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

Xionghui Qiu\textsuperscript{1,2}, Qi Ying\textsuperscript{3*}, Shuxiao Wang\textsuperscript{1,2*}, Lei Duan\textsuperscript{1,2}, Jian Zhao\textsuperscript{4}, Jia Xing\textsuperscript{1,2}, Dian Ding\textsuperscript{1,2}, Yele Sun\textsuperscript{4}, Baoxian Liu\textsuperscript{5}, Aijun Shi\textsuperscript{6}, Xiao Yan\textsuperscript{6}, Qingcheng Xu\textsuperscript{1,2}, Jiming Hao\textsuperscript{1,2}

\textsuperscript{1} State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University. Beijing 100084, China.
\textsuperscript{2} State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China
\textsuperscript{3} Zachry Department of Civil Engineering, Texas A&M University, College Station Texas, United States.
\textsuperscript{4} State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
\textsuperscript{5} Beijing Environmental Monitoring Center, Beijing 100048, China
\textsuperscript{6} Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China

*Corresponding author: shxwang@tsinghua.edu.cn & qying@civil.tamu.edu

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 HNO\textsubscript{3} and from different heterogeneous pathways. The results show that these heterogeneous reactions increase the atmospheric Cl\textsubscript{2} and ClNO\textsubscript{2} level, leading to an increase of the nitrate concentration by ~10\% in the daytime. However, these reactions also lead to a decrease the nocturnal nitrate by ~20\%. Sensitivity analyses of uptake coefficients show that the empirical uptake coefficient for the O\textsubscript{3} 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⁻ concentration dependence performs better to capture the concentration of ClNO₂ and nocturnal nitrate concentration. The reaction rate of OH and NO₂ in daytime increases by ~15% when the heterogeneous chlorine chemistry is incorporated, resulting in more nitrate formation from HNO₃ gas-to-particle partitioning. By contrast, the contribution of the heterogeneous reaction of N₂O₅ to nitrate concentrations decreases by about 27% in the nighttime when its reactions with chlorinated particles are considered. However, the generated gas-phase ClNO₂ from the heterogeneous reaction of N₂O₅ and chlorine-containing particles further decompose 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.

**Introduction**

In recent years, nitrate has become the primary component of PM₂·₅ (particulate matter with aerodynamic diameter less than 2.5μm) in Beijing with sustained and rapid reduction of SO₂ and primary particulate matter emissions (Ma et al., 2018; Li et al., 2018; Wen et al., 2018). Observations showed that the relative contributions secondary nitrate in PM₂·₅ 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 HNO₃, which happens mostly in the daytime. The reaction of OH with NO₂ produces gaseous HNO₃, which subsequently partition into the particle phase. The existence of NH₃ or basic particles enhances this process by NH₃–NH₄⁺ gas-particle equilibrium; (2) Hydrolysis of N₂O₅, which is more important at nighttime. N₂O₅ forms from the reactions of NO₂, O₃ and NO₃ and hydrolyzes to produce particulate nitrate. They can be summarized as reactions R1-R5 (Ying et al., 2011; Wang et al., 2018; Li et al., 2018):

\[
\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad \text{(R1)}
\]
However, current chemistry transport models (CTM, such as CMAQ, WRF-Chem etc.) still can’t accurately capture the spatiotemporal distributions of nitrate despite involving above chemical mechanism. For example, Chang et al. (2018) showed that the simulated nitrate concentrations derived from default CMAQ (version 5.0.2) were 1.79 to 1.95 times of the observations in summer at two sites adjacent to Beijing. Chen et al. (2017) found the high uncertainty (about 20%~50%) of simulated nitrate concentration using CMAQ in Dezhou city (Shandong province, adjacent to Beijing), which attributed to the unclear mechanism of nitrate formation. Fu et al. (2017) also found that default CMAQ (version 5.0.1) overestimated the simulated nitrate concentrations in Beijing-Tianjin-Hebei region.

