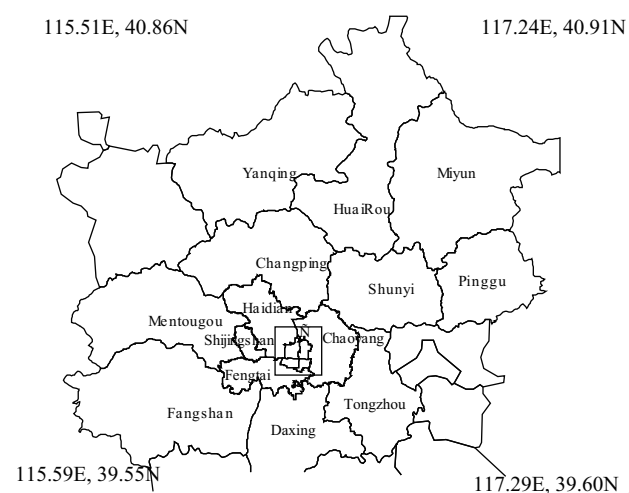


Fig. 1 Inner most mesh of the Beijing area simulation with an area of 144 km × 144 km; interior box delimits the urban area, +Olympic Center.

Table 1 Measured reaction probability (γ) of heterogeneous reactions

Heterogeneous reactions	NO ₂ ⁻	NO ₃	N ₂ O ₅	HO ₂	O ₃
γ	10 ⁻⁶ –10 ⁻³ ^a	2×10 ⁻⁴ –10 ⁻² ^b	0.01–1 ^c	0.1–1 ^d	10 ⁻⁵ –10 ⁻⁴ ^e

^a Based on reactions on both solid and aqueous solutions (Harrison and Collins, 1998; Demore et al., 1997; Jacob, 2000).

^b Uptake of NO₃ by aqueous aerosols is limited by its low Henry's Law constant; the range was based on the measurement by Rudich et al. (1996).

^c Measurement of reactions on aqueous solutions (Demore et al., 1997).

^d Measurement of reactions on aqueous solutions (Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996).

^e Based on the measurements of heterogeneous loss of O₃ on dust (Usher et al., 2002).

by the Beijing Environmental Science Institute. The basic data used for emission estimates included annual emission data from a variety of sources reported by the local Environment Protection Bureau, as well as statistical data on energy, environmental protection, social and economic factors, etc, derived from published yearbooks. The species included NO_x, VOCs, CO, SO₂, PM₁₀ and NH₃. The VOC inventory was compiled by sector, including mobile sources, transportation and marketing of petroleum products, solvent utilization, industrial processes, and stationary source combustion. For the two nested domains, the GEIA biogenic VOC emission inventory was used to determine emissions from vegetation.

2 Selection of heterogeneous reactions and reaction probability

In the urban atmosphere, heterogeneous reactions affect O₃ formation via the disturbance of the radical and NO_x cycle, or by direct O₃ removal from aerosol. The effects of the reactions are guaranteed by rapid competition with gaseous reactions; for persistent occurrence, the reactions should also refrain from poisoning the aerosol surface. Jacob (2000) provided a thorough discussion of heterogeneous reactions possibly taking place on aerosols or clouds, and recommended four reactions for inclusion in O₃ simulations. Given that only clear-sky cases were chosen for the simulation period in the current work, the study of the previously mentioned four reactions should be an appropriate choice. In addition, we can avoid processing the heterogeneous loss of some species in clouds; these species remain highly uncertain, and including the detailed aqueous-phase cloud chemistry results in highly time consuming computations.

For the parameterization of the heterogeneous reaction process in CMAQ-MADRID, the first-order rate constant is introduced following the method suggested by Jacob (2000). This rate constant is calculated using the radius and surface area of the particles, gas-phase molecular diffusion coefficient, mean molecular speed, and reaction probability. The parameterization considers the uptake by gas-phase diffusion to the aerosol surface, and uptake by free molecular collisions of gas molecules with the surface. In the uptake of gaseous species by non-cloud aerosols, the heterogeneous reaction process tends to be limited by free molecular collision (Jacob, 2000). In the parameterization, reaction probability γ represents the process of a molecule attaching the aerosol surface and undergoing reaction.

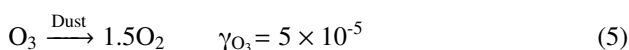
In laboratory experiments, each heterogeneous reaction

has large uncertainties in terms of measured γ value. Table 1 lists γ measured in laboratory experiments for all concerned heterogeneous reactions. The reaction probabilities are much lower on solid surfaces than on aqueous solutions. For reactions taking place on aqueous solutions, the measured γ can have values that vary by orders of magnitude for the same reaction. In the simulation of Beijing, the reaction probability of the four heterogeneous reactions used in the experiments were taken from the values proposed by Jacob (2000). All these values are the base values prescribed in CMAQ-MADRID, and are also in the range of reaction probability on aqueous solutions measured in the laboratory (Reactions (1)–(4)). The heterogeneous process parameter on aqueous solutions appropriately represents the process on moist aerosol because the relative humidity in summer is high in Beijing.

Whether O₃ uptake by aerosol is possible and the type of aerosol component or particle structure favorable to this process remain debated (Jacob, 2000). In summertime observations at the Beijing urban area (Bergin et al., 2001), organic compounds accounted for ca. 30% of PM_{2.5} mass; elementary carbon contributed 2.6%. Meanwhile, mineral aerosol contributed ca. 16% to PM_{2.5} mass, and dominated the total aerosol mass (about 44%). Current knowledge indicates that the low solubility of O₃ in water may preclude significant uptake by moist aerosols under no-cloud conditions. In urban conditions, the rapid reaction of O₃ on soot may poison the soot surface without significantly affecting O₃ (Jacob, 2000); unsaturated organic compounds have a high reactivity toward O₃, but this finding requires further exploration (Jacob, 2000). The heterogeneous loss of O₃ on dust has been verified in some experiments (Usher et al., 2002), and the uptake coefficient measured is in the range 10⁻⁵–10⁻⁴. Tang (2003a) and Denterner (1996) took $\gamma_{O_3} = 5 \times 10^{-5}$ in Sulfur Transportation Eulerian Model version 2001 (STEM-2K1) and a global model to simulate the extent to which O₃ dust removal process affects O₃ concentration. Many aspects related to O₃ uptake by urban aerosols remain uncertain; conducting sensitivity studies to detect the extent of the influence of direct O₃ loss on O₃ in Beijing is a meaningful endeavor. Such investigations can be implemented by assuming the heterogeneous reaction as a dust removal process. In observations, mineral dust accounts for an important proportion of the aerosol component in Beijing even in summer, partly supporting the above-mentioned assumption.

