Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation in Beijing, China

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Abstract:
A comprehensive chlorine heterogeneous chemistry is incorporated into the Community Multiscale Air Quality (CMAQ) model to evaluate the impact of chlorine-related heterogeneous reaction on diurnal and nocturnal nitrate formation and quantify the nitrate formation from gas-to-particle partitioning of HNO3 and from different heterogeneous pathways. The results show that these heterogeneous reactions increase the atmospheric Cl2 and ClNO2 level (~100%), which further affect the nitrate formation. Sensitivity analyses of uptake coefficients show that the empirical uptake coefficient for the O3 heterogeneous reaction with chlorinated particles may lead to the large uncertainties in the predicted Cl2 and nitrate concentrations. The N2O5 uptake...
coefficient with particulate Cl\textsuperscript{-} concentration dependence performs better to capture the concentration of Cl\textsubscript{NO}\textsubscript{2} and nocturnal nitrate concentration. The reaction of OH and NO\textsubscript{2} in daytime increases the nitrate by \sim 15\% when the heterogeneous chlorine chemistry is incorporated, resulting in more nitrate formation from HNO\textsubscript{3} gas-to-particle partitioning. By contrast, the contribution of the heterogeneous reaction of N\textsubscript{2}O\textsubscript{5} to nitrate concentrations decreases by about 27\% in the nighttime when its reactions with chlorinated particles are considered. However, the generated gas-phase Cl\textsubscript{NO}\textsubscript{2} from the heterogeneous reaction of N\textsubscript{2}O\textsubscript{5} and chlorine-containing particles further reacts with the particle surface to increase the nitrate by 6\%. In general, this study highlights the potential of significant underestimation of daytime and overestimation of nighttime nitrate concentrations for chemical transport models without proper chlorine chemistry in the gas and particle phases.

1. Introduction

In recent years, nitrate has become the primary component of PM\textsubscript{2.5} (particulate matter with aerodynamic diameter less than 2.5\textmu m) in Beijing with sustained and rapid reduction of SO\textsubscript{2} and primary particulate matter emissions (Ma et al., 2018; Li et al., 2018; Wen et al., 2018). Observations showed that the relative contributions of secondary nitrate in PM\textsubscript{2.5} could reach up to approximately 50\% during some severe haze pollution days (Li et al., 2018). The mechanism of secondary nitrate formation can be summarized as two major pathways: (1) Gas-to-particle partitioning of HNO\textsubscript{3}, which happens mostly in the daytime. The reaction of OH with NO\textsubscript{2} produces gaseous HNO\textsubscript{3}, which subsequently partition into the particle phase. The existence of NH\textsubscript{3} or basic particles enhances this process by NH\textsubscript{3}–NH\textsubscript{4}\textsuperscript{+} gas-particle equilibrium (Kleeman et al., 2005; Seinfeld and Pandis, 2006); (2) Hydrolysis of N\textsubscript{2}O\textsubscript{5}, which is more important at nighttime. N\textsubscript{2}O\textsubscript{5} forms from the reactions of NO\textsubscript{2}, O\textsubscript{3} and NO\textsubscript{3} and hydrolyzes to produce particulate nitrate. They can be summarized as reactions R1-R5 (Brown and Stutz 2012):

\[
\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad \text{(R1)}
\]
\[
\begin{align*}
\text{HNO}_3 + \text{NH}_3 & \rightarrow \text{NH}_4^+ + \text{NO}_3^- \quad \text{(R2)} \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R3)} \\
\text{NO}_3 + \text{NO}_2 & \leftrightarrow \text{N}_2\text{O}_5 \quad \text{(R4)} \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O(aq)} & \rightarrow 2\text{H}^+ + 2\text{NO}_3^- \quad \text{(R5)}
\end{align*}
\]

In addition to reactions R1 and R5, gas phase reactions of \( \text{NO}_3 \) with \( \text{HO}_2 \) and VOCs, \( \text{N}_2\text{O}_5 \) with water vapor (Tuazon et al., 1983) and the heterogeneous reaction of \( \text{NO}_2 \) with water-containing particle (Goodman et al., 1999) produce \( \text{HNO}_3 \) or nitrate as well. Theses reactions are listed in Table 2 as reactions R8, R9 and R10.

However, chemistry transport models (CTMs) incorporated with these mechanisms still can’t accurately capture the spatiotemporal distributions of nitrate in some studies in polluted northern China. For example, Chang et al. (2018) showed that the simulated nitrate concentrations derived from the default CMAQ (version 5.0.2) were significantly higher than the observations in summer at two sites adjacent to Beijing. Fu et al. (2016) also found that default CMAQ (version 5.0.1) overestimated the simulated nitrate concentrations in the Beijing-Tianjin-Hebei region.

