Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

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

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

[1] State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University. Beijing 100084, China.

[2] State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

[3] Zachry Department of Civil Engineering, Texas A&M University, College Station Texas, United States.

[4] State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[5] Beijing Environmental Monitoring Center, Beijing 100048, China

[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_3 and from different heterogeneous pathways. The results show that these heterogeneous reactions increase the atmospheric Cl_2 and $ClNO_2$ 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_3 heterogeneous reaction with chlorinated particles may lead

to the large uncertainties in the predicted Cl_2 and nitrate concentrations. The N_2O_5 uptake coefficient with particulate Cl^- concentration dependence performs better to capture the concentration of $ClNO_2$ and nocturnal nitrate concentration. The reaction rate of OH and NO_2 in daytime increases by ~15% when the heterogeneous chlorine chemistry is incorporated, resulting more nitrate formation from HNO_3 gas-to-particle partitioning. By contrast, the contribution of the heterogeneous reaction of N_2O_5 to nitrate concentrations decreases by about 27% in the nighttime when its reactions with chloriated particles are considered. However, the generated gas-phase $ClNO_2$ from the heterogeneous reaction of N_2O_5 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 $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5μm) in Beijing with sustained and rapid reduction of SO_2 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 $PM_{2.5}$ 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_3, which happens mostly in the daytime. The reaction of OH with NO_2 produces gaseous HNO_3, which subsequently partition into the particle phase. The existence of NH_3 or basic particles enhances this process by NH_3–NH_4^+ gas-particle equilibrium; (2) Hydrolysis of N_2O_5, which is more important at nighttime. N_2O_5 forms from the reactions of NO_2, O_3 and NO_3 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):

$$OH + NO_2 \rightarrow HNO_3 \qquad (R1)$$

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

$$HNO_3 + NH_3 \rightarrow NH_4^+ + NO_3^- \quad (R2)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (R3)$$

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \quad (R4)$$

$$N_2O_5 + H_2O \rightarrow 2\ NO_3^- \quad (R5)$$

However, current chemistry transport models (CTM, such as CMAQ, WRF-Chem etc.) still can't accurately capture the spatiotemporal distributions of nitrate despite of 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 Cl_2 and $ClNO_2$ reached up to 1000 pptv and 1200 pptv, respectively, during some severe air pollution period in summer. The corresponding concentrations of N_2O_5 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 N_2O_5 on chlorine-containing particle surface (CPS)(Wang et al., 2017; Simon et al., 2010; Glasow et al., 2010):

$$N_2O_5 + (1-\phi)\ H_2O + \phi\ Cl^- \rightarrow \phi\ ClNO_2 + (2-\phi)NO_3^- \quad (R6)$$

where ϕ represents the yield of $ClNO_2$. 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 ($ClNO_2$) 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 atom chlorine ($Cl^{\bullet}$); (2) the reaction of $Cl^{\bullet}$ with VOCs produces peroxy radical (HO_2 and RO_2); (3) the increased HO_2 and RO_2 prompt the formation of OH by participating into free radical cycle and NO_X cycle (Young et al., 2014; Jobson et al., 1994).

The reaction of N_2O_5 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 NO_2 and NO_3 on CPS can produce nitrate (Abbatt et al., 1998, Rudich et al., 1996). The reactions of gaseous O_3, OH, HO_2, $ClNO_2$, hypochlorous acid (HOCl), chlorine nitrate ($ClONO_2$) with CPS can produce Cl_2 and subsequently photolyze to produce $Cl^{\bullet}$ (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 $PM_{2.5}$ 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 nature gas (obtained from official website of Beijing Municipal Bureau of Statistics, available at http://edu.bjstats.gov.cn/). But another important source—cooking has received attention as its increasingly contribution to $PM_{2.5}$ (accounting for 33% of 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, high content of particulate sodium chloride was measured from the source characterization studies of $PM_{2.5}$ 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 Multiscale 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 heterogonous 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 emissionswere 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.

HCl and Cl_2: $$E_{i,j} = \sum_{i,j} A_i \times EF_{i,j} \quad (1)$$

PCl: $$E_{i,j} = \sum_{i,j} A_i \times EF_{i,j} \times \eta \quad (2)$$

where $E_{i,j}$ represents the emission of pollutant j in i sector. A represents the activity data, EF represents the emission factor. η 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 caculation 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.

$$\mathrm{E}_j = \left(V_f \times H_f \times EF_f + V_c \times H_c \times N_c \times n \times EF_c \times (1-\eta)\right) \times 365 \qquad (3)$$

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. Eff is emission factor. Hc is the cooking time for restaurant, which is set as 6h per day. The Nc is the number of restaurant, school and government department. Vc 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. η 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