Here, we took the same heterogeneous reaction and uptake coefficient of O₃ dust removal as in Tang (2003a) and Denterner's (1996) simulations to conduct sensitivity

experiments, as shown in Eq. (5).



In the next section, we discuss the sensitivity experiments conducted to separately test the effect of each of the five heterogeneous reactions on O_3 formation.

3 Effects of heterogeneous reactions

From 26 to 27 June 2000, the diurnal variations of near surface wind in the region showed a typical flow mode during summer in Beijing. Calm or light wind controlled the region in the morning hours, and a south wind with strong transportation effect prevailed in the afternoons. High O_3 concentration occurred in both the urban region and its downwind area, representing typical summertime high O_3 episodes in Beijing (Xu et al., 2008; Xu, 2006). Meanwhile, simulated hourly PM_{10} mass concentration and aerosol surface area concentration could represent the actual situation in the city (Xu et al., 2006). Thus, the effect of the heterogeneous reactions and aerosol radiative influence on O_3 formation were explored intensively during the two day period.

3.1 NO_2 , N_2O_5 , and NO_3 heterogeneous reactions

Figure 2a–d shows similar distribution patterns of O_3 changes caused by NO_2 , N_2O_5 , and NO_3 heterogeneous reactions. The reactions imposed contrasting effects on the urban and extra-urban areas. In the urban area, three heterogeneous reactions resulted in O_3 increase, whereas O_3 decrease was observed in the extra-urban area. Comparing the O_3 changes among the three heterogeneous reactions, NO_2 heterogeneous reaction had the most severe effects on O_3 .

NO_2 heterogeneous reaction caused the most significant O_3 changes in the urban area and its propagating plume. On 26 June, the NO_2 heterogeneous reaction increased O_3 to 37 ppb, occurring at the northern part of the urban area, near the Olympic Center. On 27 June, O_3 increased up to 90 ppb, occurring at the urban downwind area, as far away as Qinghe. The discrepancy in meteorological conditions between the two days caused the differences in value and distribution of the O_3 changes over Beijing. At the extra-urban area, Miyun, the O_3 changes caused by NO_2 heterogeneous reaction was weak compared with that in the urban plume, which exhibited about –10 ppb as the maximum effect.

Given that the two products of NO_2 heterogeneous reaction are HONO and HNO_3 , and HONO produces OH radicals via photolysis, the effect of NO_2 heterogeneous reaction eliminates NO_x from the NO_x cycle and adds more new radicals to the radical cycle. Both the above-mentioned processes can lead to O_3 increase in a VOC-limited regime (or radical-limited regime). Further analysis of how NO_2 heterogeneous reaction increases O_3 formation in the urban area (VOC-limited regime) has been discussed in another paper (Xu et al., 2006). Table 2 shows that both NO_x and VOC emissions were high at the urban area, but the ratio of VOC/ NO_x emission was much lower

Table 2 NO_x and VOC emission rates, and ratio of VOC/ NO_x in cells representing the Beijing urban, downwind, and extra-urban areas

	NO_x emission rate (mol/sec)	VOC emission rate (mol C/sec)	VOC/ NO_x
Urban area	2	30	15
Urban downwind area	0.076	1.811	23.8
Extra-urban area	0.01	0.829	82.9

than that in the extra-urban area, indicating that the regime of O_3 formation in the two typical regions may be different. Because both NO_x and aerosol had high concentration levels in the urban plume, NO_2 heterogeneous reaction can precede at a high efficiency. Thus, the effects were most severe in the urban plume. In the extra-urban area, where NO_x emission was low, the regime of O_3 formation may transit to an NO_x -limited case. Adding NO_2 heterogeneous reaction at the low emission area directly eliminates NO_x from the photochemical system; the O_3 decrease in the extra-urban area verifies the assumption that the regime of O_3 formation is an NO_x -limited case. Sensitivity experiments, in which NO_2 heterogeneous reaction is considered, are a better approach to examining the regime of O_3 formation than the brute force method, in which NO_x or VOC emissions are included or excluded for some areas.

In a Los Angeles 3-D simulation (urban VOC-limited case), in which the Urban Airshed Model was used (UAM; Calvert et al., 1994), O_3 increased up to about 10 ppb at 1100–1200 local standard time (LST) after the addition of a new HONO formation mechanism, i.e., the $\text{NO}_2 + \text{H}_2\text{O}$ reaction, specified in terms of gaseous species only. This O_3 increase was lower than that observed in the simulation of the present study. The discrepancy may have been caused by the differences in the parameterizations of NO_2 to HONO conversion and in the emission characteristics of the two areas. STEM-2K1 (Tang et al., 2003a) included a NO_2 heterogeneous loss process on dust, but the reaction is irreversible with no NO_x recycling, i.e., it did not produce gas-phase HONO. In areas characterized by excess NO_x , O_3 increased indirectly, but the amount was small and partly compensated for the O_3 loss from the O_3 dust removal process in the STEM-2K1 simulation.