Some studies attributed the overestimation of nitrate to the missing of chlorine chemical mechanism. According to the field measurements in June 2017 in Beijing (Zhou et al., 2018), the concentrations of reactive Cl2 and ClNO2 reached up to 1000 pptv and 1200 pptv, respectively, during some severe air pollution period in summer. The corresponding concentrations of N2O5 and nitrate rise up to 700pptv and 5μg m⁻³ from about 40 pptv and 1 μg m⁻³, which were significantly higher than those in coastal cities and the lower atmosphere in the remote Arctic region (Spicer et al., 1998; Li et al., 2017; Glasow et al., 2010; Liu et al., 2017). Some studies suggested that the reaction R5 should be revised as R6 due to the heterogeneous reaction of N2O5 on chlorine-containing particle surface (CPS)(Wang et al., 2017; Simon et al., 2010; Glasow et al., 2010):

\[
\text{N}_2\text{O}_5 + (1-\phi) \text{H}_2\text{O} + \phi \text{Cl} \rightarrow \phi \text{ClNO}_2 + (2- \phi)\text{NO}_3^- \quad (R6)
\]

where \( \phi \) represents the yield of ClNO2. By incorporating this reaction into WRF-Chem, Li et al. (2017) found that the improved model performed better to match the observed nitrate concentrations in Hongkong during 15 November and 5 December 2013. The generated gaseous nitryl chloride (ClNO2) 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 ClNO₂ produces atom
chlorine (Cl⁺); (2) the reaction of Cl⁺ with VOCs produces peroxy radical (HO₂ and
RO₂); (3) the increased HO₂ and RO₂ prompt the formation of OH by participating into
free radical cycle and NOₓ cycle (Young et al., 2014; Jobson et al., 1994).

The reaction of N₂O₅ is not the only heterogeneous reaction that influences the
nitrate formation. Some other heterogeneous reactions on CPS can also directly or
indirectly affect nitrate formation. For example, the heterogeneous uptake of NO₂ and
NO₃ on CPS can produce nitrate (Abbatt et al., 1998, Rudich et al., 1996). The reactions
of gaseous O₃, OH, HO₂, ClNO₂, hypochlorous acid (HOCl), chlorine nitrate (ClONO₂)
with CPS can produce Cl₂ and 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),
which can further accelerate the OH formation to affect the reaction R1. However, these
heterogeneous reactions are generally missing in most of the current CTMs.

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 result of PM₂.₅ 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 nature gas (obtained from official website of Beijing Municipal Bureau
cooking has received attention as its increasingly contribution to PM₂.₅ (accounting for
33% of residential sector; obtained from the official source apportionment analysis of
PM₂.₅ in Beijing in 2017; see http://www.bjepb.gov.cn/bjhr-b/index/index.html).
Moreover, high content of particulate sodium chloride was measured from the source
characterization studies of PM₂.₅ released from the cooking source (Zhang et al., 2016).
Thus, it’s important to ascertain the relationship between reactive chlorine species and
nitrate.
In this study, the Community Multi-scale Air Quality (CMAQ) model with an improved chlorine heterogeneous chemistry is applied to simulate summer nitrate concentration in Beijing. We then use the sensitivity analyses to evaluate the contribution of HNO$_3$ partitioning and heterogeneous production to nitrate formation. The results of this work can improve our understandings on nitrate formation and provide useful implications on the 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$_{10}$, BC, and OC. No data on chloride compound emissions were included. Recently, the inorganic hydrogen chloride (HCl) and fine particulate chloride (PCl) emission inventories for the sectors of coal combustion, biomass burning, and waste incineration were developed in 2014 (Qiu et al., 2017, 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 (about 75% from 2014 to 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, we develop a new emission inventory of reactive chlorine species, which includes HCl, Cl$_2$ and PCl for the year of 2017.

The emission factor method is applied to calculate the emissions of these reactive chlorine species, which can be expressed as following equations.

\[
E_{i,j} = \sum_{i,j} A_i \times EF_{i,j} \quad (1)
\]

\[
PCl: \quad E_{i,j} = \sum_{i,j} A_i \times EFi,j \times \eta \quad (2)
\]

where $E_{i,j}$ represents the emission of pollutant $j$ in $i$ sector. $A$ represents the activity data, $EF$ represents the emission factor. $\eta$ represents the content of PCl in PM$_{2.5}$.

In this study, the Cl$_2$ production is calculated based on the content of Cl in coal,
which had been measured by Deng et al (2017). In addition, the methods of emission
calculation on biomass burning, municipal solid waste (MSW) had been detailed
described by Fu et al. (2018), so we focus on demonstrating the calculation process of
cooking source.

