



Significant impact of heterogeneous reactions of reactive chlorine species on summertime atmospheric ozone and free-radical formation in north China

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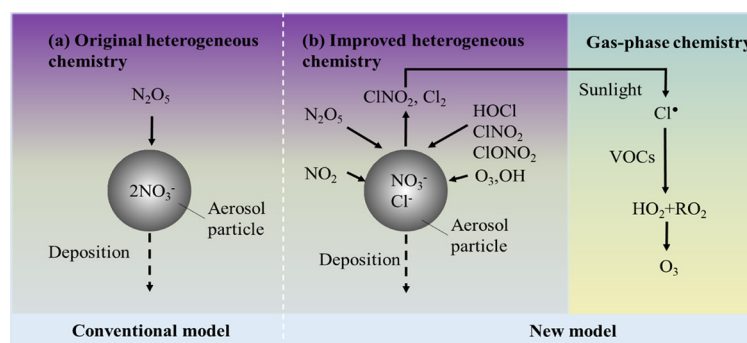
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HIGHLIGHTS

- This work represents the first high resolution regional modeling to quantify the impact of chlorine chemistry on the oxidation capacity in a polluted urban atmosphere.
- These heterogeneous reactions of reactive chlorine species increased the O₃, OH, HO₂ and RO₂ concentrations significantly for some regions in the Beijing-Tianjin-Hebei (BTH) area.
- The heterogeneous reactions of O₃ are the most important source of Cl₂ (81%).

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous reactions of N₂O₅, O₃, OH, ClONO₂, HOCl, ClNO₂, and NO₂, with chlorine-containing particles are incorporated in the Community Multiscale Air Quality (CMAQ) model to evaluate the impact of heterogeneous reactions of reactive chlorine species on ozone and free radicals. Changes of summertime ozone and free radical concentrations due to the additional heterogeneous reactions in north China were quantified. These heterogeneous reactions increased the O₃, OH, HO₂ and RO₂ concentrations by up to 20%, 28%, 36% and 48% for some regions in the Beijing-Tianjin-Hebei (BTH) area. These areas typically have a larger amount of NO_x emissions and a lower VOC/NO_x ratio. The zero-out method evaluates that the photolysis of ClNO₂ and Cl₂ are the major contributors (42.4% and 57.6%, respectively) to atmospheric Cl[•] in the early morning hours but the photolysis of Cl₂ is the only significant contributor after 10:00 am. The results highlight that heterogeneous reactions of reactive chlorine species are important to atmospheric ozone and free-radical formation. Our study also suggests that the on-going NO_x emission controls in the NCP region with a goal to reduce both O₃ and secondary nitrate can

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also have the co-benefit of reducing the formation Cl^\bullet from ClNO_2 and Cl_2 , which may also lead to lower secondary organic aerosol formation and thus the control of summertime $\text{PM}_{2.5}$ in the region.

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1. Introduction

Atmospheric chlorine radicals generated from chlorofluorocarbons (CFCs) are widely known for their active role in the destruction of the stratospheric ozone layer (Butchart and Scaife, 2001). While CFCs are generally non-reactive in the lower troposphere, high concentrations chlorine gas (Cl_2) and reactive chlorine species have been detected in coastal cities and major urban areas and even unexpectedly in the lower atmosphere in the remote Arctic region (Von Glasow, 2010; Osthoff et al., 2008; Liao et al., 2014). The Cl_2 and other reactive chlorine species, such as hypochlorous acid (HOCl), nitryl chloride (ClNO_2) and chlorine nitrate (ClONO_2), are expected to enhance the atmospheric oxidation capacity when they are photolyzed to generate the highly reactive chlorine radicals (Cl^\bullet) (see Table S1) (Thornton et al., 2010; Oum et al., 1998; Wang et al., 2005), accelerating the oxidation of volatile organic compounds (VOCs). The faster oxidation of VOCs by Cl^\bullet simultaneously enhances the production of O_3 and organic peroxy radicals (RO_2) as well as the recycling of hydroxyl (OH) and hydroperoxyl (HO_2) radicals (Wang et al., 2007; Graedel and Keene, 1995; Finley and Saltzman, 2006). In some field measurements, the occurrence of high concentrations of O_3 , OH , HO_2 and RO_2 are positively correlated with increasing Cl_2 and other chlorine compounds (Liu et al., 2017), indicating that tropospheric chlorine species are important in determining the overall atmospheric reactivity for O_3 formation.