In recent fields studies, it was found that high particulate chlorine emissions might have a significant impact on the oxidation capacity of the urban atmosphere and thus could affect nitrate concentrations. According to the field measurements in June 2017 in Beijing (Zhou et al., 2018), the 2-min averaged concentrations of reactive molecular chlorine (\( \text{Cl}_2 \)) and nitryl chloride (\( \text{ClNO}_2 \)) reached up to 1000 pptv and 1200 pptv, respectively, during some severe air pollution periods in summer. The \( \text{Cl}_2 \) concentrations were significantly higher than those observed in North American coastal cities affected by onshore flow and the lower atmosphere in the remote Arctic region (Spicer et al., 1998; Glasow et al., 2010; Liu et al., 2017). During these pollution events, the corresponding concentrations of \( \text{N}_2\text{O}_5 \) (2-min average) and nitrate (5-min average) rose from 40 pptv and 1 \( \mu \text{g} \text{ m}^{-3} \) to 700 pptv and 5 \( \mu \text{g} \text{ m}^{-3} \). To explain the high levels of \( \text{ClNO}_2 \), some studies suggested that reaction R5 should be revised to account for \( \text{ClNO}_2 \) production from the heterogeneous reaction of \( \text{N}_2\text{O}_5 \) on chloride-containing particles (CPS) (Osthoff et al., 2008; Thornton et al., 2010), as shown in reaction R6:

\[
\text{N}_2\text{O}_5 + (1-\phi) \text{H}_2\text{O} + \phi \text{Cl}^- \rightarrow \phi \text{ClNO}_2 + (2-\phi) \text{NO}_3^- \quad \text{(R6)}
\]
where $\phi$ represents the molar yield of ClNO$_2$. When Cl$^-$ is enough, this reaction leads to lower nitrate concentrations than reaction R5. By incorporating this reaction into WRF-Chem, Li et al. (2016) found that the improved model performed better to match the observed nitrate concentrations in Hong Kong during 15 November and 5 December 2013. However, ClNO$_2$ could affect the formation of nitrate indirectly by increasing the atmospheric OH after a series of chemical reactions, which are briefly summarized into three steps: (1) the photolysis of ClNO$_2$ produces chlorine radicals (Cl$^*$); (2) the reaction of Cl$^*$ with VOCs produces peroxy radical (HO$_2$ and RO$_2$); and (3) the increased HO$_2$ and RO$_2$ prompt the formation of OH through HOx cycle and lead to increased HNO$_3$ production (Young et al., 2014; Jobson et al., 1994). The overall impact of R6 on nitrate remains to be investigated.

Another related but unresolved issue is the sources of the high concentrations Cl$_2$, which could not be explained by the N$_2$O$_5$ heterogeneous reaction with Cl$^-$ and the subsequent reactions of ClNO$_2$ in the gas phase. It has been reported that the reactions of gaseous O$_3$, OH, HO$_2$, ClNO$_2$, hypochlorous acid (HOCI), chlorine nitrate (ClONO$_2$) with CPS can produce Cl$_2$, which can subsequently photolyze to produce Cl$^*$ (Knipping et al., 2000; George et al., 2010; Pratte et al., 2006; Deiber et al., 2004; Faxon et al., 2015). However, these heterogeneous reactions on CPS are generally missing in most of the current CTMs and it is unclear whether these reactions will be able to explain the observed Cl$_2$ concentrations and the overall impact of these reactions on nitrate.

Previously, biomass burning, coal combustion, and waste incineration were identified as the main sources of gaseous and particulate chlorine compounds in China from International Global Atmospheric Chemistry Program's Global Emissions Inventory Activity (GEIA) based on the year 1990 and a localized study by Fu et al. based on the year 2014 (Keene et al., 1999; Fu et al., 2018). However, recent source apportionment results of PM$_{2.5}$ in Beijing showed that the contribution of coal combustion had extremely decreased from 22.4% in 2014 to 3% in 2017 with the replacement of natural gas (obtained from official website of Beijing Municipal Bureau...
of Statistics, available at http://edu.bjstats.gov.cn/). Another important source—cooking has received attention as its increasing contribution to PM$_{2.5}$ (accounting for 33% of the residential sector; obtained from the official source apportionment analysis of PM$_{2.5}$ in Beijing in 2017; see http://www.bjepb.gov.cn/bjhr-b/index/index.html). Moreover, the high content of particulate sodium chloride was measured from the source characterization studies of PM$_{2.5}$ released from the cooking activities (Zhang et al., 2016). Thus, it is necessary to compile an updated emission inventory for Beijing to include the emissions from cooking and other sources (coal burning, solid waste incineration, biomass burning, etc.) in order to explore the emissions of the chlorine species on atmospheric nitrate formation.

In this study, a CMAQ model with an improved chlorine heterogeneous chemistry is applied to simulate summer nitrate concentration in Beijing. Sensitivity simulations are conducted to evaluate the contributions of HNO$_3$ gas-to-particle partitioning and heterogonous production to aerosol nitrate. The results of this work can improve our understandings on nitrate formation and provide useful information on nitrate pollution control strategies in Beijing.

2. Emissions, chemical reactions and model description

2.1 Emissions

Generally, the conventional emission inventories of air pollutants in China only include the common chemical species, such as SO$_2$, NO$_X$, VOCs, PM$_{2.5}$, PM$_{10}$, NH$_3$, BC, and OC (Wang et al., 2014). Chloride compound emissions were not included. However, the emissions of chlorine species are vital for studying the chlorine chemical mechanism. Recently, the inorganic hydrogen chloride (HCl) and fine particulate chloride (PCI) emission inventories for the sectors of coal combustion, biomass burning, and waste incineration were developed for the year of 2014 (Qiu et al., 2016, Fu et al., 2018, Liu et al., 2018). However, the gaseous chlorine emission was not estimated in these studies. In addition, these studies did not account for the rapid decrease of coal consumption in recent years in Beijing, from 2000 Mt in 2014 to 490 Mt in 2017. More
importantly, the cooking source, as one of the major contributors to particulate chlorine in Beijing, is not included in current chlorine emission inventories. Thus, a new emission inventory of reactive chlorine species, which includes HCl, Cl₂ and PCl, were developed in this study for the year of 2017.