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

In addition to reactions R1 and R5, gas phase reactions of NO_3 with HO_2 or VOCs (R8 and R9, see Table 2), N_2O_5 with H_2O and the heterogeneous reaction of NO_2 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 $ClNO_2$ is represented as (Li et al., 2016):

$$\phi_{ClNO_2} = \left(1 + \frac{[H_2O]}{483 \times [Cl^-]}\right)^{-1} \tag{4}$$

where ϕ_{ClNO_2} is the yield of $ClNO_2$, $[H_2O]$ 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 O_3 and OH) and reactive chlorine species (such as $ClNO_2$, HOCl, and $ClONO_2$) could occur on CPS to produce Cl_2 (R13-R18), which affected the atmospheric OH level after a series of chemical reactions. Note that the products from heterogeneous uptake of $ClNO_2$ on CPS vary with particle acidity. It generats Cl_2 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):

$$\frac{dC}{dt} = -\frac{1}{4}(\bar{c}\gamma A)C = -k^{\mathrm{I}}C \tag{5}$$

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}), γ represents the uptake coefficient. Thus, k^{I} is considered as a constant. The parameters of A and $\bar{c}$ are calculated by CMAQ. Considering the consumption and generation of $ClNO_2$, the concentration of $ClNO_2$ can be calculated with equation (3):

$$\begin{aligned}\frac{d[\mathrm{ClNO_2}]}{dt} &= -k_{\mathrm{i}}^{\mathrm{I}}[\mathrm{ClNO_2}] + k_6^{\mathrm{I}}\phi_{\mathrm{ClNO2}}[\mathrm{N_2O_5}] \\ &= -k_{\mathrm{i}}^{\mathrm{I}}[\mathrm{ClNO_2}] + k_6^{\mathrm{I}}\phi_{\mathrm{ClNO2}}[\mathrm{N_2O_5}]_0\exp(-k_6^{\mathrm{I}}t)\end{aligned} \tag{6}$$

Assuming ϕ_{ClNO2} is a constant, an analytical solution can be found for equation (7).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

$$[\mathrm{ClNO_2}] = [\mathrm{ClNO_2}]_0 \exp(-k_\mathrm{i}^\mathrm{I} t) + \frac{k_6^\mathrm{I} \phi_{\mathrm{ClNO2}} [\mathrm{N_2O_5}]_0}{k_\mathrm{i}^\mathrm{I} - k_6^\mathrm{I}} \left[\exp(-k_6^\mathrm{I} t) - \exp(-k_\mathrm{i}^\mathrm{I} t)\right] \quad (7)$$

Where k_i^I represents the reaction constant of reaction R17 or R18. The variable t represents the time.

The uptake coefficients γ 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 $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 (Davis et al., 2008). In this study, the PCl and NO_3^- 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.

$$\gamma_{N_2O_5} = \begin{cases} 0.02, & for\ frozen\ aerosols \\ \frac{4}{v}\frac{V}{S} K_h K_f \left(1 - \frac{1}{\left(\frac{K_3[\mathrm{H_2O}]}{K_2[\mathrm{NO_3^-}]}\right) + 1 + \left(\frac{K_4[\mathrm{Cl^-}]}{K_2[\mathrm{NO_3^-}]}\right)}\right) \end{cases} \quad (8)$$

In the above equation, V represents the particle volume concentration ($m^3\ m^{-3}$); S represents the particle surface area concentration ($m^2\ m^{-3}$); v represents the thermal velocity of N_2O_5 ($m\ s^{-1}$); K_h represents the dimensionless Henry's law coefficient. K_f represents a parameterized function based on water concentration and K_3/K_2 and K_4/K_2 are constants obtained by fitting data. The uptake coefficient of OH is expressed with a function of the concentration of PCl following the IUPAC (International Union of Pure and Applied Chemistry) (available at http://iupac.poleether.fr/htdocs/datasheets/pdf/O-H_halide_solutions_VI.A2.1.pdf).

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

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

The uptake coefficients of O_3, NO_3, NO_2, HOCl, $ClNO_2$, and $ClONO_2$ are treated as constants. Among of them, the γ value of NO_3, NO_2, HOCl and $ClONO_2$ are set as 3×10^{-3}, 1×10^{-4}, 1.09×10^{-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 10^{-3} in the daytime and 10^{-5} at nighttime is chosen for the O_3 uptake coefficient (Keene et al., 1999). The uptake coefficient of $ClNO_2$ depends on the particle acidity, with the value of $2.65\ \times10^{-6}$ for reaction R17 and $6\ \times10^{-3}$ for reaction R18 (Robert et

al., 2008).