Most current chemical transport models (CTMs) have difficulties in simulating the concentrations of chlorine compounds and thus correctly quantifying the effects of chlorine chemistry on atmospheric reactivity and O_3 formation because the models have inadequate representation of the chlorine chemistry, especially the heterogeneous reactions involving the particulate chloride (PCL) and the production of reactive gaseous chlorine species (Finlayson-pitts et al., 1989; Thornton and Abbatt, 2005). In most CTMs the heterogeneous uptake of dinitrogen pentoxide (N_2O_5) on aqueous aerosols and water droplets only leads to the production of particulate nitrate, regardless of the concentrations of PCL . However, recent studies suggest that N_2O_5 produces nitrate and ClNO_2 on chlorine-containing aerosol surfaces, such as sea salt particles (Li et al., 2016; Osthoff et al., 2008; Yu et al., 2010). Various studies added this reaction into the model and the reported increase in O_3 in regional photochemical modeling studies for northern China varied from 3 to 6% by Sarwar et al. (2014) to ~11.5% by Zhang et al. (2017). Box model simulations by Wang et al. (2016) for southern China and by Liu et al. (2017) for northern China concluded that ozone production rate increased by 11–41% and 19%, respectively. The cause of the large variations in the model assessments is unclear and needs to be further investigated.

In addition to ClNO_2 production through the N_2O_5 reaction, other heterogeneous reactions related to reactive chlorine species have been reported in the literature. For example, laboratory observations found that Cl_2 production could occur from irradiated mixtures of O_3 and PCL (Behnke and Zetzsch, 1989; Keene et al., 1990). Sander and Crutzen (1996) and Gebel and Finlayson-Pitts (2001) suggested that Cl_2 could also be produced by heterogeneous uptake of HOCl , OH , ClNO_2 and ClONO_2 on particle surface under different atmospheric conditions. Abbatt and Waschewsky (1998) concluded that gaseous NO_2 could also react with chlorine-containing aerosol to produce reactive chlorine species. These missing chlorine heterogeneous reactions contribute to the additional formation of Cl^\bullet from Cl_2 during daytime hours but the amount of Cl_2 that can be generated from these reactions and their

synergetic effects on O_3 and peroxy radical concentrations in a polluted urban atmosphere have not been subject to rigorous assessments using a unified comprehensive modeling framework.

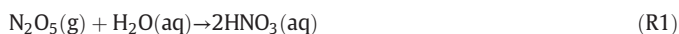
Atmospheric chlorine in polluted areas mainly originates from combustion sources. According to the chlorine emission inventory developed by the International Global Atmospheric Chemistry Program's Global Emissions Inventory Activity (GEIA) based on the year 1990, biomass burning (42%), coal combustion (37%), and waste incineration (21%) were the major sources of inorganic chlorine in China (Keene et al., 1999). A number of local measures also detect high content of PCL in $\text{PM}_{2.5}$ (particulate matter with an aerodynamic diameter $<2.5 \mu\text{m}$) from power plants, residential combustion, and biomass burning sources (Li et al., 2017; Qiu et al., 2016; Shen et al., 2010). Coal and biomass burning are regarded as the culprit of the severe air pollution events in north China. According to statistics (Cai et al., 2017), about 300 megatons (MT) of coal is consumed for industrial production and residential heating and nearly 40 MT of biomass is burned during post-harvest in north China in 2014. These two sources lead to 35 Gg of particulate chlorine emissions in the North China Plain region. Consequently, Liu et al. (2017) observed high concentrations of Cl_2 (up to 450 pptv) and ClNO_2 (~3640 pptv) in June 2014 in Wangdu, a city in the polluted NCP. Thus, it's necessary to explore the effects of high concentrations of Cl_2 , ClNO_2 and other reactive chlorine species on the atmospheric oxidation capacity in polluted urban areas.

In this study, a three-dimensional (3D) CTM, the Community Multiscale Air Quality (CMAQ) model, is improved to include a more complete description of the gas phase reactions of the chlorine species and the heterogeneous reactions associated with the production and destruction of these reactive chlorine species. The updated model is applied to study summer ozone concentrations in north China. This work represents the first regional CTM modeling study that includes a complete treatment of gas phase and heterogeneous chlorine chemistry to evaluate their impacts on chlorine of O_3 , HO_x ($\text{OH} + \text{HO}_2$) and organic peroxy radicals ($\text{RO}_2 = \text{RO}_2\text{C} + \text{RO}_2\text{XC} + \text{MEO}_2$) in north China. The results of this study also have significant implications for designing future emission control strategies.

2. Methods

2.1. Heterogeneous chemistry for reactive chlorine species

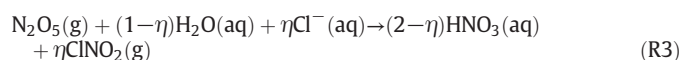
CMAQ version 5.0.1 is used as the framework to implement the chlorine mechanisms. The SAPRC-11 gas-phase chemical mechanism with an extension of comprehensive chlorine gas-chemistry is implemented in the model (detailed description in Table S1) (Ying et al., 2015). In the original CMAQ model, the heterogeneous uptake of N_2O_5 on wet aerosol surfaces occurs via reaction (R1):



In this study, gaseous ClNO_2 production on the chlorine-containing aerosols via reaction (R2) is considered (Roberts et al., 2009; Sarwar et al., 2012):



Reactions R1 and R2 are represented in the model as an overall reaction (R3):



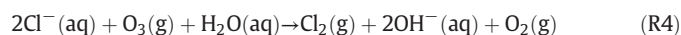
in which the parameter η represents the yield of ClONO_2 and is calculated by Eq. (1) (Bertram and Thornton, 2009):

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

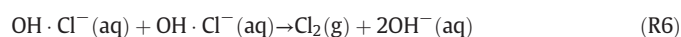
In the above formula, $[\text{H}_2\text{O}]$ and $[\text{Cl}^-]$ are the molarities of liquid water and chloride in aerosol volume (mol m^{-3}).