The emission factor method (equation (1)) is applied to calculate the emissions of these reactive chlorine species from coal combustion, biomass burning, municipal solid waste incineration and industrial processes:

\[ E_{i,j} = A_i \times EF_{i,j} \]  

where \( E_{i,j} \) represents the emission factor of pollutant \( j \) in sector \( i \); \( A \) represents the activity data; \( EF \) represents the emission factor. \( EF \) for PCl is estimated by \( EF_{i,\text{PM2.5}} \times f_{\text{Cl}}, \) where \( f_{\text{Cl}} \) represents the mass fraction of PCl in primary PM\textsubscript{2.5}. Activity data are obtained from the Beijing Municipal Bureau of Statistics (available at http://tjj.beijing.gov.cn/). The Cl\textsubscript{2} emission factor for coal combustion is calculated based on the content of Cl in coal, which had been measured by Deng et al (2017). The PM\textsubscript{2.5} emission factors and mass fractions of PCl in PM\textsubscript{2.5} to calculate the emissions of Cl had been described in detail by Fu et al. (2018). PCl in PM\textsubscript{2.5} for coal combustion and biomass burning are taken as 1% and 9.0%, respectively, based on local measurements in Beijing.

Emissions of PCl from cooking, including contributions from commercial and household cooking, are estimated using equation (2):

\[ E_{\text{PCl}} = [N_f \times V_f \times H_f \times EF_{f,\text{PCl}} + V_c \times H_c \times N_c \times n \times EF_{c,\text{PCl}} \times (1 - \eta)] \times 365 \]  

where \( N_f \) is the number of households, \( V_f \) is the volume of exhaust gas from a household stove (2000 m\textsuperscript{3} h\textsuperscript{-1}); \( H_f \) is the cooking time for a family (0.5 h day\textsuperscript{-1}); \( EF_{f,\text{PCl}} \) and \( EF_{c,\text{PCl}} \) are the emission factors (kg m\textsuperscript{-3}) of PCl for household and commercial cooking, respectively; \( H_c \) is the cooking time in a commercial cooking facility (6 h day\textsuperscript{-1}); \( N_c \) is the number of restaurants, schools and government departments. \( V_c \) is the volume of exhaust gas from a commercial cooking stove (8000 m\textsuperscript{3} h\textsuperscript{-1}); \( n \) is the number of stoves for each unit, which equals to 6 for a restaurant and is calculated as one stove per 150 students for each school. \( \eta \) is the removal efficiency of fume scrubbers (30%). \( EF_{c,\text{PCl}} \) is the emission factor (kg m\textsuperscript{-3}) of PCl in commercial cooking. These constants are all
based on Wu et al. (2018). The PCl fraction in PM$_{2.5}$ from cooking is taken as 10%, based on local measurements. HCl and Cl$_2$ emissions from cooking are not considered in this study.

The sectoral emissions of HCl, Cl$_2$ and PCl are summarized in Table 1. The estimated HCl, Cl$_2$ and PCl emissions in Beijing are 1.89 Gg, 0.07 Gg and 0.63 Gg respectively. The Cl emissions estimated for 2014 by Fu et al. (2018) were used for other areas. This simplification is a good approximation because replacing coal with natural gas only occurred in Beijing, and reduction of coal consumption in surrounding regions was generally less than 15%. In addition, strict control measures for biomass burning, cooking and municipal solid waste incineration have not been implemented in most regions yet. Emissions of conventional species for this study period are developed in a separate study that is currently under review and are summarized in Table S1.

2.2 Chlorine-related heterogeneous reactions

The heterogeneous reactions in original CMAQ (version 5.0.1) are not related to chlorine species. In this study, the original heterogeneous reactions of N$_2$O$_5$ and NO$_2$ (R5 and R10 in Table 2) are replaced with a revised version which includes production of ClNO$_2$ from CPS (R6 and R11 in Table 2). In reaction R6, the molar yield of ClNO$_2$ ($\phi_{\text{ClNO}_2}$) is represented as equation (3) (Bertram and Thornton, 2009):

$$\phi_{\text{ClNO}_2} = \left(1 + \frac{[\text{H}_2\text{O}]}{483 \times [\text{Cl}^-]}\right)^{-1}$$

where [H$_2$O] and [Cl$^-$] are the molarities of liquid water and chloride (mol m$^{-3}$).

In addition, laboratory observations confirmed that the heterogeneous uptake of some oxidants (such as O$_3$ and OH) and reactive chlorine species (such as ClNO$_2$, HOCI, and ClONO$_2$) could also occur on CPS to produce Cl$_2$. These reactions are implemented in the model and summarized in Table 2 as R13-R18. Note that the products from the heterogeneous uptake of ClNO$_2$ on CPS vary with particle acidity (Riedel et al., 2012; Rossi, 2003). It generates Cl$_2$ under the condition of pH lower than 2 but produces nitrate and chloride under higher pH conditions. The reaction rates of the heterogeneous
reactions are parameterized as first-order reactions, with the rate of change of gas phase species concentrations determined by equations (4) (Ying et al., 2015):

$$\frac{dC}{dt} = -\frac{1}{4} (\nu y A) C = -k^I C$$

(4)

where \(C\) represents the concentration of species; \(\nu\) represents the thermal velocity of the gas molecules (m s\(^{-1}\)); \(A\) is the CMAQ-predicted wet aerosol surface area concentration (m\(^2\) m\(^{-3}\)); \(y\) represents the uptake coefficient. For all gas phases species (except ClNO\(_2\)) involved in the heterogeneous reactions (R6 and R11-R18), a simple analytical solution can be used to update their concentrations from time \(t_0\) to \(t_0+\Delta t\):

\[[C]_{t_0+\Delta t} = [C]_{t_0} \exp(-k^I \Delta t),\] where \(\Delta t\) is the operator-splitting time step for heterogeneous reactions.