Given that the product of N_2O_5 and NO_3 heterogeneous reactions is solely HNO_3 , both reactions correspond to the direct NO_x removal process. Both reactions increased O_3 because NO_x was in excess in the urban area (VOC-limited regime of O_3 formation). By contrast, for the NO_x -limited case in the extra-urban area, the reactions resulted in O_3 decrease. However, N_2O_5 heterogeneous reaction caused a weak O_3 increase by only 1–2 ppb in the urban area, much lower than that caused by NO_2 heterogeneous reaction. In the extra-urban area (Miyun and Huairou), the effects were stronger, decreasing O_3 to 6 ppb, despite the opposite effects. In a 3-D model simulation in summer over the southwestern part of Germany (Riemer et al., 2003), the N_2O_5 heterogeneous reaction decreased O_3 concentration to 5 ppb over the NO_x -limited region, which is the same level as that of the result for the extra-urban area in the current study. The effects of NO_3 heterogeneous reaction

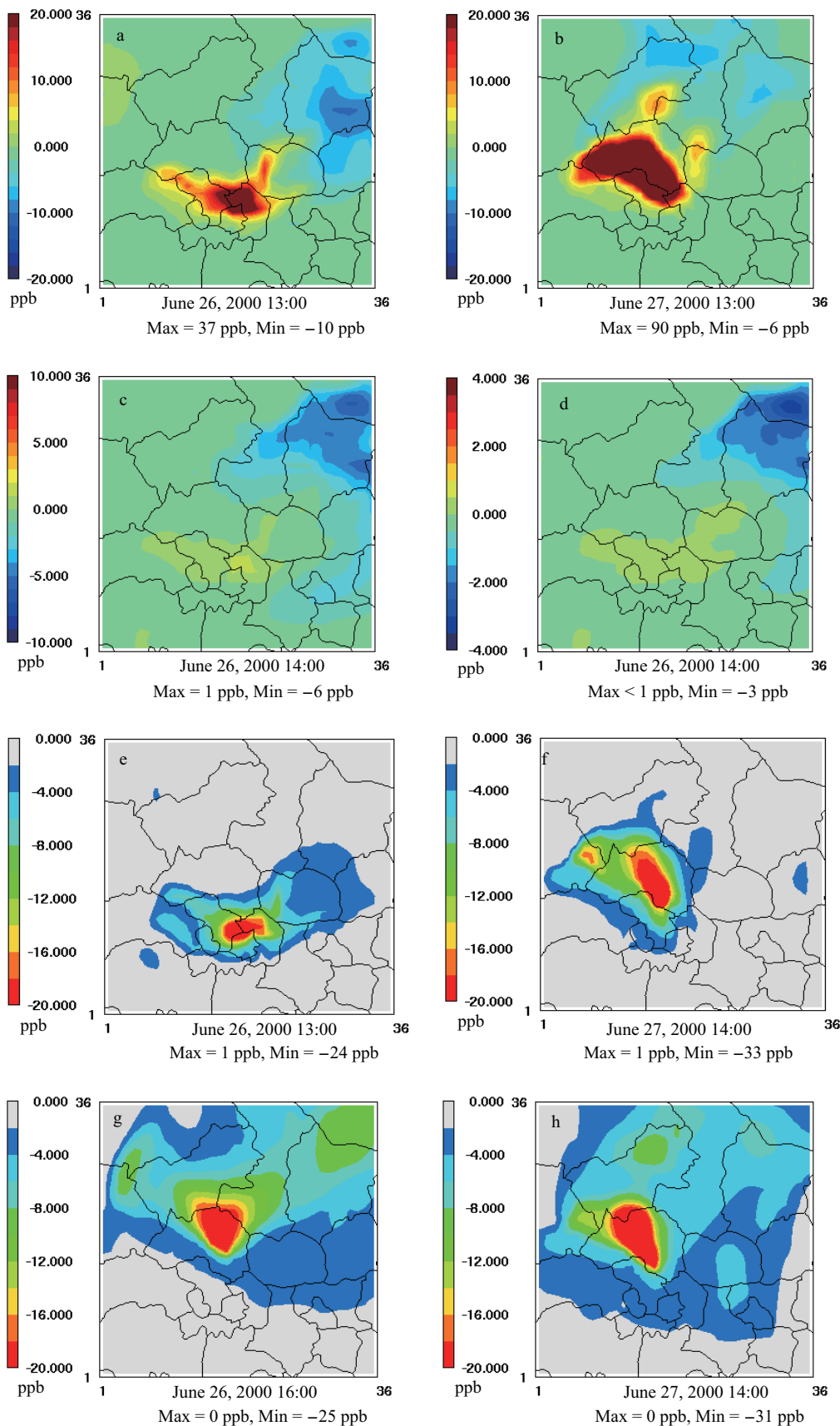


Fig. 2 O₃ concentration changes caused by NO₂ (a) and (b), N₂O₅ (c), NO₃ (d), HO₂ heterogeneous reactions (e) and (f), and O₃ heterogeneous loss (g) and (h) in the Beijing area simulation on 26 and 27 June 2000.

were weaker than those of N₂O₅ heterogeneous reaction. In the urban area, NO₃ heterogeneous reaction resulted in only minimal O₃ increase, less than 1 ppb. In the extra-

urban area, O₃ decreased to 3 ppb.

Figure 3a and b shows the hourly mean reaction rate of NO₂, N₂O₅, and NO₃ heterogeneous reactions from 26 to

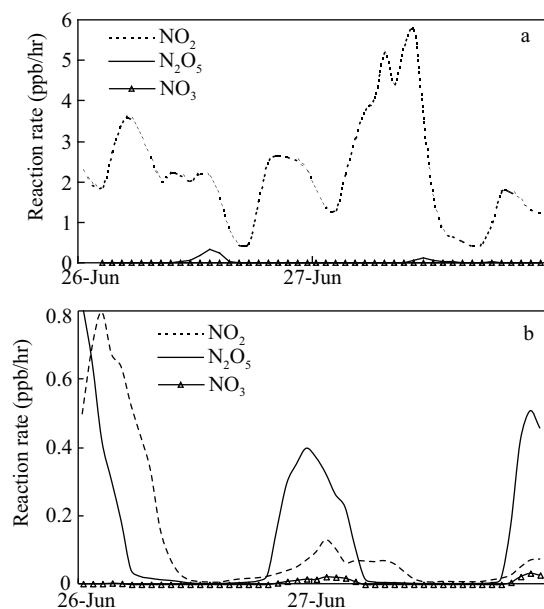


Fig. 3 Hourly mean reaction rates of NO_2 , N_2O_5 , and NO_3 heterogeneous reactions from 26 to 27 June 2000 in the urban (a) and extra-urban areas (b).