Additional heterogeneous reactions involving reactive chlorine species such as Cl_2 are included in the CMAQ model based on a literature search of experimental studies. A summary of these additional reactions is given below, followed by a discussion of the parameterization of their uptake coefficients.

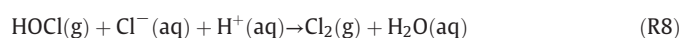
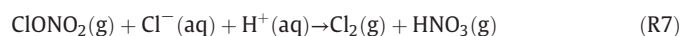
It was observed in previous experiments that the concentration of Cl_2 increased rapidly from irradiated mixtures of O_3 and chloride-containing aerosols (Knipping et al., 2000), which could be explained by the heterogeneous uptake of gas phase O_3 on the particle surface via reaction (R4):



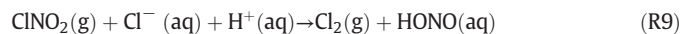
Knipping et al. (2000) suggested that the formation of Cl_2 in a chamber experiment that exposed chloride-containing aerosols to OH could be modeled with the heterogeneous reaction of gaseous OH with particulate Cl^- . The reaction intermediates $\text{OH} \cdot \text{Cl}^-$ subsequently self-reacts to produce Cl_2 , as shown in reactions R5 and R6 (Faxon et al., 2015; George and Abbatt, 2010):



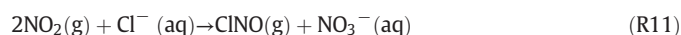
Heterogeneous reactions of ClONO_2 and HOCl at the acidic particle surface can also lead to Cl_2 production (Deiber et al., 2004; Pratte and Rossi, 2006), as shown in reactions R7 and R8, respectively:



For ClONO_2 , the production of Cl_2 was shown to follow reaction R9 in acidity condition ($\text{pH} < 2$) and decompose to produce PCI at higher pH as shown in R10 (Riedel et al., 2012; Rossi, 2003).



Lastly, as shown in reaction R11, the surface uptake of NO_2 on chlorinated particle surface was considered to produce gaseous ClNO (Abbatt and Waschewsky, 1998), an intermediate species which subsequently produces $\text{Cl} \cdot$ radicals through gas phase reactions (the reactions M03 and M21 in Table S1).



In summary, the heterogeneous reactions (R3–R11) involving gaseous N_2O_5 , O_3 , OH, ClONO_2 , HOCl , ClNO_2 , and NO_2 uptake on particle surface are included in the revised CMAQ model. These irreversible heterogeneous reactions are treated as gas phase diffusion limited first-

order reactions, with the overall reaction rate is parameterized according to Ying et al. (2015), as shown in Eq. (2),

$$R = -\frac{d\rho_m}{dt} = \frac{1}{4} \gamma v \rho_m S \quad (2)$$

where γ is the uptake coefficient of the gas phase species; v is its thermal velocity (m s^{-1}); ρ_m is the species concentration ($\mu\text{g m}^{-3}$) in the gas phase; and S is the aerosol surface area concentration ($\text{m}^2 \text{m}^{-3}$). The values of ρ_m and S are obtained from the gas and aerosol phase simulations, and the γ for air pollutants are based on the laboratory measurements reported in the literature, which are summarized below.

The uptake coefficient γ for N_2O_5 in the original CMAQ model was based on the parameterization of Davis et al. (2008), which increases with increasing of RH and decreasing of T and depends on the particulate concentrations of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4NO_3 . However, this parameterization does not include particle chlorine, which was shown to affect the uptake coefficient of N_2O_5 in several experimental studies (McDuffie et al., 2018; Sarwar et al., 2014). Thus, the parameterization by Bertram and Thornton (2009), as shown in Eq. (3), is used in this study,

$$\gamma_{\text{N}_2\text{O}_5} = \begin{cases} 0.02, & \text{for frozen aerosols,} \\ 3.2 \times 10^{-8} K_f \left[1 - \left(1 + \frac{6 \times 10^{-2} [\text{H}_2\text{O}]}{[\text{NO}_3^-]} + \frac{29 [\text{Cl}^-]}{[\text{NO}_3^-]} \right)^{-1} \right] & \end{cases} \quad (3)$$