The rate of change of ClNO\(_2\) includes both removal and production terms, as shown in equation (5):

$$\frac{d[\text{ClNO}_2]}{dt} = -k^I_{i1}[\text{ClNO}_2] + k^I_{b6} \phi_{\text{ClNO}_2} [\text{N}_2\text{O}_5]$$

(5)

Assuming \(\phi_{\text{ClNO}_2}\) is a constant, an analytical solution for equation (5) can be obtained, as shown in equation (6):

\[[\text{ClNO}_2]_{t_0+\Delta t} = [\text{ClNO}_2]_{t_0} \exp(-k^I_{i1} \Delta t) + \frac{k^I_{b6} \phi_{\text{ClNO}_2} [\text{N}_2\text{O}_5]_{t_0}}{k^I_{i1} - k^I_{b6}} \left[ \exp(-k^I_{i1} \Delta t) - \exp(-k^I_{b6} \Delta t) \right]$$

(6)

where \(k^I_{i1}\) represents the pseudo first-order rate coefficient of either reaction R17 or R18, depending on pH.

The uptake coefficients \(y\) of gaseous species are obtained from published laboratorial studies. In the original CMAQ, the uptake coefficient of N\(_2\)O\(_5\) is determined as a function of the concentrations of (NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)HSO\(_4\) and NH\(_4\)NO\(_3\) (Davis et al., 2008). In this study, the PCl and NO\(_3^-\) dependent parameterization by Bertram and Thornton (2009) (equation (7)) is used:

$$y_{\text{N}_2\text{O}_5} = \begin{cases} 
0.02, & \text{for frozen aerosols} \\
3.2 \times 10^{-8} K_f \left[ 1 - \left( 1 + 6 \times 10^{-2} \frac{[\text{H}_2\text{O}]}{[\text{NO}_3^-]} + 29 \frac{[\text{Cl}^-]}{[\text{NO}_3^-]} \right)^{-1} \right]
\end{cases}$$

(7)

In the above equation, \(K_f\) is parameterized function based on molarity of water: \(K_f = \)
\[ \gamma = \min\left(0.04 \times \frac{[Cl^-]}{1000 \times M}, 1\right) \]  

(8)

where \( M \) represents the volume of liquid water in aerosol volume (m\(^3\) m\(^{-3}\)). For frozen particles, the uptake coefficient is limited to 0.02, as used in the original CMAQ model.

The uptake coefficients of O\(_3\), NO\(_3\), NO\(_2\), HOCl, ClNO\(_2\), and ClONO\(_2\) are treated as constants. Among of them, the \( \gamma \) values of NO\(_3\), NO\(_2\), HOCl and ClONO\(_2\) are set as 3\( \times \) 10\(^{-3}\), 1\( \times \) 10\(^{-4}\), 1.09\( \times \) 10\(^{-3}\) and 0.16 based on laboratory measurements (Rudich et al., 1996; Abbatt et al., 1998; Pratte et al., 2006; Gebel et al., 2001). A preliminary value of 10\(^{-3}\) in the daytime and 10\(^{-5}\) at nighttime is chosen for the O\(_3\) uptake coefficient. The daytime \( \gamma_{O_3} \) is based on the analysis of Cl\(_2\) production rate in a hypothesized geochemical cycle of reactive inorganic chlorine in the marine boundary layer by Keene et al. (1990). The lower nighttime value was also recommended by Keene et al. (1990) who noted that Cl\(_2\) production in the marine boundary layer are lower at night. The uptake coefficient of ClNO\(_2\) depends on the particle acidity, with the value of 2.65 \( \times \) 10\(^{-6}\) for reaction R17 and 6 \( \times \) 10\(^{-3}\) for reaction R18 (Robert et al., 2008).

2.4 CMAQ model configuration

These heterogeneous reactions of chlorine are incorporated into a revised CMAQ based on the CMAQ version 5.0.1 to simulate the distribution of nitrate concentration in Beijing from 11 to 15 June 2017. The revised CMAQ model without heterogeneous reactions of chlorine has been described in detail by Ying et al. (2015) and Hu et al. (2016, 2017). In summary, the gas phase chemical mechanism in the revised CMAQ model is based on the SAPRC-11 (Cater et al., 2012) with a comprehensive inorganic chlorine chemistry. Reactions of Cl radical with several major VOCs, which lead to production of HCl, are also included. The aerosol module is based on AERO6 with an
updated treatment of NO₂ and SO₂ heterogeneous reaction and formation of secondary organic aerosol from isoprene epoxides. Three-level nested domains with the resolutions of 36km, 12km, and 4km using Lambert Conformal Conic projection (173×136, 135×228 and 60×66 grid cells) are chosen in this work (the domains see Figure S1). The two true latitudes are set to 25°N and 40°N and the origin of the domain is set at 34°N, 110°E. The left-bottom coordinates of the outmost domain are positioned at x = -3114 km, y = -2448 km. The BASE case (heterogeneous reactions of Cl turned off) and HET case (all heterogeneous reactions enabled) are compared to evaluate the impact of heterogeneous chlorine chemistry on nitrate formation.