2.4 CMAQ model configuration

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 ºN and 40ºE and the origin of the domain is set as 34ºN, 110ºE. 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_2O_5 concentrations were compared with observations measured at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39.98N°, 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)). The

simulations of Cl_2 and $ClNO_2$ are improved because the newly added heterogeneous reactions prompt the conversions of chlorine from particle state to gaseous state. Overall, the Cl_2 and $ClNO_2$ concentrations are still underestimated. The underestimation of Cl_2 may be associated with insufficient chemical conversion from $ClNO_2$ to produce Cl_2 at nighttime. The uncertainty in the uptake coefficient of O_3 in daytime could also be an important factor as we believe that the uptake of O_3 is the major source of Cl_2 during this period of time (see discussion in Section 3.2). According to equation (7), the underestimation of $ClNO_2$ concentration may be due to two factors, that is, reaction rate K_6 and N_2O_5 concentration. Because the N_2O_5 concentration is not substantially underestimated (see Figure 1(c)), we believe that the deviation of reaction rate K_6 is the curprit to result in the underestimation of $ClNO_2$, thus the uptake coefficient of N_2O_5 which significantly affects K_6 may be an important factor to affect the accuracy of $ClNO_2$ simualtion(see further discussion in Section 3.2). The improved CMAQ can accurately capture the diurnal variation of N_2O_5 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 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, 40.00N°, 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 NH_3 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 O_3 and N_2O_5

The uptake coefficients of O_3 and N_2O_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 coefficient of O_3. The uptake coefficient of O_3 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 Cl_2 production and nitrate formation. 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 consider the influence of PCl concentrations, meteorology conditions, etc., similar to those of OH and N_2O_5, might be needed. Further laboratory studies should be conducted to confirm this conclusion.

As described above, the uptake coefficient of N_2O_5 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 N_2O_5 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 coffecient used in this study. We conclude that a chlorine-related coffecient 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_2O_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 sourthern 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_2O_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_2O_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_2O_5 concentrations decrease by about 16% because more N_2O_5 is converted into nitrate. Although the added PCl prompts the conversion from N_2O_5 to nitrate, the nitrate concentration in these regions has not presented significant increase. In contrast, the nitrate concentration decreases signficantly by about 22% due to the reduction of 2 mol NO_3^- in R5 to 1 mol in R6 for each mole of N_2O_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_2O_5 (0.01~0.09 for N_2O_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 signficantly 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_2O_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 N_2O_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_2O has less contribution to nitrate (15.2%).

When the chlorine chemistry is included, the gaseous HNO_3 produced by OH reacting with NO_2 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 NO_3 with HO_2 does not increase obviously even through the chlorine chemistry also leads to higher atmospheric HO_2 levels (increase by more than 20%, Li et al., (2016)) because the atmospheric NO_3 radical level is rather low. The heterogeneous production of nitrate from the reaction of N_2O_5 uptake decreases dramatically (about 27%) due to the inclusion of heterogeneous reactions of chlorine species. The contributions of NO_2 uptake to nitrate also decrease by 22% because of the lower rate constant of the reaction of NO_2 with PCl. In contrast, the contribution of $ClNO_2$ 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 HNO_3 and from different heterogeneous reactions.

This results show four meaningful conclusions: (1) the emission inventories of reactive chlorine species are important becase it is the cornerstones of studying chlorine chemistry; (2) The sensitivity analysis shows that a non-constant parameterization of the uptake coefficients of O_3 that consider the influence of PCl concentrations, meteorology conditions, etc., might be needed, N_2O_5 uptake coefficient expressed as a function of the concentrations of chlorine can capture the nitrate concentration better than others; (3) Cl_2 and $ClNO_2$ are easy to transport among cities because high

concentrations of them are not found in sourthern 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 understnadings 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 sufferred 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.

***Acknowledgements*.** This work was supported by National Natural Science Foundation of China (21625701), China Postdoctoral Science Foundation (2018M641385), National Research Program for Key Issue in Air Pollution Control (DQGG0301, DQGG0501) and National Key R&D Program of China (2018YFC0213805, 2018YFC0214006). The simulations were completed on the “Explorer 100” cluster system of Tsinghua National Laboratory for Information Science and Technology.

References

Abbatt, J. P., Waschewsky, G. C., et al.: Heterogeneous interactions of HOBr, HNO_3, O_3, and NO_2 with deliquescent NaCl aerosols at room temperature. J. Phys. Chem, A., 102, 3719-3725, 1998.

Bertram, T. H., Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride. Atmos. Chem. Phys., 9, 8351-8363, 2009.

Cater, W. P. L., Heo, G.: Development of revised SAPRC aromatics mechanisms. Final Report to the California Air Resources Board, Contracts No. 07-730 and 08−326, April 12, 2012

Chang, X., Wang, S., Zhao, B., et al.: Assessment of inter-city transport of particulate matter in the Beijing–Tianjin–Hebei region, Atmos. Chem. Phys., 18, 4843-4858, https://doi.org/10.5194/acp-18-4843-2018, 2018.

Chen, D.S., Liu, X.X., Lang, J.L., et al.: Estimating the contribution of regional transport to $PM_{2.5}$ air pollution in a rural area on the North China Plain. Sci. Total. Environ., 583, 280-291, 2017.

Davis, J. M., Bhave, P. V., Foley, K. M.: Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate. Atmos. Chem. Phys. 8, 5295-5311, 2008.

Deng, S., Zhang, C., Liu, Y., et al.: A Full-Scale Field Study on Chlorine Emission of Pulverized Coal-Fired Power Plants in China. Research of Environmental Science. In Chinese, 27, 127-133, 2014.