In the above equation, K_f is a parameterized function based on molarity of water: $K_f = 1.15 \times 10^6 (1 - e^{-0.13[\text{H}_2\text{O}]})$. NO_3^- and Cl^- concentrations are also in molarity. The γ value of O_3 used in this study follows the suggestions by Keene et al. (Keene et al., 1990), with a daytime value of 10^{-3} and a nighttime value of 10^{-5} . Several laboratory measurements reported that the γ value of OH was strongly associated with RH and ranged from 0.1 to 0.2 (George and Abbatt, 2010; Laskin et al., 2006). The IUPAC (International Union of Pure and Applied Chemistry) recommends that OH heterogeneous uptake γ be parameterized as a function of the molarity of Cl^- (available at http://iupac.poleether.fr/htdocs/datasheets/pdf/OH_halide_solutions_V1.A2.1.pdf) as shown in Eq. (4):

$$\gamma = \min\left(0.04 \times \frac{[\text{Cl}^-]}{1000 \times M}, 1\right) \quad (4)$$

where M is the volume of liquid water in aerosol volume ($\text{m}^3 \text{m}^{-3}$). This equation was derived based on experiments using aqueous sea salt aerosol and is used in this study to calculate the uptake coefficient of OH on wet aerosol surfaces. HOCl reacts on aerosol with a γ ranging from 0.39×10^{-3} to 1.79×10^{-3} at a RH at 40%–85% (Pratte and Rossi, 2006). The average value of 1.09×10^{-3} is used in this work. The uptake coefficient of ClONO_2 used in this study is a constant value of 0.16 according to the suggestion of Gebel and Finlayson-Pitts (2001), which is lower than the initial uptake coefficient of up to 0.42 determined using fresh sea salt aerosols but higher than the lower limit of 0.02–0.04 for aged sea salt aerosols. The uptake coefficient of ClNO_2 for reaction R9 depends on particle acidity (Roberts et al., 2008). For neutral particles, the reported γ ranges from 0.3×10^{-6} to 5×10^{-6} , and the average value of 2.65×10^{-6} is used in this study. For acidic aerosols, a much higher value of γ (6×10^{-3}) is used. The γ of NO_2 takes a constant value of 10^{-4} , following the study of Abbatt and Waschewsky (1998).

2.2. Model setup

The CMAQ model with the modified heterogeneous chlorine chemistry is applied to simulate the regional concentrations of Cl_2 , PCI and related gaseous chlorine species (ClONO_2 , HCl and ClONO_2 ,

etc.) and evaluate the impact of chlorine chemistry on ozone and free radicals in northern China. The model setup, preparation of emissions (without chlorine) and meteorological inputs have been described in previous publications (Cai et al., 2017; Chang et al., 2017). Three-level nested domains with spatial resolutions of 36 km, 12 km, and 4 km are used in this work (for the innermost domain, see Fig. S2). The chloride emission inventory, including inorganic hydrogen chloride (HCl) and fine particulate chloride, is obtained from Fu et al. (2018). Two cases, a base case (BASE) without chlorine heterogeneous chemistry and a case with chlorine heterogeneous chemistry (HET) are compared to reveal the differences due to the inclusion of the heterogeneous reactions. In both cases, emissions of HCl and PCl and the extended gas-phase chlorine chemistry are included.

3. Results

3.1. Model performance evaluation

Predicted O₃, SO₂, NO₂ and PM_{2.5} concentrations from the BASE case simulation are evaluated against monitoring data in 13 major cities in the Beijing-Tianjin-Hebei (BTH) region (Table S2). The average NMB/NME values for O₃, NO₂ and PM_{2.5} across the 13 cities are -15%/31.5%, 0.5%/31% and -16%/32%, respectively, which are similar to the model performance reported in previous modeling studies in this region (Chang et al., 2017).

Simulated hourly Cl₂ and ClNO₂ concentrations from 12 to 30 June 2014, are compared with observations measured by Liu et al. (2017) using a Chemical Ionization Mass Spectrometer (CIMS) in Wangdu (38.67°N, 115.20°E). Fig. 1(a) and (b) show that the simulated Cl₂ and ClNO₂ concentrations in the BASE case are close to zero, indicating that emissions HCl and PCl and gas phase chlorine chemistry alone is not enough to explain the observed Cl₂ and ClNO₂ concentrations. By contrast, the HET case predicts significantly higher Cl₂ and ClNO₂ concentrations, which reduce the NMB and NME of both species (Table S3). However, the simulated Cl₂ mixing ratio is higher than the observations, while the simulated ClNO₂ mixing ratio is underestimated. The possible causes are further discussed in Section 4. Direct measurements of PCl are not available at this site. However, PCl measurements are available at the Liulihe monitoring site in Beijing (39.65°N, 116.25°E, about 120 km from the Wangdu site, see Fig. S2) from July 24 to July 31 in 2014. PCl predictions from both the BASE and HET simulations agree well with the observed high concentrations throughout the week (see Panel 1c). Time series of O₃ at Wanliu (a state controlling air sampling site in Beijing, 39.96°N, 116.30°E) are shown in Fig. 1(d) as an example to illustrate its hour-to-hour variations. On average, the HET case reduces the NMB and NME by 2.4%. Concentrations of another chlorine species ClONO₂ have not been measured in the troposphere. A plot of the episode average hourly ClONO₂ concentrations and a brief discussion is included in Fig. S1.