3. Results

3.1 Model performance evaluation

Predicted O₃, NO₂ and PM₂.₅ concentrations from the BASE case simulation are evaluated against monitoring data at 12 sites in Beijing (Table S2) in 11 to 15, June 2017. The average NMB/NME values for O₃, NO₂ and PM₂.₅ across the 12 sites are -8%/29%, -7%/59% and -8%/53%, respectively. Predicted hourly Cl₂, ClNO₂ and N₂O₅ concentrations were compared with observations measured at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39.98°N, 116.37°E) using a high-resolution time-of-flight chemical ionization mass spectrometer (CIMS) from 11 to 15 June 2017 (for site description, instrument introduction, and analytical method, please refer to the study by Zhou et al. (2018)). Figure 1 shows that the concentrations of Cl₂ and ClNO₂ in BASE case are rather low (close to 0), proving that the gas-phase chemistry is not the major pathway to produce Cl₂ and ClNO₂. By contrast, the simulated Cl₂ and ClNO₂ concentrations in HET case increase significantly, correspondingly the NMB and NME changes from -100% to -54% and 100% to 61% for Cl₂, and from -100% to -58% and 100% to 62% for ClNO₂, respectively (the particle surface area concentrations is scaled up by a factor of 5 in daytime and 10 in nighttime because this parameter is underestimated compared to the measured concentrations reported by Zhou et al. (2018)). The simulations of Cl₂ and ClNO₂ are improved as the
additional heterogeneous reactions prompt the production of gas phase molecular chlorine. Overall, however, the Cl$_2$ and ClNO$_2$ concentrations are still underestimated. Both BASE and HET simulations generally capture the hourly N$_2$O$_5$ concentrations as well as the peak values (Figure 1(c)) with similar overall NMB and NME values.

The uptake coefficient of O$_3$ could be an important factor affecting the predicted Cl$_2$ concentrations as it is found that the heterogeneous reaction of O$_3$ is the major source of Cl$_2$ during this period (see discussion in Section 3.2). The influence of different parametrizations of the uptake coefficient of N$_2$O$_5$ on ClNO$_2$ and nitrate concentrations are also discussed in Section 3.2.

Predicted NO$_3^-$ and PCl concentrations are compared with observations measured at an adjacent monitoring site located at the rooftop of School of Environment building in Tsinghua University (THU, 40.00°N, 116.34°E, about 5 km from IAP) using an Online Analyser of Monitoring of Aerosol and Gases (MARGA) from 11 to 15 June 2017. According to Figure 1(d), the simulated nitrate concentration is slightly lower than the observations most of the time. From the evening hours of 12 June to morning hours of 13 June, observed and simulated nitrate concentration both increase significantly. The NMB and NME values of hourly nitrate for the HET case (-5% and 39%, respectively) are slightly lower than those for the BASE case -10% and 46%) during this high concentration period. The HET case also generally captures the day-to-day variation of PCl concentration and perform better than the BASE case, correspondingly the NMB and NME are reduced from -48% and 72% to -37% and 67%. The substantial underestimation of PCl in the daytime on 15 June is likely caused by missing local emissions during this period.

3.2 Impact of uptake coefficients of O$_3$ and N$_2$O$_5$ on chlorine species and nitrate

The uptake coefficients of O$_3$ and N$_2$O$_5$ may be important factors affecting the accuracy of simulated nitrate concentrations. Some studies have confirmed that the reaction of O$_3$ on CPS can indirectly affect the nitrate formation by increasing the atmospheric Cl$_2$ and OH level (Li et al., 2016; Liu et al., 2018). According to Figure 1(a), the improved model still substantially underestimates the concentration of Cl$_2$, which may be
associated with the underestimation of the uptake coefficients of $O_3$, which are empirical and have not been confirmed by laboratory studies. The uptake coefficients were increased by a factor of 10 (0.01 for daytime and $10^{-4}$ for nighttime) to evaluate the sensitivity of Cl$_2$ production and nitrate formation to this parameter. Figure 2 shows that the simulated Cl$_2$ and nitrate concentrations in daytime increase significantly (especially for Cl$_2$) and sometimes can capture the peak value (such as the daytime peak on 14 June). However, although the NMB and NME of Cl$_2$ and nitrate improve from -18% and 39% to 1% and 28% when the new uptake coefficients are used, the simulated Cl$_2$ concentrations are still quite different from the observations such as during the daytime in 11 and 12 June, see Figure 2). A non-constant parameterization of the uptake coefficients of $O_3$ that considers the influence of PCl concentrations, meteorology conditions, etc., similar to those of OH and N$_2$O$_5$, might be needed. Further laboratory studies should be conducted to provide a better estimation of this important parameter.