Deiber, G., George, C., Le Calve, S., Schweitzer, F., Mirabel, P.: Uptake study of $ClONO_2$ and $BrONO_2$ by Halide containing droplets. Atmos. Chem. Phys. 4, 1291-1299, 2004.

Faxon, C. B., Bean, J. K., Hildebrandt R.L.: Inland Concentrations of Cl_2 and $ClNO_2$ in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity. Atmosphere, 6, 1487-1506, 2015.

Fu, X., Wang, S.X., Xing, J., et al.: Increasing Ammonia Concentrations Reduce the Effectiveness of Particle Pollution Control Achieved via SO_2 and NO_X Emissions Reduction in East China. Environ. Sci. Technol. Lett. 4, 221-227, 2017.

Fu, X., Wang, T., Wang, S. X., et al.: Anthropogenic Emissions of Hydrogen Chloride and Fine Particulate Chloride in China. Environ. Sci. Technol. 52, 1644-1654, 2018.

George, I. J., Abbatt, J. P.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals. Nat. Chem. 2, 713-722, 2010.

Gebel, M. E., Finlayson-Pitts, B. J.: Uptake and reaction of $ClONO_2$ on NaCl and synthetic sea salt. J. Phys. Chem. A, 105, 5178-5187, 2001.

Glasow, V.R. Atmospheric chemistry: wider role for airborne chlorine. Nature. 464, 168-169. 2010.

Li, H.Y., Zhang, Q., Zheng, B., et al.: Nitrate-driven urban haze pollution during summertime over the North China Plain. Atmos. Chem. Phys.,18, 5293-5306, 2018.

Li, Q.Y., Zhang, L., Wang, T., et al. Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China. Atmos. Chem. Phys.,16, 14875-14890, 2016.

Liu, X. X., Qu, H., Huey, L. G., et al.: High Levels of Daytime Molecular Chlorine and Nitryl Chloride at a Rural Site on the North China Plain. Environ. Sci. Technol., 51, 9588-9595, 2017.

Liu, Y.M., Fan, Q., Chen, X.Y.: Modeling the impact of chlorine emissions from coal combustion and prescribed waste incineration on tropospheric ozone formation in China. Atmos. Chem. Phys., 18, 2709-2724, 2018.

Keene, W. C., Khalil, M. A. K., Erickson, D. J., et al.: Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory. J. Geophys. Res-Atmos., 104, 8429-8440, 1999.

Jobson, B. T., Niki, H., Yokouchi, Y., et al.: Measurements of C2-C6 hydrocarbons during the Polar Sunrise 1992 experiment: Evidence for Cl atom and Br atom chemistry, J. Geophys. Res., 99, 25355-25368, 1994.

Keene, W. C.; Pszenny, A. A. P.; Jacob, D. J.; Duce, R. A.; Galloway, J. N.; Schultz-Tokos, J. J.; Sievering, H.; Boatman, J. F.: The Geochemical Cycling of Reactive Chlorine through the Marine Troposphere. Global. Biogeochem., 4, 407-430, 1990.

Knipping, E. M., Lakin, M. J., Foster, K. L., Jungwirth, P., Tobias, D. J., Gerber, R. B., Dabdub, D., Finlayson-Pitts, B. J.: Experiments and simulations of ion-enhanced interfacial chemistry on aqueous NaCl aerosols. Science, 288, 301-306, 2000.

Ma, X.Y., Sha, T., Wang, J.Y., et al.: Investigating impact of emission inventories on $PM_{2.5}$ simulations over North China Plain by WRF-Chem. Atmos. Environ., 195, 125-140. 2018.

Pratte, P., Rossi, M. J.: The heterogeneous kinetics of HOBr and HOCl on acidified sea salt and model aerosol at 40-90% relative humidity and ambient temperature. Phys. Chem. Chem. Phys. 8, 3988-4001, 2006.

Qiu, X.H., Chai, F.H., Duan, Lei., et al.: Deriving High-Resolution Emission Inventory of Open Biomass Burning in China based on Satellite Observations. Environ. Sci. Technol., 50, 11779-11786, 2017.

Rudich, Y., Talukdar, R.K., Ravishankara, A.R., et al.: Reactive uptake of NO3 on pure water and ionic solutions. J. Geophy. Res. 101, 21023-21031, 1996.

Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A. R.: N_2O_5 oxidizes chloride to Cl_2 in acidic atmospheric aerosol. Science, 321, 1059-1059, 2008.

Simon, H., Kimura, Y., McGaughey, G., et al.: Modeling heterogeneous $ClNO_2$ formation, chloride availability, and chlorine cycling in Southeast Texas. Atmos. Environ., 44, 5476-5488, 2010.

Spicer, C.W., Chapman, E.G., Finlayson-Pitts., et al.: Unexpectedly high concentrations of molecular chlorine in coastal air. Nature, 394, 353-356, 1998.

Song, S. J., Gao, M., Xu, W. Q.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models. Atmos. Chem. Phys., 18, 7423-7438, 2018.