27 June 2000 in the urban and extra-urban areas, calculated by Integrated Reaction Rate analysis (IRR) provided in CMAQ. In the urban area, NO_2 heterogeneous reaction had a much higher reaction rate than did N_2O_5 and NO_3 heterogeneous reactions, and remained at a high level both at night and during the day. NO_3 production (via $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$) was also low, because the simulated O_3 concentration was low at night; N_2O_5 production (via $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$) was also low at night. During the daytime, some NO_3 was produced, but the majority was lost in rapid reactions with NO , HC , and NO_2 (the product is N_2O_5). The rapid photolysis of NO_3 also contributed to the loss. Thus NO_3 could not accumulate. In this case, NO_3 heterogeneous reaction remained only at a low level in the full-day simulation. Meanwhile, N_2O_5 heterogeneous reaction reached only a relatively high level during the period of O_3 peak formation, but remained at a low level during the other hours. Therefore, both N_2O_5 and NO_3 heterogeneous reactions imposed minimal effects on O_3 formation in the urban area.

In the extra-urban area, both the value and diurnal variations of the reaction rates for three heterogeneous reactions differed from those in the urban area. The reaction rate of NO_2 heterogeneous reaction was much lower in the extra-urban area than in the urban area; this result was determined by the low NO_x concentration level. The high value was observed only at night and during the morning hours. Thus, the resultant O_3 change was much lower in the extra-urban region than in the urban area. During the daytime, NO_3 could not accumulate in the extra-urban area because of its fast photolytic reaction. O_3 could remain at a certain concentration level at night because of the low titration effect given that the NO_x emission was low. Therefore, NO_3 could be produced and accumulated, and N_2O_5 could also be produced at night. Then, both N_2O_5 and NO_3 heterogeneous reactions could take place at a high

level only during the night and early morning hours. The comparison of the reaction rates of the three heterogeneous reactions showed that NO_2 and N_2O_5 reaction rates were at the same level at night and early morning hours. In addition, the reaction rates of all three reactions were at the same level during the daytime, although the values were all low. The three heterogeneous reactions could proceed at a comparable rate because NO_x concentration was low in the extra-urban area. Thus, their effects on O_3 formation were at the same level. In the urban area, NO_x concentration was high. N_2O_5 heterogeneous reaction imposed only a small perturbation on the NO_x cycle, resulting in weak O_3 increase. Given the low NO_x concentration in the extra-urban area, N_2O_5 heterogeneous reaction could have a relatively heavy effect on the NO_x cycle, leading to a relatively high O_3 decrease.

3.2 HO_2 heterogeneous reaction

Figure 2e and f shows that HO_2 heterogeneous reaction also had significant effect on O_3 concentration in Beijing. O_3 decrease resulted in the domain, and the effect was most prominent in the urban plume. Given that HO_2 heterogeneous reaction eliminates radicals from the photochemical system, additional radical removal would accelerate radical termination, and then lower the atmospheric activity in a radical-limited regime, thereby decreasing O_3 formation in the urban area and its propagating plume. HO_2 heterogeneous reaction exhibited the highest efficiency because radical concentration reached the highest level during the O_3 peak period. On 26 June, the HO_2 heterogeneous reaction decreased O_3 concentration to 24 ppb, and the maximum effect was observed near the Olympic Center at the O_3 peak hour. On 27 June, O_3 decreased to 33 ppb, occurring at the urban downwind area, Changping County.

Compared with global- (Dentener et al., 1996) and regional-scale (Horowitz & Collins, 1998) simulations, that conducted in the present study showed considerably stronger effects on O_3 concentration. In the global simulation, γ_{HO_2} on dust was assumed equally fast as that on moist aerosols. The study is focused on the effects of dust on troposphere photochemistry; thus, the strong effects were observed near the dust region. However, the low emission led to weak photochemistry, so that HO_2 heterogeneous reaction did not impose heavy effects on O_3 formation. In the North American summertime simulation, adding HO_2 heterogeneous reaction led to a 1–3 ppb decrease in mean O_3 over the Eastern United States, even when $\gamma_{\text{HO}_2} = 1$ in the test run. This value is the upper limit in the range of γ_{HO_2} . The above work by Horowitz aimed at a seasonal average by regional-scale simulation with coarse resolution (4° latitude \times 5° longitude), whereas the simulation in the current work focused on the extremely high O_3 events in summer with high horizontal resolution. These differences may have caused the discrepancy in results.

3.3 O_3 heterogeneous reaction

As a sensitivity experiment on an urban air pollution case, the simulation showed that the presumed O_3 heterogeneous

loss on aerosol remarkably decreased O_3 concentration in Beijing (Figs. 2g, h). The effect was most prominent in the urban plume. On 26 June, the O_3 heterogeneous loss process decreased O_3 to 25 ppb, occurring at the urban downwind area, and the maximum effect was observed at the local O_3 peak hour. On 27 June, the O_3 removal process decreased O_3 to 31 ppb. The concentration of O_3 precursors was high in the urban plume; thus, O_3 concentration constantly increased via photochemistry with plume propagation. Consequently, both high O_3 and aerosol concentration occurred in the urban plume, and the O_3 heterogeneous loss proceeded at high efficiency.

The results for the Beijing area are generally in agreement with those of previous works, although the previous simulations were carried out mostly on a global or regional scale. In a global simulation for the dust season (Dentener et al., 1996), the included heterogeneous reactions decreased mean O_3 concentration to 10%, but most of the effects resulted from the O_3 heterogeneous loss on dust. In a box model simulation conducted by Zhang and Carmichael (1999), O_3 heterogeneous loss on dust contributed to 74%–87% of the O_3 decrease, which was the major contributor compared with the other heterogeneous reactions and aerosol radiative influence. In the East Asia simulation by STEM-2K1 (Tang et al., 2003), the O_3 heterogeneous loss on dust decreased O_3 to about 20 ppb, which is the same level as our results. As discussed in Section 3, high uncertainties are associated with O_3 heterogeneous reaction on aerosol, especially on urban aerosol, in which the composition and structure may have large discrepancies among cities in different regions. The urban case experiment in this study can only be viewed as a tentative result.