Several parameterizations for the uptake coefficient of N$_2$O$_5$ have been developed for regional and global models and have been evaluated in several previous studies (Tham et al., 2019, McDuffie et al., 2018a, 2018b). In addition to the parameterization of Bertram and Thornton (2009) used in the HET case, two additional simulations were performed to assess the impact of the uptake coefficient of N$_2$O$_5$ on nitrate formation. The first simulation uses the original CMAQ parameterization of Davis et al. (2008) and second simulation uses a constant value of 0.09, which is the upper limit of the N$_2$O$_5$ uptake coefficient derived by Zhou et al. (2018) based on observations. The results from the simulations with the parameterization of Bertram and Thornton (2009) generally agree with the results using those based on Davis et al. (2008) and the larger constant N$_2$O$_5$ leads to slightly better results, which might reflect the fact that the N$_2$O$_5$ concentrations are underestimated. Using the uptake coefficient of 0.09 can generally increase the concentration of nitrate in some periods, but it also leads to significant increase of the nitrate level (such as nighttime on 12-13 June and 13-14 June), which is 4-6 times higher than those based on Bertram and Thornton (2009). Overall, predicted nitrate concentrations are sensitive to changes in the changes in $\gamma_{N_2O_5}$, with approximately 50% increase in the nitrate when a constant of $\gamma_{N_2O_5}$ of 0.09 is used.
3.3 Spatial distributions of nitrate and chlorine species concentrations

The regional distributions of averaged Cl\(_2\), ClNO\(_2\), N\(_2\)O\(_5\) and NO\(_3^-\) concentration from 11 to 15 June for the HET case are shown in Figure 3. Compared to the BASE case, the episode average concentrations of Cl\(_2\) and ClNO\(_2\) from the HET case increase significantly in the eastern region of Beijing, reaching up to 23 ppt and 71 ppt from near zero (Figure 3a and 3b). High concentrations are not found in the southern region with intensive emissions of chlorine species (Figure S2). The production of ClNO\(_2\) requires the presence of chloride, NO\(_2\), and O\(_3\). In the areas close to the fresh emissions, O\(_3\) is generally low (Figure S3), and the production of NO\(_3\) (hence N\(_2\)O\(_5\) and ClNO\(_2\)) is limited. Therefore, the production rate of ClNO\(_2\) is generally low in areas affected by fresh emissions. Since the contribution of direct emissions to Cl\(_2\) is low and it is predominantly produced secondarily in the atmosphere, high levels of Cl\(_2\) are also found away from the fresh emissions.

The spatial distribution of N\(_2\)O\(_5\) concentrations differs from that of other species (Figure 3c). While the concentrations of most of the species are higher in the southern region, the N\(_2\)O\(_5\) concentrations are lower in some parts of this region. This is because the O\(_3\) concentration in the core urban areas is low due to high NO\(_x\) emissions. The N\(_2\)O\(_5\) concentrations from the HET case are approximately 16% lower on average (Figure 3d) because the Bertram and Thornton (2009) parameterization used in the HET case generally gives higher uptake coefficients than the parameterization of Davis et al. (2008) used in the BASE case (Table 3).

Although the higher uptake coefficients of N\(_2\)O\(_5\) in the HET case facilitate faster conversion of N\(_2\)O\(_5\) to nitrate, the nitrate concentrations do not always increase. During daytime hours, nitrate concentrations in the HET case increase due to higher OH (Figure 3e and Figure 3f). At nighttime, in contrast, the nitrate concentration decreases significantly in some regions by about 22%, mainly due to lower molar yield of nitrate from the N\(_2\)O\(_5\) heterogeneous reaction in the HET case (Figure 3g and Figure 3h). Although ClNO\(_2\) produced in the N\(_2\)O\(_5\) reaction also produces nitrate through a heterogenous reaction when the particle pH is above 2, which is true for most regions (see Figure S4), the uptake coefficient of ClNO\(_2\) is significantly lower than that of N\(_2\)O\(_5\).
(0.01~0.09 for N₂O₅ and 6 ×10⁻³ for ClNO₂), leading to an overall decrease of nitrate production. As the ClNO₂ production from the heterogeneous reaction leads to less N₂O₅ conversion to non-relative nitrate, it may change the overall lifetime of NOx and their transport distances. The magnitude of this change and its implications on ozone and PM2.5 in local and downwind areas should be further studied.

3.4 Relationship between nitrate formation and chlorine chemistry

Nitrate productions from the homogeneous and heterogeneous pathways in Beijing are approximated by the difference in predicted nitrate concentrations between the BASE or HET case and a sensitivity case without heterogenous reactions. Averaging over the five-day period, approximately 58% of the nitrate originates from HNO₃ gas-to-particle partitioning and 42% is from heterogeneous reactions (Figure 4). This conclusion generally agrees with measurements at Peking University (PKU) (52% from the heterogeneous process and 48% from HNO₃ partitioning) on four polluted days (average in September 2016 reported by Wang et al. (2017). Slightly higher contributions of the homogeneous pathway in this study is expected because of high OH concentrations during the day and lower particle surface areas at night.

The nitrate formation from different homogeneous and heterogeneous pathways in the BASE case and HET case are further studied. Contributions of different gas phase pathways are determined using the process analysis tool in CMAQ. Contributions of different heterogeneous pathways are determined using a zero-out method that turns off one heterogeneous pathway at a time in a series of sensitivity simulations. Figure 4 shows that the reaction of OH and NO₂ is always the major pathway for the formation of nitrate through homogeneous formation of HNO₃ and gas-to-particle partitioning. However, its nitrate production rate through this homogeneous pathway decreases significantly from daytime to nighttime (from 1.81 µg m⁻³ h⁻¹ to 0.33 µg m⁻³ h⁻¹ on average). The nitrate production from other HNO₃ partitioning pathways in the daytime is negligible. At nighttime, homogeneous reaction of N₂O₅ with water vapor accounts for approximately 5% of the overall homogeneous nitrate formation. For the heterogeneous pathways, daytime production rate is approximately 0.6 µg m⁻³ h⁻¹ with
1/3 of the contributions from NO
2 and 2/3 from N2O5. Nighttime production on nitrate from the heterogeneous pathways is approximately 3.1 μg m⁻³ h⁻¹, of which 85% is due to N2O5 and 15% is due to NO2.