The cooking emissions are separately estimated due to the differences of
calculation method between social cooking (including school, corporation and
restaurant etc.) and household cooking emissions, which are expressed as equation 3.

\[
E_f = \left( V_f \times H_f \times EF_f + V_c \times H_c \times N_c \times n \times EF_c \times (1 - \eta) \right) \times 365
\]  
(3)

where \( V_f \) is the volume of exhaust gas from household stove, which equals to 2000 m\(^3\)/h,
\( H_f \) is the cooking time for a family, which is set as 3h per day. \( EF_f \) is emission factor. \( H_c \)
is the cooking time for restaurant, which is set as 6h per day. The \( N_c \) is the number of
restaurant, school and government department. \( V_c \) is the volume of exhaust gas, which
is set as to 8000 m\(^3\)/h. \( n \) is the number of stove for each unit, which equals to 6 for
restaurant and is calculated as the number of students divide 150 for school. \( \eta \) is the
remove efficient of fume scrubbers, a constant of 30\% is chose.

Activity data, such as coal consumptions, population, crop yields, and production
of each industrial sector are obtained from Beijing Municipal Bureau of Statistics
(available at http://tjj.beijing.gov.cn/). This official data shows that coal combustion has
dramatically decrease from more than 2000 Mt from 2014 to 490 Mt in 2017, which
indicates that significant reduction of emissions of air pollutants. Part of localized data
of PCl, such as the content of PCl in PM\(_{2.5}\) discharged from cooking, power plant and
biomass burning (10\%, 1\% and 9.0\%, respectively), are obtained based on the localized
measurement. Others emission factors are obtained from the study by Fu et al. Finally,
the sectoral emissions of HCl, Cl\(_2\) and PCl, including power plant, industry, residential,
biomass burning, MSW and cooking, are estimated and listed in Table 1. Finally, estimated
HCl, Cl\(_2\) and PCl missions in Beijing are 1.89 Gg, 0.065Gg and 0.63Gg
respectively. Emissions of other species for this study period were derived by Ding et
al. (under-review; emissions are summerized in Table S1).

2.2 Chlorine-related heterogeneous reactions
In addition to reactions R1 and R5, gas phase reactions of NO3 with HO2 or VOCs (R8 and R9, see Table 2), N2O3 with H2O and the heterogeneous reaction of NO2 with water-containing particle are included in current CMAQ model (Zheng et al., 2015). However, these heterogeneous reactions in original CMAQ (version 5.0.1) are not related to chlorine species. This study revises the reactions R5 and R10 as R6 and R11 by considering the impact of heterogeneous uptake on CPS. In reaction R6, the yield of ClNO2 is represented as (Li et al., 2016):

$$\phi_{\text{ClNO2}} = \left(1 + \frac{[\text{H}_2\text{O}]}{483 \times [\text{Cl}^-]}\right)^{-1}$$  \hspace{1cm} (4)

where $\phi_{\text{ClNO2}}$ is the yield of ClNO2, [H2O] and [Cl] are the molarities of liquid water and chloride in aerosol volume (mol/m$^3$).

In addition, Laboratorial observations confirmed that heterogeneous uptakes of some oxidants (such as O3 and OH) and reactive chlorine species (such as ClNO2, HOCl, and ClONO2) could occur on CPS to produce Cl2 (R13-R18), which affected the atmospheric OH level after a series of chemical reactions. Note that the products from heterogeneous uptake of ClNO2 on CPS vary with particle acidity. It generates Cl2 under the condition of pH lower than 2 while produces nitrate when the pH is higher than 2. These heterogeneous reaction rates are parameterized as first-order reactions, with the rate of change of gas phase species concentrations determined by equations (2) (Ying et al., 2015):

$$\frac{dC}{dt} = -\frac{1}{\bar{c} \gamma A}C = -k^1C$$  \hspace{1cm} (5)

where $C$ represents the concentration of species, $\bar{c}$ represents its thermal velocity (m s$^{-1}$), $A$ represents aerosol surface area concentration (m$^2$ m$^{-3}$), $\gamma$ represents the uptake coefficient. Thus, $k^1$ is considered as a constant. The parameters of $A$ and $\bar{c}$ are calculated by CMAQ. Considering the consumption and generation of ClNO2, the concentration of ClNO2 can be calculated with equation (3):

$$\frac{d[\text{ClNO2}]}{dt} = -k^1[C\text{ClNO2}] + k^6 \phi_{\text{ClNO2}}[\text{N}_2\text{O}_5]$$  \hspace{1cm} (6)