Wang, H.C., Lu, K.D., Chen, X.R., et al.: High N_2O_5 concentrations observed in urban Beijing: implications of a large nitrate formation pathway. Environ. Sci. Technol. Lett. 4, 416-420, 2017.

Wang, H.C., Lu, K.D., Chen, X.R., et al.: Fast particulate nitrate formation via N_2O_5 uptake aloft in winter in Beijing. Atmos. Chem. Phys., 18, 10483-10495, 2018.

Wen, L., Xue, L.K., Wang, X.F., et al.: Summertime fine particulate nitrate pollution in the North China Plain: increasing trends, formation mechanisms and implications for control policy. Atmos. Chem. Phys., 18, 11261-11275, 2018.

Ying, Q.: Physical and chemical processes of wintertime secondary nitrate aerosol formation. Front.Environ.Sci.Eng., 5, 348-361, 2011.

Ying, Q., Li, J. Y., Kota, S. H.: Significant Contributions of Isoprene to Summertime Secondary Organic Aerosol in Eastern United States. Environ. Sci. Technol., 49, 7834-7842, 2015.

Young, C.J., Washenfelder, R.A., Edwards, P.M., et al.: Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles. Atmos. Chem. Phys. 14, 3247-3440, 2014.

Zhang, T., Peng, L., Li, Y.H.: Chemical characteristics of $PM_{2.5}$ emitted from cooking fumes. Res. Environ. Sci., 29, 183-191, 2016. In Chinese.

Zheng, B., Zhang, Q., He, K.B., et al.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. Atmos. Chem. Phys., 15, 2013-2049, 2015.

Zhou, W., Zhao, J., Ouyang, B., et al.: Production of N_2O_5 and $ClNO_2$ in summer in urban Beijing, China., Atmos. Chem. Phys., 18,11581-11597, 2018.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

Figure captions

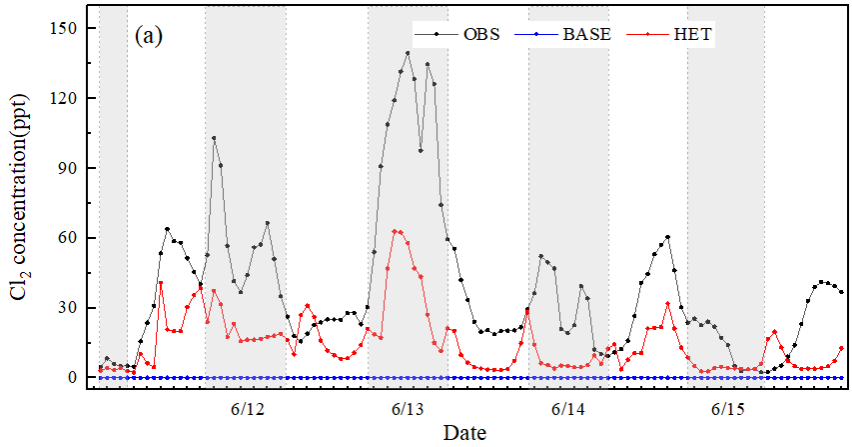
Figure 1. Comparison of simulated and observed Cl_2, $ClNO_2$, N_2O_5, NO_3^- and PCl using original and improved CMAQ (the gray presents nighttime)

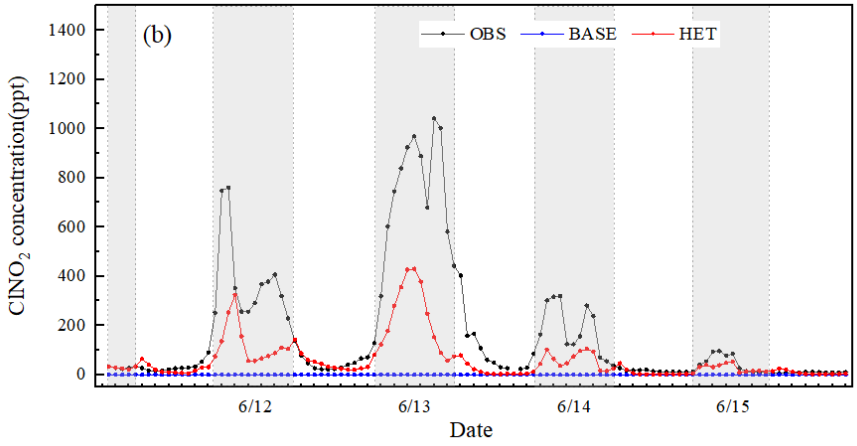
Figure 2. Comparison of simulated Cl_2 and NO_3^- concentrations under different uptake coefficient of O_3 (HET-Co: the scenario of uptake coefficients).