3.4 Aerosol radiative influence

In most O_3 simulations thus far, aerosol radiative influence was not included in the calculation of photolysis rates. The simulations considered only clear-sky conditions, which may be applicable in the low-aerosol conditions observed in Europe or North America. In CMAQ, the photolysis processor (JPROC) produces clear-sky photolysis rates, and then a correction is made only for the cloud cover effect. For the two typical high O_3 events in Beijing, no observable cloud process occurred at the area. Thus, the simulation results of the present study represent only the results for clear-sky conditions. However, the observed aerosol exhibited high light extinction properties in the Beijing urban area in summer (Bergin et al., 2001), roughly greater by a factor of four than the measurement in Atlanta, USA. Such strong aerosol extinction properties may affect the rates of photolytic reactions. The clear-sky presumption used in previous O_3 simulations may not be valid for the Beijing simulation.

To validate aerosol radiative influence on photolytic reactions, the Tropospheric Ultraviolet-Visible (TUV) model (Madronich, 1987) was used to calculate the photolysis rates when the aerosol optical properties were considered. This approach was adopted because no photolysis rate observation was available during the study period. In our

TUV calculation, 0.8 was taken as the value of 550 nm aerosol optical depth (AOD), which was referenced from the retrieved monthly mean AOD in the Beijing urban area in summer (Li et al., 2003). Single scattering albedo ω was measured at 0.81 in summer 1999 (Bergin et al., 2001), and at 0.8 in June and July 2003 (Mao and Li, 2005) in the Beijing urban area. Hence, ω was set to 0.8 in the calculation.

Figure 4 shows the comparison of the photolysis rates for the clear-sky condition and the case that considers aerosol extinction properties. When the aerosol extinction properties were included, all the photolysis rates decreased sharply. The rates reached the maximum at noontime because solar radiation was the strongest at this period; thus, aerosol radiative influence caused the highest decrease in photolysis rates at noon. At ground level, NO_2 photolysis rate decreased by 27% at noontime, while O_3 photolysis rate decreased by 33%. At a height of 1000 m, the effects on the photolysis rates were lower than those at ground level. NO_2 photolysis rate decreased by 17% at noontime, whereas O_3 photolysis rate decreased by 23%. Aldehyde photolysis rate exhibited a decrease ratio similar to that of NO_2 when aerosol radiative influence was included. In the STEM-2K1 simulation of East Asia coupled with TUV calculation (Tang et al., 2003), UV-absorbing aerosol decreased the rate of NO_2 photolysis by 35% below 1 km on average. For the Los Angeles basin simulation (Jacobson, 1998), UV-absorbing aerosol caused the photolysis rates to decrease by 10% to 25% at noontime at the near-surface layer. The aerosol optical properties presented strong UV-absorbing characteristics in the Beijing urban area, and they decreased the photolysis rates at a level comparable with those of previous works.

The decreased photolysis rate in the CMAQ-MADRID simulation was used to check the extent of aerosol radiative influence on O_3 concentration changes. In the simulation, only the photolysis rate decreasing below 1 km was considered. The assumption should be reasonable given that the high aerosol loading may occur only in the boundary layer in the summertime case (no dust event) over Beijing. In theory, the decrease in photolysis rate will lower O_3 formation in two steps. First, the decreased photolysis of aldehyde, O_3 , etc. will create fewer new radicals, lowering the atmospheric activity and reducing the occurrence of $NO \rightarrow NO_2$ conversion. These could be further illustrated in a radical cycle comparison (Bowman and Seinfeld, 1994; Xu et al., 2006, 2008) of sensitivity runs in the urban area (Fig. 5). The aerosol radiative influence reduced new radical creation by 32%, which decreased the conversion among radicals by more than 30%, with a 31% decrease in $NO \rightarrow NO_2$ conversion. Second, the decreased NO_2 photolysis will produce less O_3 . Figure 6 shows that the aerosol radiative influence decreased O_3 in the domain. The effects were most significant in the urban plume. The O_3 precursors, such as NO_2 and aldehyde, had higher concentrations in the urban plume than in other area, where the decreased photolysis rate had the most severe effects. On 26 June, the maximum O_3 decrease reached 55 ppb, which occurred at the urban downwind area. On 27