Assuming $\phi_{\text{ClNO2}}$ is a constant, an analytical solution can be found for equation (7).
\[
[C\text{INO}_2] = [C\text{INO}_2]_0 \exp(-k_1^i t) + \frac{k_6^i \phi [N_2O_5]_0}{k_1^i - k_6^i} \left[ \exp(-k_6^i t) - \exp(-k_1^i t) \right]
\] (7)

Where \( k_1^i \) represents the reaction constant of reaction R17 or R18. The variable \( t \) represents the time.

The uptake coefficients \( \gamma \) of gaseous species are obtained from published laboratorial studies. In the original CMAQ, the uptake coefficient of \( N_2O_5 \) is determined as a function of the concentrations of \((\text{NH}_2)\text{SO}_4, \text{NH}_4\text{HSO}_4 \) and \( \text{NH}_4\text{NO}_3 \) (Davis et al., 2008). In this study, the PCI and \( N_2O_5 \) concentration dependent parameterization (eq. 8) by Bertram et al. for \( N_2O_5 \) is used instead (Bertram et al., 2009). For frozen particles, the uptake coefficient is limited to 0.02, as used in the original CMAQ model.

\[
\gamma_{N_2O_5} = \begin{cases} 
0.02, & \text{for frozen aerosols} \\
\frac{4 V}{v S} K_h K_f \left( 1 - \frac{1}{\frac{K_3[H_2O]}{K_2[N_2O_5]} + 1 + \frac{K_4(Cl^-)}{K_2[N_2O_5]}} \right)
\end{cases}
\] (8)

In the above equation, \( V \) represents the particle volume concentration \((\text{m}^3 \text{ m}^{-3})\); \( S \) represents the particle surface area concentration \((\text{m}^2 \text{ m}^{-3})\); \( v \) represents the thermal velocity of \( N_2O_5 \) \((\text{m} \text{ s}^{-1})\); \( K_h \) represents the dimensionless Henry’s law coefficient. \( K_f \) represents a parameterized function based on water concentration and \( K_s/K_2 \) and \( K_d/K_2 \) are constants obtained by fitting data. The uptake coefficient of \( \text{OH} \) is expressed with a function of the concentration of PCI following the IUPAC (International Union of Pure and Applied Chemistry) (available at http://iupac.poleether.fr/bt/docs/datasheets/pdf/O-H_halide_solutions_VI.A2.1.pdf).

\[
\gamma = \min(0.04 \times \frac{[Cl^-]}{1000 \times M}, 1)
\] (9)

where \( M \) represents the volume of liquid water in aerosol volume \((\text{m}^3/\text{m}^3)\).

The uptake coefficients of \( \text{O}_3, \text{NO}_3, \text{NO}_2, \text{HOCl}, \text{CINO}_2 \), and \( \text{ClONO}_2 \) are treated as constants. Among of them, the \( \gamma \) value of \( \text{NO}_3, \text{NO}_2, \text{HOCl} \) and \( \text{ClONO}_2 \) are set as \( 3 \times 10^{-3}, 1 \times 10^{-4}, 1.09 \times 10^{-3} \) and 0.16 based on the laboratory measurements (Rudich et al., 1996; Abbatt et al., 1998; Pratte et al., 2006; Gebel et al., 2001). A preliminary value of \( 3 \times 10^{-3} \) in the daytime and \( 1.0 \times 10^{-3} \) at nighttime is chosen for the \( \text{O}_3 \) uptake coefficient (Keene et al., 1999). The uptake coefficient of \( \text{CINO}_2 \) 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
These heterogeneous reactions of chlorine are incorporated into revised CMAQ (version 5.0.1) to simulate the distribution of nitrate concentration in Beijing in June. The gas phase chemical mechanism is based on the SAPRC-11 with a comprehensive gas-phase chemistry of chlorine (Cater et al., 2012; Ying et al., 2015). 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 (see Figure 3 for the inner most domain). The two true latitudes is set as 25°N and 40°E and the origin of the domain is set as 34°N, 110°E. The left-bottom coordinates of the outmost domain are positioned at x = -3114 km, y = -2448 km. The BASE case (simulation using default CMAQ) and HET case (with improved CMAQ) are compared to evaluate the impact of heterogeneous chlorine chemistry on nitrate formation.