Comparing the BASE case and the HET case shows that, when the chlorine chemistry is included, the gaseous HNO3 produced by OH reacting with NO2 increases significantly in the HET case. Correspondingly, the nitrate production rate reaches up to 2.04 μg m⁻³ h⁻¹ in the daytime due to increased atmospheric OH concentrations predicted by the chlorine reactions. Similar conclusions are also obtained by Li et al. (2016) and Liu et al. (2017) based on observations and model simulations. The heterogeneous production of nitrate from the reaction of N2O5 uptake decreases by approximately 27% in the HET case due to the production of gas phase ClNO2. According to the study by Sarwar et al. (2012; 2014), including the heterogeneous reaction of N2O5 with PCl decreased the nocturnal nitrate concentration by 11-21% in the United States, which was slightly less than the current study for Beijing. It is likely because PCl concentrations in the United States are significantly lower than those in Beijing (the monthly PCl concentration is 0.06 μg m⁻³ in the United State against ~1 μg m⁻³ in Beijing) so that PCl is depleted quickly. The contributions of NO2 uptake to nitrate also decrease by 22% because of the lower rate constant of the reaction of NO2 with PCl. In contrast, the contribution of ClNO2 reacts with particle surface to nitrate production increases by 6% in the HET case. The overall nitrate concentration in the HET case is about 22% higher than that in the BASE case during this study period.

4. Conclusions
In this work, a modified CMAQ model incorporated with heterogeneous reactions for the production of molecular chlorine and other reactive chlorine species is developed and its impact on of the nitrate formation predictions are evaluated. The contributions from different homogenous and heterogeneous pathways to nitrate formation are also quantified. High concentration of Cl2 and ClNO2 do not occur in the southern part of the Beijing-Tianjin-Hebei region with intensive emissions of chlorine species as higher concentrations of O3 and N2O5 associated with the heterogeneous formation of these
species generally occurred in the downwind areas. CTMs without a complete treatment of the chlorine chemistry can underestimate daytime nitrate formation from the homogeneous pathways, particularly from HNO$_3$ gas-to-particle partitioning due to underestimation of OH concentrations and overestimate the nighttime nitrate formation from the heterogeneous pathways due to missing chlorine heterogeneous chemistry.

**Data availability.** The data in this study are available from the authors upon request (shxwang@tsinghua.edu.cn)

**Author contributions.** XQ, QY, SW and JH designed the study; YS, BL, AS, XY provided observation data; XQ, QY, SW, JZ, QX, DD, LD and JX analyzed data. XQ, QY and SW wrote the paper.

**Competing interests.** The authors declare that they have no conflict of interest.

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Figure 1 Comparison of observed hourly Cl\textsubscript{2}, ClNO\textsubscript{2}, N\textsubscript{2}O\textsubscript{5} (at the Institute of Atmospheric Physics, Chinese Academy of Sciences), NO\textsubscript{3}\textsuperscript{-} and PCl (at Tsinghua University) in urban Beijing with predictions from the BASE and the HET cases during 11-15 June 2017.
Figure 2 Comparison of observed and predicted Cl₂ and NO₃⁻ concentrations under different uptake coefficient of O₃ (HET: daytime $\gamma_{O_3} = 1 \times 10^{-3}$, nighttime $\gamma_{O_3} = 1 \times 10^{-5}$; HET-Co: daytime $\gamma_{O_3} = 1 \times 10^{-2}$, nighttime $\gamma_{O_3} = 1 \times 10^{-4}$).
Figure 3 Spatial distributions of episode-average (a) Cl\(_2\), (b) CINO\(_2\), (c) N\(_2\)O\(_5\), (e) daytime (8:00 – 20:00 hours) nitrate (ANO\(_3\)) and (g) nighttime nitrate concentrations from 11-15 June 2017, and the differences in the episode-average (d) N\(_2\)O\(_5\) (HET case – BASE case), (f) daytime nitrate and (g) nighttime nitrate. Units are µg m\(^{-3}\).
Figure 4 Contributions of different homogeneous and heterogeneous pathways to nitrate formation.
Table 1 The sectoral emissions of HCl, Cl₂ and PCl in Beijing in 2017. Unit: Mg year⁻¹

<table>
<thead>
<tr>
<th>Sector</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl</td>
</tr>
<tr>
<td>Power plant</td>
<td>22.8</td>
</tr>
<tr>
<td>Industry</td>
<td>587.3</td>
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<tr>
<td>Residential</td>
<td>202.4</td>
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<tr>
<td>Biomass burning</td>
<td>0.182</td>
</tr>
<tr>
<td>Municipal solid waste</td>
<td>1080.2</td>
</tr>
<tr>
<td>Cooking</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>1892.9</td>
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</table>
Table 2 Major gas-phase and heterogeneous pathway of producing nitrate in original CMAQ and newly added or revised heterogeneous reactions in improved CMAQ.