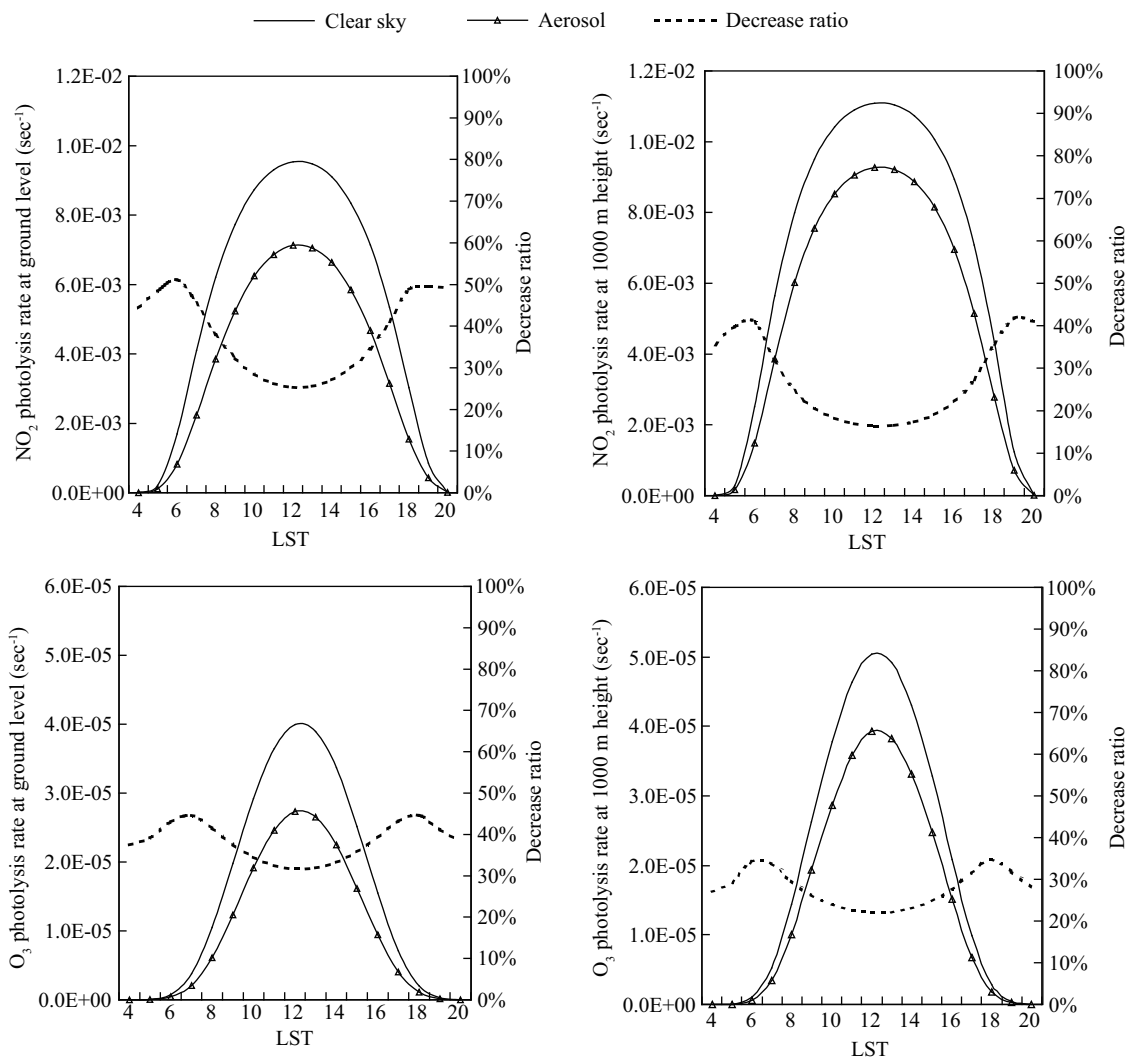


Fig. 4 Comparison of NO_2 and O_3 photolysis rate for the clear-sky conditions and when aerosol radiative influence was considered on 26 June 2000.

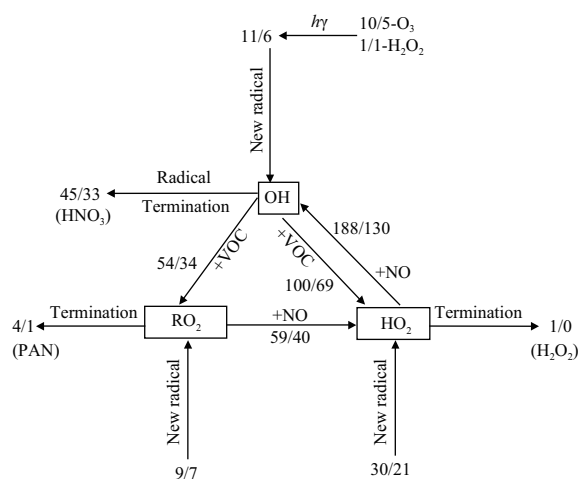


Fig. 5 Effect of radiative influence on radical cycle in the urban area at 0800–1600 LST on 26 June (each pair of numbers denotes simulation results with gaseous-only chemistry considered and aerosol radiative influence included; unit: ppb).

June, the maximum O_3 decrease was 73 ppb, which also occurred at the urban downwind area, as far as Changping County.

O_3 decrease by UV-absorbing aerosols has been investigated in previous simulations. In the 1-D column

simulation (He and Carmichael, 1999), the urban aerosol with strong absorbing properties caused a reduction in O_3 to about 40 ppb in the boundary layer, a result comparable with ours. For a spring season simulation in East Asia, UV-absorbing aerosol decreased O_3 concentration to 12 ppb in pollutant plumes (Tang et al., 2003b). The coarse horizontal resolution of 80 km and the unfavorable season for high O_3 formation caused O_3 decrease lower than those derived in the current work. In an urban case simulation by Jacobson (1998), UV-absorbing aerosol decreased O_3 by 5% to 8%, corresponding to a decreasing value of 10–20 ppb derived from the simulated O_3 peak of about 200 ppb in Claremont, California. Dickerson et al. (1997) obtained results by UAM-V simulation, in which UV-absorbing aerosol reduced O_3 to 24 ppb in the downwind area of New York City. The discrepancy in the prescribed aerosol optical properties and emission scenarios caused the differences between their results and those of the present study.

4 Discussion

Ordinary O_3 models consider gaseous-only chemistry. In a low-aerosol atmosphere, aerosol-related processes may