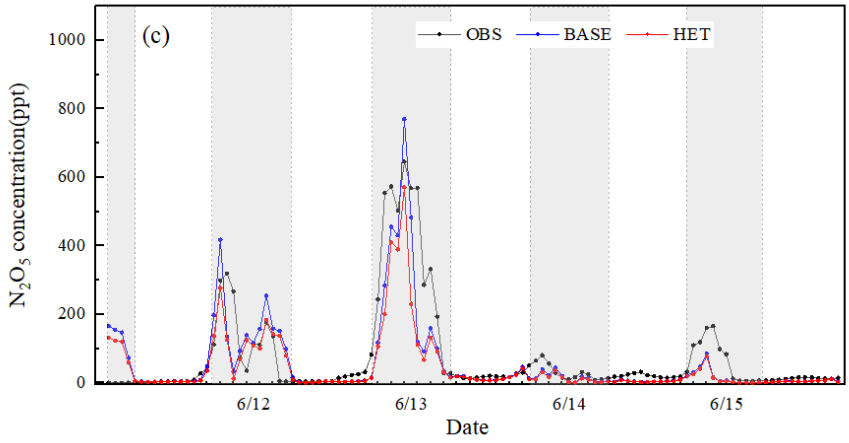
Figure 3. Spatial distributions of Cl_2, $ClNO_2$, N_2O_5 and NO_3^- concentration in daytime and nighttime (a-b: concentrations of Cl_2 and $ClNO_2$ in HET case; c-d: the concentration of N_2O_5 in HET case and difference between HET case and BASE case; e-f: the diurnal concentration of NO_3^- in HET 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.

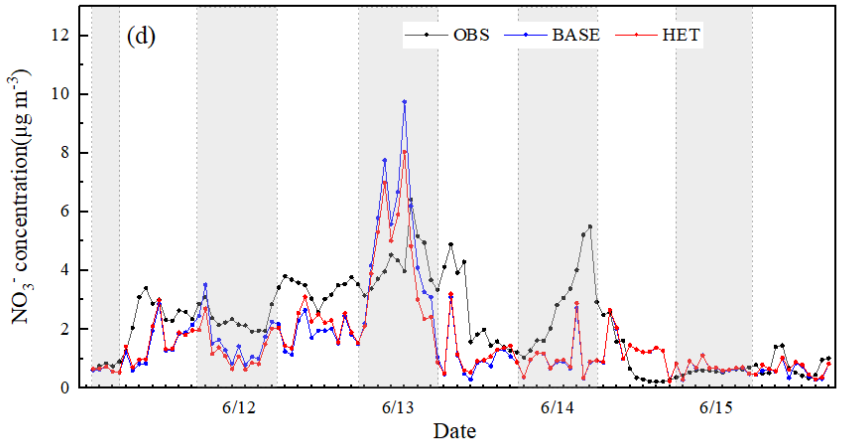
Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018







Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018



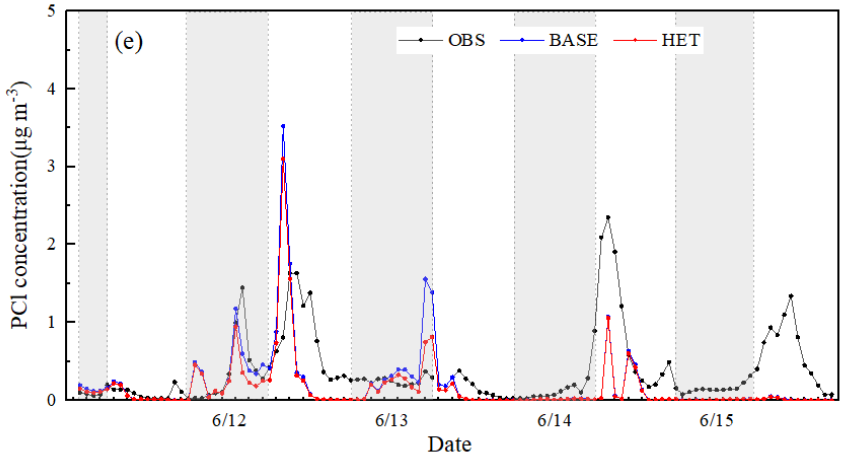


Figure 1

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

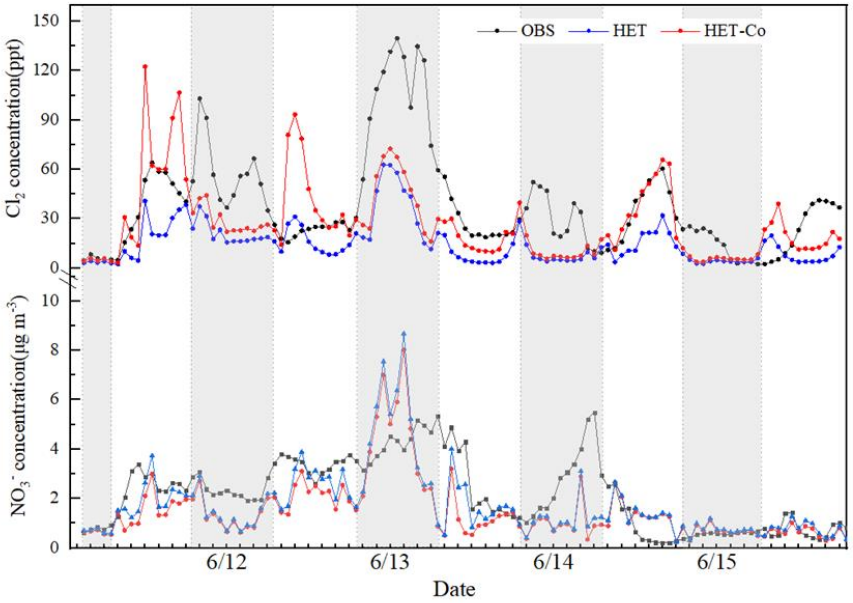


Figure 2

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

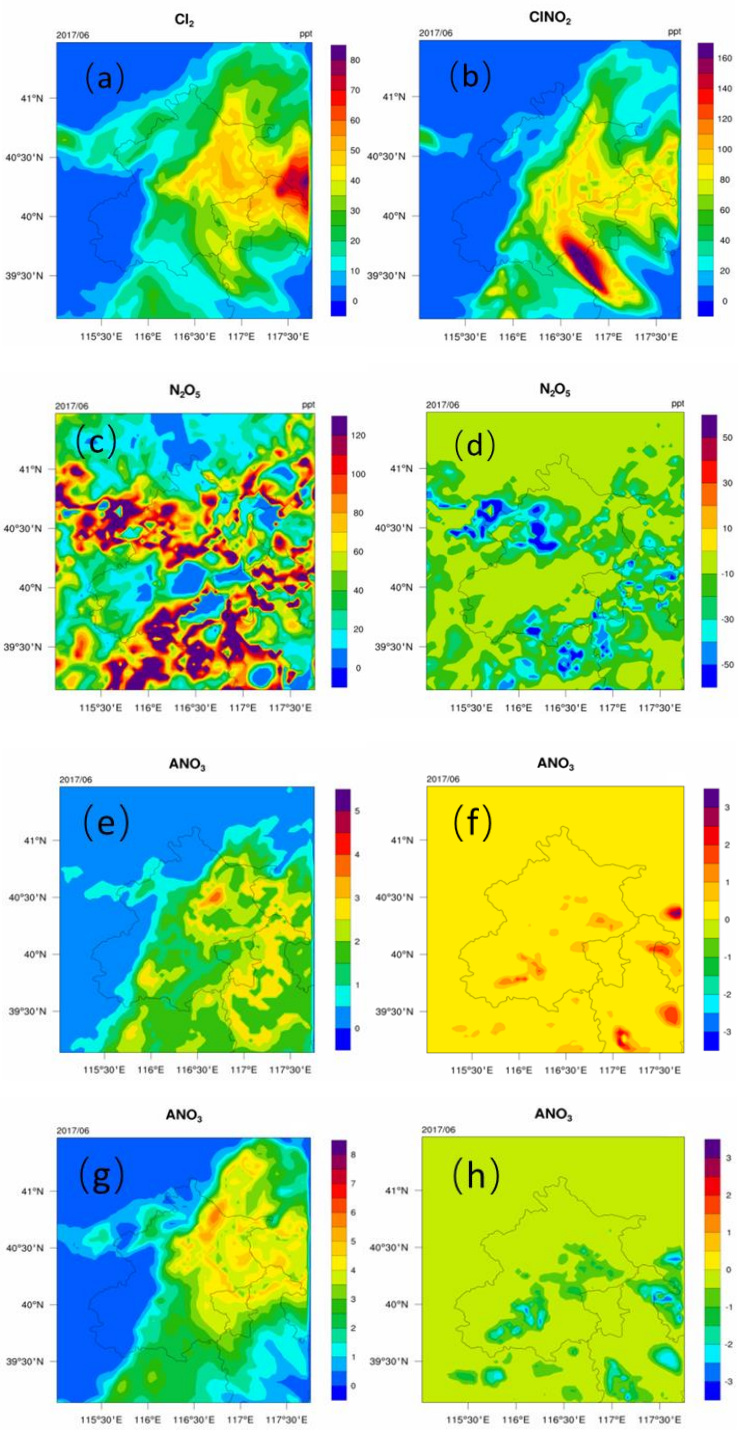


Figure 3

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

Note: the distribution of Cl_2 and $ClNO_2$ in HET minus BASE have not been shown because their concentrations in BASE case are rather low (close to 0)