During the summer 2014 field campaign, N₂O₅ and HCl concentrations were not measured. In order to more comprehensively evaluate the model, an additional set of simulation was performed for June 11 to 15, 2017, during which N₂O₅, Cl₂, ClNO₂, and HCl concentrations were measured at the Institute of Atmospheric Physics (IAP) in urban Beijing (Fig. S2) by Zhou et al. (2018) using CIMS. For this episode, the averaged concentrations of ClNO₂, N₂O₅, and HCl are well represented by the model even though the concentrations are under-predicted. The detailed process sees our previous study (Qiu et al., 2019). The NMB/NME values for ClNO₂ in the HET case in Wangdu are -58%/64%, which are similar or slightly better than the those reported by Li et al. (2016) (-50%/109%) for southern China and Simon et al. (2009) (NME~-80%) for Houston, USA. That's because the emission of chloride compound in China is significant higher than that in USA.

3.2. Impacts of chlorine heterogeneous chemistry on ozone and free-radical

The heterogeneous production of Cl₂ and ClNO₂ also leads to increases in Cl• and OH radical concentrations, causing a significant increase in the oxidation capacity of the urban atmosphere. Fig. 2 shows the regional distribution of monthly concentrations of Cl•, O₃, OH, HO₂ and RO₂ from the HET simulation and the relative difference between the BASE and HET simulations for July 2014. The monthly average Cl• concentrations in the HET simulation ranges from 10³ to 10⁴ molecules cm⁻³. Significant increases in Cl• concentrations are found in most regions, as high as 3000–7000 times in eastern and southern areas of the Beijing-Tianjin-Hebei (BTH) region and 100–400 times in other areas, indicating the important role of chlorine heterogeneous chemistry on Cl• production. Although direct measurements of Cl• concentrations are not available, some other simulations using box-models constrained by observed Cl₂ and/or ClNO₂ roughly agree with the predictions from this study. For example, averaged concentration Cl• of about 4 × 10⁴ molecules cm⁻³ from 11 June to 1 July in 2014 in north China were predicted by Liu et al. (2017) and approximately 0.85 × 10⁴ molecules cm⁻³ of morning peak Cl• averaged from 15 May to 15 June in 2010 in Los Angeles were estimated by Young et al. (2014).

Higher concentrations of Cl• lead to higher concentrations of RO₂ and HO₂ radicals due to the reactions of Cl• with VOCs (M24-M31 in Table S1), as shown in Fig. 2(c–d) and (e–f). Higher relative increases of RO₂ (>40%) and HO₂ (>30%) occur in eastern and southern BTH where the RO₂ concentrations are low in the BASE case. These areas typically have a larger amount of NO_x emissions and thus a lower VOC/NO_x ratio (Cai et al., 2017; Zhao et al., 2018). The increased Cl₂ and Cl radical lead to faster VOC oxidation, and thus higher concentrations of HO₂ and RO₂ radicals. While these radicals can contribute to the ozone formation by recycling NO to NO₂, their impacts are highest in regions where O₃ formation is VOC-limited. In NO_x-limited regions, where O₃ formation rate is mostly controlled by the NO₂ photolysis rate, their impacts on O₃ are diminished. Spatial distributions of OH and its increase are similar to that of HO₂ with a relative increase of up to approximately 30% in the eastern and southern BTH areas, due to the sequential conversion from RO₂ and HO₂ and to OH. Fig. 2(i–j) show that O₃ concentrations from the HET case are higher than those from the BASE case. The higher relative increases (10%–25%) also occur in the southern BTH region.

Take an observation site with high growth rates of ozone and free radicals concentrations as an example (red circle in Fig. 2(j), located in Handan), hourly O₃, OH, HO₂ and RO₂ concentrations in July 2014 from the BASE and the HET cases are compared in Fig. 3 in order to have an insight into their association with Cl•. The temporal variations of O₃, OH, HO₂ and RO₂ concentrations are similar, with the highest values occur at 13:00–14:00 local time. Moreover, the relative difference of hourly O₃, OH, HO₂ and RO₂ between the HET and BASE case shows a bimodal distribution with two peaks on 7:00–8:00 and 18:00–19:00, with peak values of 45.7% and 22.8% (O₃), 88.9% and 30.1% (OH), 148% and 72.1% (HO₂), and 152% and 99.0% (RO₂). This bimodal distribution matches the bimodal distribution of the concentrations of Cl• (Fig. 4). At early morning with the appearance of sunlight, Cl• quickly increases due to the photolysis of Cl₂ and reactive chlorine species accumulated at night. Its reaction with VOCs prompts the production of O₃, OH, HO₂ and RO₂. However, the concentration of Cl• is quickly depleted and accordingly the relative changes of O₃, OH, HO₂ and RO₂ between the two cases reduce. Later during the day, stronger solar radiation and higher O₃ prompt and sustain the production of Cl• from Cl₂ leading to higher O₃ and radicals in the HET case. After 18:00, the photolysis rate of Cl₂ and reactive chlorine species recede, decreasing the growth rates of Cl•, O₃, OH, HO₂ and RO₂.