3. Results

3.1 Model performance evaluation

Predicted hourly Cl$_2$, ClNO$_2$ and N$_2$O$_5$ concentrations were compared with observations measured at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39.98°N, 116.37E°) 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 Cl$_2$ and ClNO$_2$ in BASE case are rather low (close to 0), proving that the gas-phase chemistry is not the major pathway to produce Cl$_2$ and ClNO$_2$. By contrast, the simulated Cl$_2$ and ClNO$_2$ concentrations in HET case increase significantly, correspondingly the NMB and NME changes from -100% to -54% and 100% to 61% for Cl$_2$, and from -100% to -58% and 100% to 62% for ClNO$_2$, respectively (the parameter of total particle surface area (TOTSURFA) in CMAQ is revised by multiplying a factor of 5 in daytime and 10 in nighttime because this parameter is underestimated compared with the study of Zhou et al. (2018)).
simulations of Cl₂ and ClNO₂ are improved because the newly added heterogeneous reactions prompt the conversions of chlorine from particle state to gaseous state. Overall, the Cl₂ and ClNO₂ concentrations are still underestimated. The underestimation of Cl₂ may be associated with insufficient chemical conversion from ClNO₂ to produce Cl₂ at nighttime. The uncertainty in the uptake coefficient of O₃ in daytime could also be an important factor as we believe that the uptake of O₃ is the major source of Cl₂ during this period of time (see discussion in Section 3.2). According to equation (7), the underestimation of ClNO₂ concentration may be due to two factors, that is, reaction rate $K₆$ and N₂O₅ concentration. Because the N₂O₅ concentration is not substantially underestimated (see Figure 1(c)), we believe that the deviation of reaction rate $K₆$ is the curpit to result in the underestimation of ClNO₂, thus the uptake coefficient of N₂O₅ which significantly affects $K₆$ may be an important factor to affect the accuracy of ClNO₂ simualtion(see further discussion in Section 3.2). The improved CMAQ can accurately capture the diurnal variation of N₂O₅ concentration as well as the peak values (Figure 1(c)). In general, although the overall NMB and NME of BASE case (-20% and 38%) are slightly better than the HET case (-21% and 41%), the improved CMAQ (with the NMB and NME of -3% and 14%) perform better than original CMAQ (with the NMB and NME of -33% and 52%) in some period of heavy air pollution (such as the nighttime on 12 June and 13 June).

Predicted NO₃⁻ and PCI concentrations are compared with observations measured at an adjacent monitoring site located at the rooftop of School of Environment building in Tsinghua University (THU, 40.00N°, 116.34E°, 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), excluding the very high nitrate level in 13 June, the simulated nitrate concentration is commonly lower than the observations, probably as the result of the unreasonable NH₃ gas-particle partitioning model in our developed CMAQ model (Song et al., 2018). Comparing with the very high nitrate concentrations in 12 June and 13 June, we find that the simulated nitrate concentration using improved CMAQ is superior to use original CMAQ, while the nitrate level is higher in daytime and lower in nighttime, with the NMB and NME improve from -10% and 46% to -5%.
and 39%. Excluding the daytime on 15 June, the improved CMAQ also capture the hourly variation of PCl concentration and perform better than using original CMAQ, correspondingly the NMB and NME change from -48% and 72% to -37% and 67%.

The substantial underestimation of PCl in the daytime on 15 June is likely caused by some local emissions during this period.