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

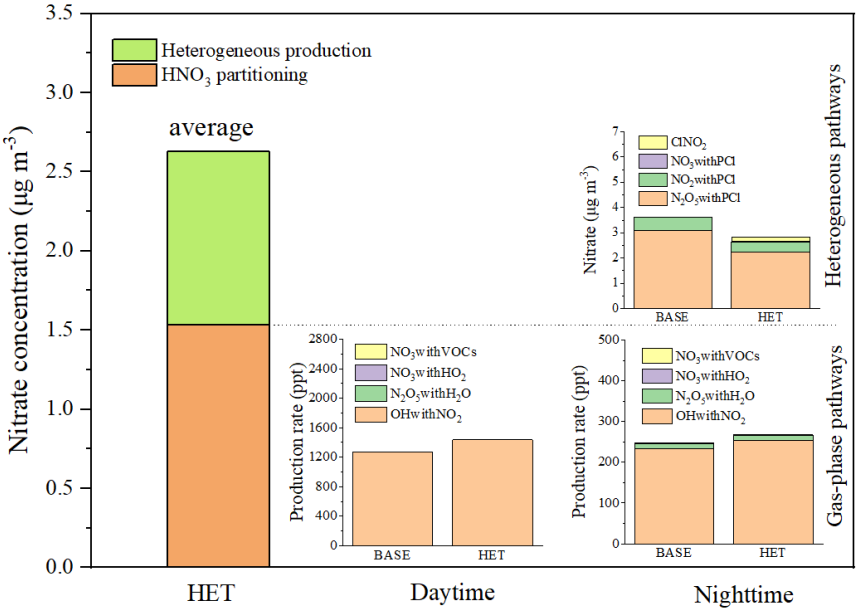


Figure 4

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

Table 1 The sectoral emissions of HCl, Cl_2 and PCl. Unit: Mg

Sector	Emissions		
	HCl	Cl_2	PCl
Power plant	22.8	1.2	6.75
Industry	587.3	20.1	89.2
Residential	202.4	8.1	34.7
Biomass buring	0.182	0	0.14
MSW	1080.2	0	8.47
Cooking	0	0	426.8
Total	1892.9	29.4	566.1

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

Table 2 Major gas-phase and heterogeneous pathway of producing nitrate in original CMAQ and newly added or revised heterogeneous reactions in improved CMAQ.

Type	Reactions	No.	Comment
Original CMAQ			
Gas-phase chemistry	$OH + NO_2 \rightarrow HNO_3$	R1	
	$N_2O_5 + H_2O \rightarrow HNO_3$	R7	
	$HO_2 + NO_3 \rightarrow HNO_3 + OH + NO_2$	R8	
	$NO_3 + VOCs^a \rightarrow HNO_3$	R9	
Heterogeneous chemistry	$N_2O_5\,(g) + H_2O\,(aq) \rightarrow 2HNO_3(g)$	R5	
	$NO_2(g) + H_2O\,(aq) \rightarrow HONO(g) + HNO_3(g)$	R10	
Improved CMAQ			
Newly added or revised heterogeneous reactions	$N_2O_5(g) + H_2O(aq) + Cl^-(aq) \rightarrow ClNO_2 + NO_3^-(aq)$	R6	Revise R5
	$2NO_2(g) + Cl^-\,(aq) \rightarrow ClNO(g) + NO_3^-(aq)$	R11	Revise R10
	$NO_3 + 2Cl^-\,(aq) \rightarrow Cl_2(g) + NO_3^-(aq)$	R12	Increase NO_3^-
	$2Cl^-(aq) + O_3(g) + H_2O(aq) \rightarrow Cl_2(g) + 2OH^-(aq) + O_2(g)$	R13	Affect OH
	$OH(g) + Cl^-(aq) \rightarrow Cl_2(g) + 2OH^-\,(aq)$	R14	Affect OH
	$ClONO_2(g) + Cl^-(aq) + H^+(aq) \rightarrow Cl_2(g) + HNO_3(g)$	R15	Affect OH
	$HOCl(g) + Cl^-(aq) + H^+(aq) \rightarrow Cl_2(g) + H_2O(aq)$	R16	Affect OH
	$ClNO_2(g) + Cl^-\,(aq) + H^+(aq) \rightarrow Cl_2(g) + HONO(aq)$ (PH < 2.0)	R17	Affect OH
	$ClNO_2(g) \rightarrow Cl^- + NO_3^- + 2H^+$ (pH ≥ 2.0)	R18	Increase NO_3^-

[a]: 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).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2018

Table 3 The uptake coefficient of N_2O_5 in different Scenarios and its impact on nitrate (unit: μg m^{-3}) (uptake coefficient of N_2O_5 detrives from Bertram et al. (Scenario1), Davie et al.(Scenario2), and Zhou et al.(2018), repectively)

		Scenario1		Scenario2		Scenario3	
	Obs	γ_{N2O5}	NO_3^-	γ_{N2O5}	NO_3^-	γ_{N2O5}	NO_3^-
06/11-D	2.54	0.033	1.59	0.008	1.32	0.09	2.17
06/11-12-N	2.42	0.043	1.67	0.037	1.37	0.09	2.12
06/12-D	3.39	0.028	2.16	0.032	2.74	0.09	3.13
06/12-13-N	4.24	0.021	4.02	0.022	4.05	0.09	6.04
06/13-D	2.57	0.012	1.18	0.008	1.06	0.09	2.47
06/13-14-N	4.10	0.022	4.45	0.022	4.45	0.09	7.13
06/14-D	0.95	0.001	1.34	0.001	1.33	0.09	1.64
06/14-15-N	2.75	0.013	1.00	0.007	0.96	0.09	2.33
06/15-D	0.75	0.001	0.66	0.001	0.66	0.09	1.11