The hourly HONO concentrations are not available at this work. However, Tan et al. (2017) detected that the averaged concentration of HONO was about 0.8 ppb in the daytime and 1.5 ppb in the nighttime measured at Wangdu site from June 7 to July 8, 2014. By contrast, we find that the simulated HONO concentration estimated by original

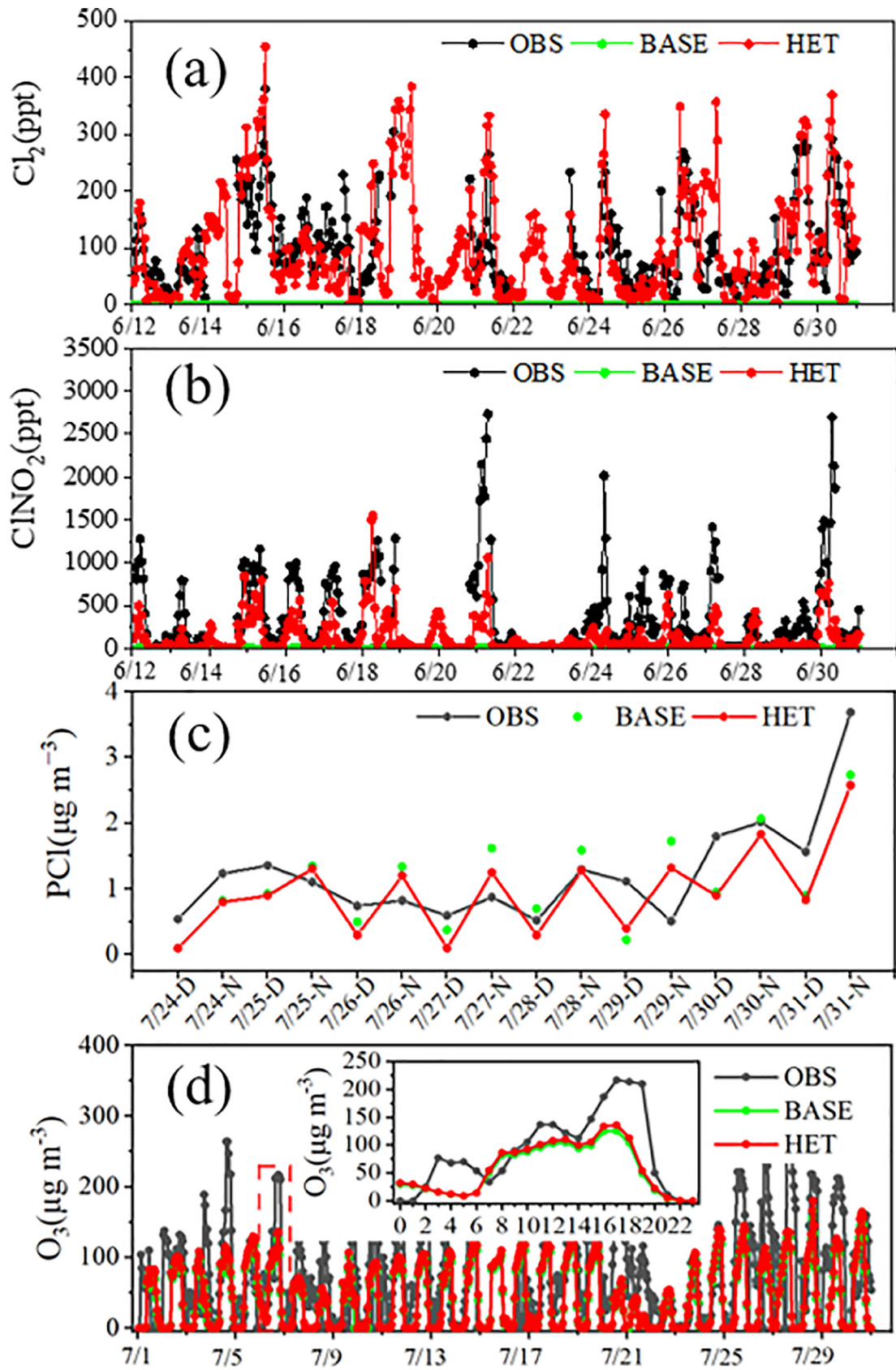


Fig. 1. Observed and simulated (a) hourly Cl_2 at Wangdu, (b) hourly $ClNO_2$ at Wangdu, (c) day and nighttime particulate chloride (PCI) at Liulihe and (d) hourly ozone at Wanliu using the original (BASE) and improved CMAQ (HET) (-D: daytime, -N: nighttime). The results of panels (a) and (b) are for June 12 to 30, 2014. The inset figure in panel (d) shows the hourly concentration time series on July 6.