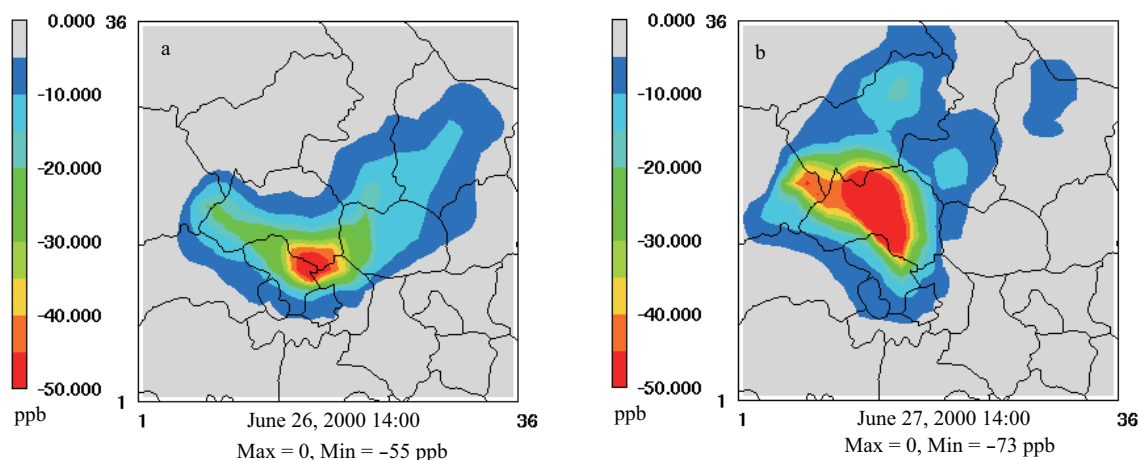


Fig. 6 O₃ changes caused by aerosol radiative influence in the Beijing area on 26 June (a) and 27 June 2000 (b).

have only minimal effects on O₃ formation; thus, O₃ can be effectively simulated using gas-only chemistry. However, when the aerosol in atmosphere has high loads and strong light extinction properties, both the heterogeneous reactions and aerosol radiative influence may have visible effects on O₃ formation. Table 3 shows the simulated maximum changes in O₃ concentration caused by each of the heterogeneous reactions and aerosol radiative influence in some representative locations in Beijing, i.e., the urban, urban downwind, and extra-urban areas. Both the heterogeneous reactions and aerosol radiative influence had clearly observable effects on O₃ concentration at each representative location in our simulation. Although some processes caused O₃ to increase or decrease, the magnitudes of each effect were comparable at each location. The simulation implies that the interaction between O₃ photochemistry and aerosol may be important under the ubiquitous high aerosol conditions in China. Thus, aerosol-related processes should be considered in O₃ simulations.

We compared the observations with the simulated O₃ in series with the combined effects of heterogeneous reactions and aerosol radiative influence at the Beijing urban area (Fig. 7). The simulated O₃ in all the experiments well represented the observed O₃ variation trend, which implies that although aerosol-related process remarkably affected O₃, the essential O₃ variation should be generally guided by the emission inventory and meteorological conditions in the area. For the four heterogeneous reactions, NO₂, NO₃, N₂O₅, and HO₂, O₃ increased compared with the gas-only case, and the results were close to the observations. However, after considering aerosol radiative influence and O₃ heterogeneous loss process consecutively, O₃ decreased sharply, causing an even worse simulation result (simulated O₃ was much lower than that in the observation).

The above-mentioned findings can be explained through the following aspects.

The study of the interaction between the O₃ photochemistry and aerosol is currently at a tentative stage. Some uncertainties regarding the identification of possible heterogeneous reactions on the aerosol surface, reaction condition and products, reaction parameters obtained from the experiments, and aerosol optical properties exist. These uncertainties determine the quality of the parameterization of aerosol-related processes, thereby imposing significant effects on the simulation results. For example, the reaction probability of heterogeneous reaction γ may be highly uncertain, and is always assumed with a range of orders of magnitude. To explore the effects of the uncertainty on O₃ simulation, we conducted a series of test runs to detect how O₃ changes respond to varying γ for each heterogeneous reaction. The results are shown in Table 3, with the range of O₃ changes simulated at each of the low and high bounds of the reaction probabilities. For each reaction, the range of γ takes the value mentioned in Section 3. Among the five heterogeneous reactions, O₃ changes were insensitive to the reaction probabilities for NO₃ and N₂O₅ heterogeneous reactions. Meanwhile, O₃ change was most sensitive to the reaction probability of NO₂ heterogeneous reaction. When γ_{NO_2} varied, the resultant O₃ change could be as low as 1 ppb at the low bound and can reach as high as 126 ppb at the high bound. For O₃ heterogeneous loss, the range of O₃ change was from -7 to -56 ppb at the low and high bounds of reaction probability. For HO₂ heterogeneous reaction, the range of O₃ change was from -15 to -44 ppb at each bound. The uncertainties in reaction probabilities of some heterogeneous reactions could lead to a wide range of O₃ changes, which may have important effects on the model performance.

Table 3 Maximum O₃ changes caused by each heterogeneous reaction and aerosol radiative influence in Beijing area

	Heterogeneous reaction					Aerosol radiative influence
	NO ₂ (ppb)	HO ₂ (ppb)	NO ₃ (ppb)	N ₂ O ₅ (ppb)	O ₃ (ppb)	
Urban area	67 (1, 106)*	-24 (-14, -43)	< 1 (0, < 1)	1 (0, 2)	-14 (-3, -26)	-52
Urban downwind area	90 (1, 126)	-33 (-15, -44)	0 (0, 0)	2 (0, 3)	-31 (-7, -56)	-73
Exurban area	-10 (0, -40)	< 1 (< 1, < 1)	-3 (-2, -3)	-9 (-4, -11)	-5 (-1, -9)	-9

* Three numbers account for the range of O₃ changes for each reaction; the first indicates the result for the base value, while each pair of numbers in parentheses indicates the sensitivity results at the low and high bounds in the range of reaction probabilities.