3.2 Estimation of uptake coefficients of O₃ and N₂O₅

The uptake coefficients of O₃ and N₂O₅ may be important factors affecting the accuracy of simulated nitrate concentrations. Some studies have confirmed that the reaction of O₃ on CPS can indirectly affect the nitrate formation by increasing the atmospheric Cl₂ 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 Cl₂, which may be associated with the underestimation of the uptake coefficient of O₃. The uptake coefficient of O₃ used in this study is empirical and has 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 Cl₂ production and nitrate formation. Figure 2 shows that the simulated Cl₂ and nitrate concentrations in daytime increase significantly (especially for Cl₂) and sometimes can capture the peak value (such as the daytime peak on 14 June). However, although the NMB and NME of Cl₂ and nitrate improve from -18% and 39% to 1% and 28% when the new uptake coefficients are used, the simulated Cl₂ 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 O₃ that consider the influence of PCl concentrations, meteorology conditions, etc., similar to those of OH and N₂O₅, might be needed. Further laboratory studies should be conducted to confirm this conclusion.

As described above, the uptake coefficient of N₂O₅ can be expressed in multiple forms. In addition to the parameterization of Bertram et al. (2009) used in the HET case, two additional simulations were performed to assess the impact of uptake coefficient of N₂O₅ on nitrate formation: (1) using the original CMAQ parameterization of Davis et
al. (2008), and (2) the maximum value of 0.09 from the study by Zhou et al. (2018). The results show that the HET case has better agreement with the observations than the two additional simulations (Table 3). The Davis et al. parameterization is dependent on the concentration of nitrate and sulfate concentration, which is inferior to the coefficient used in this study. We conclude that a chlorine-related coefficient is more reasonable for the application of simulating reactive chlorine species and nitrate concentrations in high chlorine emission region. Using the uptake coefficient of 0.09 can generally increase the concentration of nitrate in some periods, but it also leads to significant overestimations of the nitrate level (such as nighttime on 12-13 June and 13-14 June).

3.3 Spatial distributions of nitrate and chlorine species concentrations

The distributions of averaged Cl$_2$, ClNO$_2$, N$_2$O$_5$ and NO$_3^-$ concentration from 11 to 15 June in the BASE case and HET case are shown in Figure 3. Compared to original CMAQ, the averaged concentrations of Cl$_2$ and ClNO$_2$ derived from improved CMAQ increase significantly in the eastern region of Beijing, reaching up to 23 ppt and 71 ppt from near zero. High concentrations are not found in in southern region with intensive emissions of chlorine species, implying that Cl$_2$ and ClNO$_2$ are easy to transport among cities.

The spatial distribution of N$_2$O$_5$ concentration in nighttime differs from that of other species. While the concentrations of most of the species are higher in the southern region, the N$_2$O$_5$ concentration is low 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. By incorporating the chlorine heterogeneous reaction, the N$_2$O$_5$ concentrations decrease by about 16% because more N$_2$O$_5$ is converted into nitrate. Although the added PCl prompts the conversion from N$_2$O$_5$ to nitrate, the nitrate concentration in these regions has not presented significant increase. In contrast, the nitrate concentration decreases significantly by about 22% due to the reduction of 2 mol NO$_3^-$ in R5 to 1 mol in R6 for each mole of N$_2$O$_5$ reacted. Although the generated ClNO$_2$ also further produces nitrate, the particle pH in most time is higher than 2 (see Figure S1) and the uptake coefficient of ClNO$_2$ is significantly lower than N$_2$O$_5$ (0.01~0.09 for N$_2$O$_5$ and $6 \times 10^{-3}$ for ClNO$_2$).
leading to an overall decrease of nitrate production.

3.4 Relationship between nitrate formation and chlorine chemistry

A CMAQ-tagged method (tagging the nitrate concentration produced by the heterogeneous reaction, the rest of nitrate is produced by HNO$_3$ partitioning) is used to estimate the nitrate production from heterogeneous pathways and HNO$_3$ partitioning pathways. In general, about 58.3% of nitrate originates from HNO$_3$ partitioning and 41.7% of nitrate are produced from heterogeneous reaction (Figure 4). This conclusion generally agrees with measurements at a nearby observation site in Peking University (PKU) (Wang et al., 2017), which indicates 52% from the heterogeneous process and 48% from HNO$_3$ partitioning. Two factors may lead to the differences between our simulation and the measurement at PKU. One is the chlorine heterogeneous chemistry and the other is the pollution level. More nitrate is expected to be produced by HNO$_3$ gas-to-particle partitioning in cleaner days whereas the heterogeneous process is more important in haze days. The averaged nitrate level at PKU site during the measurement was 14.2 μg m$^{-3}$, about 4 times higher than that in this study.