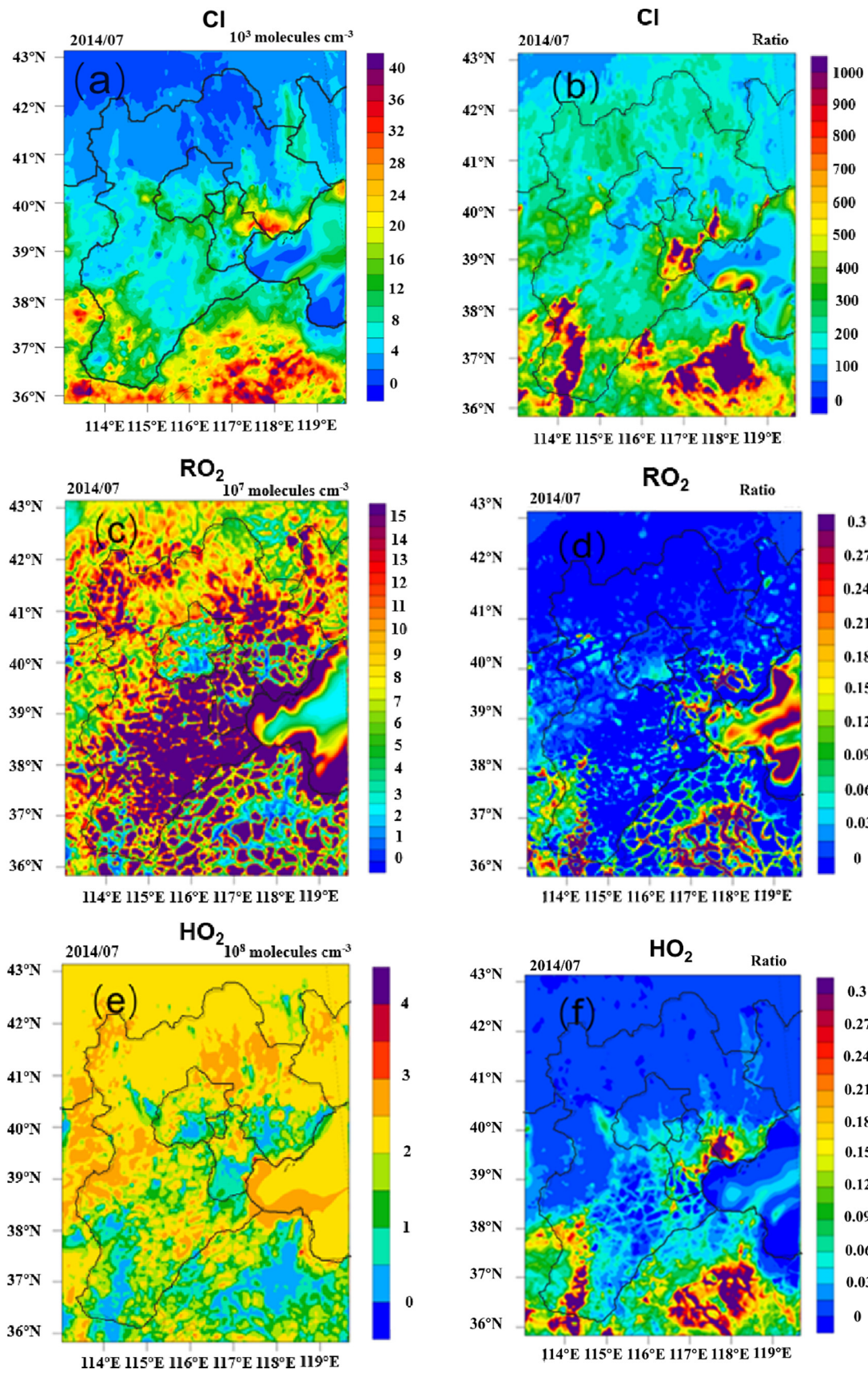


Fig. 2. Spatial distribution of simulated Cl, RO_2 , HO_2 , OH, and O_3 using improved CMAQ (HET case, left column) and the relative changes between original (BASE case) and improved CMAQ [(HET-BASE)/BASE, right column]. The results are based on averaged concentrations during the entire month of July 2014.