<table>
<thead>
<tr>
<th>Type</th>
<th>Reactions</th>
<th>No.</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Original CMAQ</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-phase chemistry</td>
<td>OH + NO₂ → HNO₃</td>
<td>R1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N₂O₅ + H₂O → 2HNO₃</td>
<td>R7</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>HO₂⁺ + NO₃ → 0.2HNO₃ + 0.8OH⁻ + 0.8NO₂</td>
<td>R8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₃⁻ + VOCs⁺→ HNO₃</td>
<td>R9</td>
<td></td>
<td></td>
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<tr>
<td>Heterogeneous chemistry</td>
<td>N₂O₅(g) + H₂O(aq) → 2H⁺ + 2NO₃⁻</td>
<td>R5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2NO₂(g) + H₂O(aq) → HONO(g) + H⁺ + NO₃⁻</td>
<td>R10</td>
<td></td>
<td></td>
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<tr>
<td><strong>Improved CMAQ</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Newly added or revised heterogeneous reactions</td>
<td>N₂O₅(g) + H₂O(aq) + Cl⁻(aq)→ ClNO₂(g) + NO₃⁻</td>
<td>R6</td>
<td>Bertram and Thornton (2009)</td>
<td>Revise R5</td>
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<tr>
<td></td>
<td>2NO₂(g) + Cl⁻→ ClNO(g) + NO₃⁻</td>
<td>R11</td>
<td>Abbatt et al. (1998)</td>
<td>Revise R10</td>
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<tr>
<td></td>
<td>NO₃(g) + 2Cl⁻→ Cl₂(g) + NO₃⁻</td>
<td>R12</td>
<td>Rudich et al. (1996)</td>
<td>Increase NO₃⁻</td>
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<tr>
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<td>O₃(g) + 2Cl⁻ + H₂O(aq) → Cl₂(g) + O₂(g) + 2OH⁻</td>
<td>R13</td>
<td>Abbatt et al. (1998)</td>
<td>Affect OH</td>
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<tr>
<td></td>
<td>2OH(g) + 2Cl⁻→ Cl₂(g) + 2OH⁻</td>
<td>R14</td>
<td>George et al. (2010)</td>
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<tr>
<td></td>
<td>ClONO₂(g) + Cl⁻→ Cl₂(g) + NO₃⁻</td>
<td>R15</td>
<td>Deiber et al. (2004)</td>
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<tr>
<td></td>
<td>HOCl(g) + Cl⁻ + H⁺→ Cl₂(g) + H₂O</td>
<td>R16</td>
<td>Pratte et al. (2006)</td>
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<td></td>
<td>ClNO₂(g) + Cl⁻ + H⁺→ Cl₂(g) + HONO(g) (pH &lt; 2.0)</td>
<td>R17</td>
<td>Riedel et al. (2012)</td>
<td>Affect OH</td>
</tr>
<tr>
<td></td>
<td>ClNO₂(g) + H₂O(aq)→ Cl⁻ + NO₃⁻ + 2H⁺ (pH ≥ 2.0)</td>
<td>R18</td>
<td>Rossi (2003)</td>
<td>Increase NO₃⁻</td>
</tr>
</tbody>
</table>

*: presents different VOCs species. In the SAPRC-11 mechanism, the VOCs species include CCHO (Acetaldehyde), RCHO (Lumped C3+ Aldehydes), GLY (Glyoxal), MGLY (Methyl Glyoxal), PHEN (phenols), BALD (Aromatic aldehydes), MACR (Methacrolein), IPRD (Lumped isoprene product species).
Table 3 Observed day (D) and night (N) NO$_3^-$ concentrations (Obs.) and predicted uptake coefficient of N$_2$O$_5$ ($\gamma_{N2O5}$) and nitrate concentrations (Pred.) using the parameterizations of $\gamma_{N2O5}$ by Bertram and Thornton (2009) (Scenario 1), Davis et al., (2008) (Scenario 2) and the upper-limit value derived by Zhou et al. (2018) (Scenario 3).

<table>
<thead>
<tr>
<th></th>
<th>NO$_3^-$</th>
<th>Scenario1</th>
<th>Scenario2</th>
<th>Scenario3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>$\gamma_{N2O5}$</td>
<td>Pred.</td>
<td>$\gamma_{N2O5}$</td>
</tr>
<tr>
<td>06/11-D</td>
<td>2.54</td>
<td>0.033</td>
<td>1.59</td>
<td>0.008</td>
</tr>
<tr>
<td>06/11-12-N</td>
<td>2.42</td>
<td>0.043</td>
<td>1.67</td>
<td>0.037</td>
</tr>
<tr>
<td>06/12-D</td>
<td>3.39</td>
<td>0.028</td>
<td>2.16</td>
<td>0.032</td>
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<tr>
<td>06/12-13-N</td>
<td>4.24</td>
<td>0.021</td>
<td>4.02</td>
<td>0.022</td>
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<tr>
<td>06/13-D</td>
<td>2.57</td>
<td>0.012</td>
<td>1.18</td>
<td>0.008</td>
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<tr>
<td>06/13-14-N</td>
<td>4.10</td>
<td>0.022</td>
<td>4.45</td>
<td>0.022</td>
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<tr>
<td>06/14-D</td>
<td>0.95</td>
<td>0.001</td>
<td>1.34</td>
<td>0.001</td>
</tr>
<tr>
<td>06/14-15-N</td>
<td>2.75</td>
<td>0.013</td>
<td>1.00</td>
<td>0.007</td>
</tr>
<tr>
<td>06/15-D</td>
<td>0.75</td>
<td>0.001</td>
<td>0.66</td>
<td>0.001</td>
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