The production rates of gaseous HNO$_3$ from different gas-phase reactions and nitrate formation from different heterogeneous reaction pathways in the BASE case and HET case are further studied using process analysis. Figure 4 shows that the reaction of OH and NO$_2$ is always the major pathway to produce gaseous HNO$_3$ regardless of daytime or nighttime. However, its reaction rate decreases significantly from daytime to nighttime (from 1272 ppt h$^{-1}$ to 234 ppt h$^{-1}$ on average). The other HNO$_3$ production pathways in daytime can be ignored because their reaction rates are rather low. But at nighttime the reaction rate of N$_2$O$_5$ with water vapor presents a rapid increase, reaching up to 12.2 ppt h$^{-1}$ from 1.7 ppt h$^{-1}$, which accounts for approximately 5% of the HNO$_3$ formation in the gas phase. For the heterogeneous pathways, all of the reactions can be neglected in the daytime. At nighttime, the heterogeneous uptake of N$_2$O$_5$ on the particle surface is the major pathway to nitrate formation (about 3.07 μg m$^{-3}$ h$^{-1}$, account for 84.8% in heterogeneous formation). By contrast, heterogeneous uptake of NO$_2$ on particulate H$_2$O has less contribution to nitrate (15.2%).
When the chlorine chemistry is included, the gaseous HNO₃ produced by OH reacting with NO₂ increases significantly (up to 1487 ppb h⁻¹ in the daytime and 253 ppt h⁻¹ at nighttime) 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 simulation. Note that the reaction of NO₃ with HO₂ does not increase obviously even through the chlorine chemistry also leads to higher atmospheric HO₂ levels (increase by more than 20%, Li et al., (2016)) because the atmospheric NO₃ radical level is rather low. The heterogeneous production of nitrate from the reaction of N₂O₅ uptake decreases dramatically (about 27%) due to the inclusion of heterogeneous reactions of chlorine species. 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 decomposition to nitrate production increases by 6% in the HET case. Generally, the overall nitrate concentrations estimated by original CMAQ is about 22% higher than the modified CMAQ during this study period.

4. Conclusions

Current chemistry transport models are evaluated to have high uncertainty in the simulation of nitrate, especially for the period of heavy air pollution. In this work, an improved CMAQ model incorporated with chlorine heterogeneous chemistry is developed to evaluate the impact of chlorine-related heterogeneous reaction on nitrate formation and quantify the contributions from gas-to-particle partitioning of HNO₃ and from different heterogeneous reactions.

This results show four meaningful conclusions: (1) the emission inventories of reactive chlorine species are important because it is the cornerstones of studying chlorine chemistry; (2) The sensitivity analysis shows that a non-constant parameterization of the uptake coefficients of O₃ that consider the influence of PCl concentrations, meteorology conditions, etc., might be needed, N₂O₅ uptake coefficient expressed as a function of the concentrations of chlorine can capture the nitrate concentration better than others; (3) Cl₂ and ClNO₂ are easy to transport among cities because high
concentrations of them are not found in southern region with intensive emissions of chlorine species. (4) more importantly, current CTMs without a complete treatment of the chlorine chemistry can significantly underestimate the nitrate level from HNO$_3$ partitioning due to underestimation of the reaction rate of OH with NO$_2$ and overestimate the heterogeneous formation due to missing chlorine heterogeneous chemistry.

This study aims to improve our understandings on the chlorine chemistry and its impact on nitrate formation, which can provide useful implications on the nitrate pollution control strategies for those regions that suffered serious nitrate pollution.

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

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

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

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References


Figure captions

Figure 1. Comparison of simulated and observed Cl\(_2\), ClNO\(_2\), N\(_2\)O\(_5\), NO\(_3^-\) and PCl using original and improved CMAQ (the gray presents nighttime).

Figure 2. Comparison of simulated Cl\(_2\) and NO\(_3^-\) concentrations under different uptake coefficient of O\(_3\) (HET-Co: the scenario of uptake coefficients).