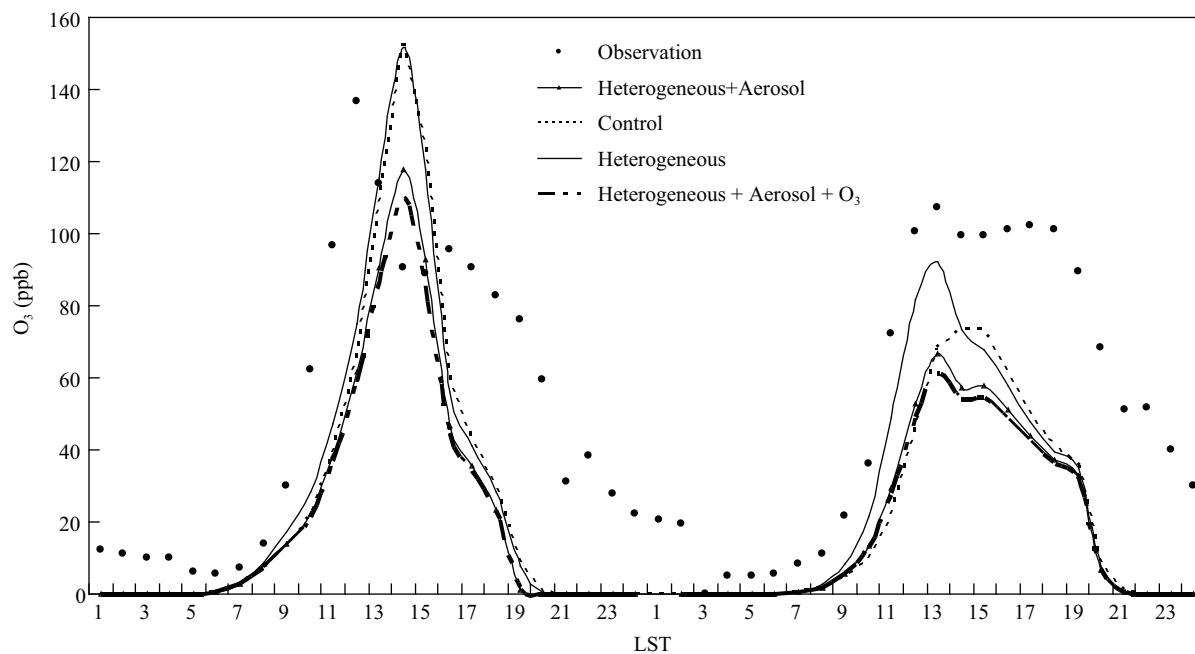


Fig. 7 Observed and simulated surface layer O_3 diurnal variations over the Beijing urban area in a series of sensitivity experiments from 26 to 27 June 2000, where control stands for the simulation with gaseous chemistry only. Heterogeneous represents the simulation in which four heterogeneous reactions, i.e., NO_2 , N_2O_5 , NO_3 , and HO_2 , were considered; Heterogeneous + Aerosol denotes the simulation in which the four heterogeneous reactions and aerosol radiative influence were considered; Heterogeneous + Aerosol + O_3 represents the simulation that included all aerosol-related processes, i.e., the four heterogeneous reactions, aerosol radiative influence, and O_3 heterogeneous loss process.

If we presume that the parameterization of the heterogeneous reactions and aerosol radiative influence in our simulation could accurately represent actual processes, the underestimated O_3 may be attributed to the underestimated VOC emission or chemical reactivity of VOC species because the urban area was in a VOC-limited regime of O_3 formation. The analysis of sampled VOC indicated that the chemical reactivity of ambient VOC was rather high at the Beijing urban area, even higher than that of ethane (Shao et al., 2005), whereas the reactivity is similar to pentane in New England, USA. Unlike Europe and the US, detailed VOC species profiles sampled from each type of source are unavailable in China. Thus, the profiles used for the emission preprocessing was taken from a reference of the US database. This may have underestimated the chemical reactivity of VOC when applied in Beijing. Another uncertainty of VOC emission may have stemmed from biogenic sources. GEIA biogenic VOC emission was estimated for the year 1990, while vegetation may change during a 10-year period. In the simulation, the biogenic VOC contribution was low in the Beijing urban area, which accounted for only 4.6% of total VOC emission. The emission is probably underestimated, causing some discrepancy in the O_3 simulation. To represent the actual status of Biogenic VOC (BVOC) emission in Beijing, new emission models should use an updated vegetation map; BVOC emissions should be predicted with diurnal variations, which are calculated online using hourly meteorological and solar radiation variables. This will yield emission rates at a higher temporal and spatial resolution than that generated using GEIA.

According to the analysis of Li et al. (2003), monthly mean AOD is about 0.7 in June over the Beijing area.

Setting AOD value as 0.8 could represent the polluted air quality case in summertime over the Beijing urban area. The simulated effects can be viewed as the upper limit of the effects. Newly released CMAQ include online AOD calculation based on simulated aerosol components; using these components as bases improves the estimation of aerosol radiative influence. However, the performance of AOD prediction is dependent on aerosol component prediction, an area that still requires further study.

Apart from the importance of aerosol radiative effects on photolysis rate, the meteorological feedback brought forth by aerosol, such as temperature decrease, stability increase, etc. can change O_3 simulation. The effects may be comparable with or exceed the influence of sole changes in photolysis rate in the Beijing urban area. The above-mentioned processes cannot be addressed using offline CTM. Only fully coupled chemistry and meteorology models can treat such types of feedback. The effects of both processes are involved in the simulation results; thus, detailed work on result analysis are needed to discern the effects of aerosol and meteorology.

5 Summary

Models-3/CMAQ-MADRID was employed to test the effects of two aerosol-related processes, namely, heterogeneous reactions occurring on the aerosol surface and photolysis rate changes caused by aerosol radiative influence on O_3 formation in typical high O_3 episodes in summer over the Beijing area. The results showed that the heterogeneous reactions affected O_3 formation significantly in the Beijing area. Among the five heterogeneous reactions, NO_2 , HO_2 , and O_3 reaction altered

O₃ concentration more considerably. When aerosol radiative influence was considered, the photolysis rate decreased, thereby remarkably reducing O₃. Comparing the O₃ changes caused by each heterogeneous reaction and aerosol radiative influence showed that their effects on the Beijing area are comparable.

Most standard O₃ simulations were based only on gaseous phase photochemistry. However, some aerosol-related processes may affect O₃ photochemistry under high aerosol loads. Both the heterogeneous reactions and aerosol radiative influence should be considered in O₃ and aerosol simulations because high aerosol concentration is a ubiquitous condition in China. As the primary topics in both atmospheric chemistry and global climate change research, aerosol-related processes are characterized by numerous uncertainties. A better understanding and parameterization of aerosol-related processes are highly desirable to improve simulations.

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