Figure 3. Spatial distributions of Cl\(_2\), ClNO\(_2\), N\(_2\)O\(_5\) and NO\(_3^-\) concentration in daytime and nighttime (a-b: concentrations of Cl\(_2\) and ClNO\(_2\) in HET case; c-d: the concentration of N\(_2\)O\(_5\) in HET case and difference between HET case and BASE case; e-f: the diurnal concentration of NO\(_3^-\) in HET case and difference between HET case and BASE case; g-h: the nocturnal concentration of NO\(_3^-\) in HET case and difference between HET case and BASE case).

Figure 4. Contributions of different gas-phase reaction pathways and heterogeneous reaction to nitrate formation.
Figure 1

(d) NO$_3^-$ concentration (μg m$^{-3}$)

(e) PCI concentration (μg m$^{-3}$)

Date: 6/12, 6/13, 6/14, 6/15
Figure 2
Figure 3

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Discussion started: 20 December 2018
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Note: the distribution of Cl₂ and ClNO₂ in HET minus BASE have not been shown because their concentrations in BASE case are rather low (close to 0).
Figure 4
Table 1 The sectoral emissions of HCl, Cl₂ and PCl. Unit: Mg

<table>
<thead>
<tr>
<th>Sector</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl</td>
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<tr>
<td>Power plant</td>
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<tr>
<td>Industry</td>
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<tr>
<td>Residential</td>
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<tr>
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<td>MSW</td>
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<td>Cooking</td>
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<tr>
<td>Total</td>
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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>
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<th>Type</th>
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<th>Comment</th>
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<td><strong>Original CMAQ</strong></td>
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<tr>
<td>Gas-phase chemistry</td>
<td>OH + NO₂ → HNO₃</td>
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<td></td>
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<tr>
<td></td>
<td>N₂O₅ + H₂O → HNO₃</td>
<td>R7</td>
<td></td>
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<tr>
<td></td>
<td>HO₂ + NO₃ → HNO₃ + OH + NO₂</td>
<td>R8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₃ + VOCsₘ → HNO₃</td>
<td>R9</td>
<td></td>
</tr>
<tr>
<td>Heterogeneous chemistry</td>
<td>N₂O₅(g) + H₂O (aq) → 2HNO₃(g)</td>
<td>R5</td>
<td></td>
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<tr>
<td></td>
<td>NO₂(g) + H₂O (aq) → HONO(g) + HNO₃(g)</td>
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<tr>
<td><strong>Improved CMAQ</strong></td>
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<tr>
<td>Newly added or revised heterogeneous reactions</td>
<td>N₂O₅(g) + H₂O(aq) + Cl⁻(aq) → ClNO₂ + NO₃⁻(aq)</td>
<td>R6</td>
<td>Revise R5</td>
</tr>
<tr>
<td></td>
<td>2NO₂(g) + Cl⁻(aq) → ClNO(g) + NO₃⁻(aq)</td>
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<td>Revise R10</td>
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<td>NO₃ + 2Cl⁻(aq) → Cl₂(g) + NO₃⁻(aq)</td>
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<td>Increase NO₃⁻</td>
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<td>2Cl⁻(aq) + O₃(g) + H₂O(aq) → Cl₂(g) + 2OH⁻(aq) + O₂(g)</td>
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<td>Affect OH</td>
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<td>ClONO₂(g) + Cl⁻(aq) + H⁺(aq) → Cl₂(g) + HNO₃(g)</td>
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<td>HOCl(g) + Cl⁻(aq) + H⁺(aq) → Cl₂(g) + H₂O(aq)</td>
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<td>CINO₂(g) + Cl⁻(aq) + H⁺(aq) → Cl₂(g) +</td>
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<td></td>
<td>HONO(aq) (PH &lt; 2.0)</td>
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<td></td>
<td>CINO₂(g) → Cl⁻ + NO₃⁻ + 2H⁺ (PH ≥ 2.0)</td>
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</table>

*: presents different VOCs species. In 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 The uptake coefficient of N$_2$O$_5$ in different Scenarios and its impact on nitrate (unit: μg m$^{-3}$) (uptake coefficient of N$_2$O$_5$ derives from Bertram et al. (Scenario 1), Davie et al. (Scenario 2), and Zhou et al. (2018), respectively)

<table>
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<td>(\gamma_{\text{N}_2\text{O}_5})</td>
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