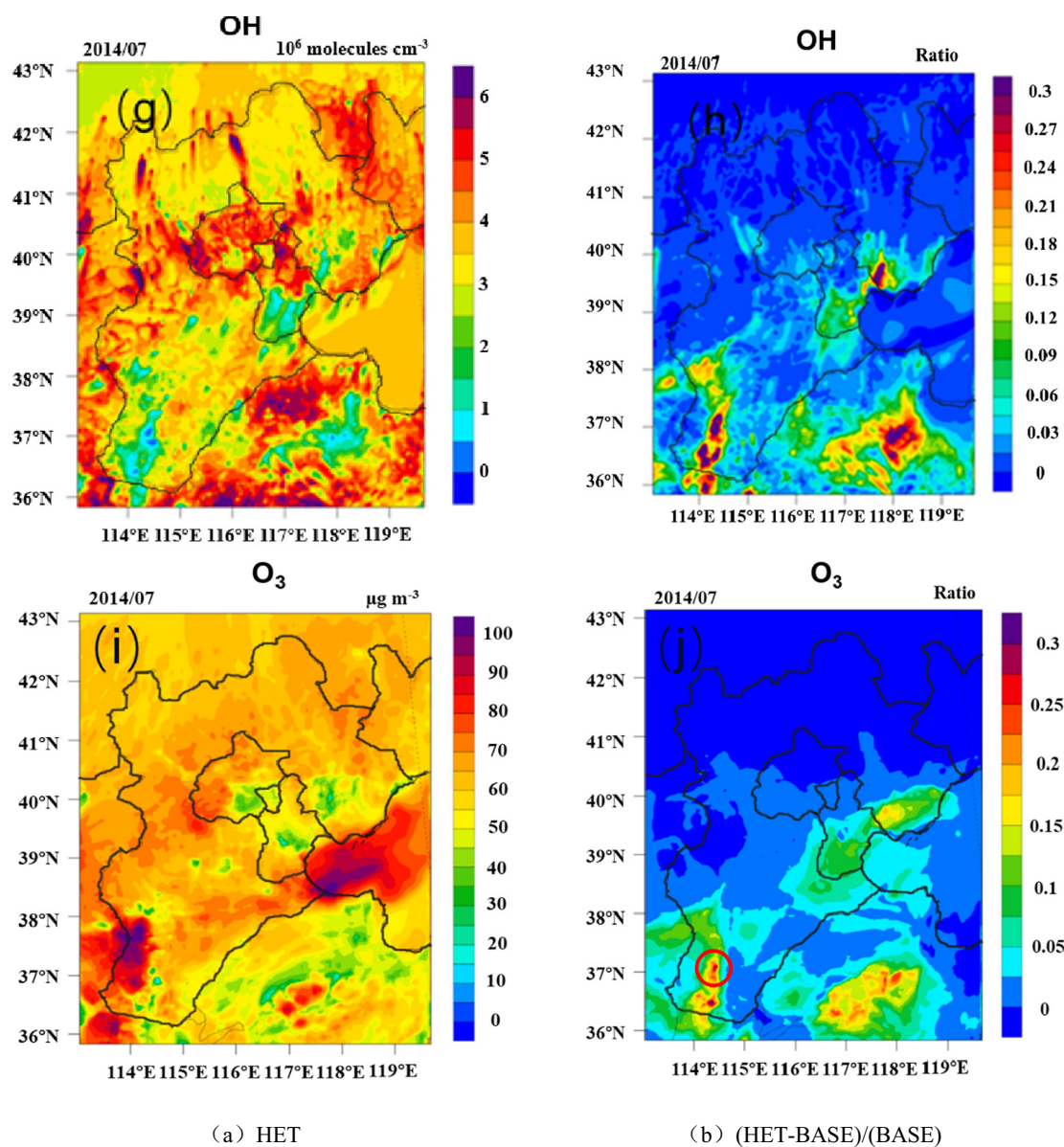


Fig. 2 (continued).

CMAQ is overestimated (about 3 ppb in the nighttime and 1 ppb in the daytime). Since the reaction of NO₂ with PCl is improved (NO₂ reacts with H₂O in original model), the simulated HONO concentration decreases to 1.2 ppb in nighttime and 0.7 ppb in the daytime, which indicates that this improved model is suitable for applying in this work. A sensitivity simulation is designed by revising the NO₂ with H₂O or not (aim to evaluate the difference of OH generated by HONO and ClNO photolysis). The results show that this improvement can elevate the OH concentration by about 1.3 times in the daytime but decrease by 2 times in the nighttime, concluding that this improvement is more favorable for producing OH in the daytime.

The impacts on peak hour O₃ levels is higher than the study by Sarwar et al. (2012) (~6%) and comparable to the study by Li et al. (2016) (~17%). This is expected because higher daytime Cl₂ and Cl• with the inclusion of these additional heterogeneous reactions lead to a large increase in the OH, HO₂ and RO₂ concentrations. Additionally, Sarwar et al. (2012) only evaluated the impact of sea-salt heterogeneous reactions on the improvement of O₃ concentration, the anthropogenic emission of chlorine species are not involved.

The nighttime increase of O₃ is mainly due to the increased O₃ during daytime hours. In regions without large direct NO emissions to titrate O₃ at night, elevated O₃ concentration can persist. Regional transport of higher O₃ from other regions (which are also due to daytime chlorine chemistry) can also lead to higher O₃ concentrations in downwind area at night. As the Cl₂ generated from heterogeneous reactions does not react at night based on the current mechanism, the slight increase of RO₂, HO₂ and OH at night shown in Fig. 3 is not due to chlorine chemistry. Instead, it is mainly due to increased gas phase O₃ reaction rates with unsaturated organic compounds such as alkenes and monoterpenes in the HET case.

3.3. Sources of chlorine radical

Previously, most literature reported that Cl• was originated from the photolysis of ClNO₂ (e.g. Young et al. (2014) and Li et al. (2016)). However, direct observations of Cl₂ made by Liu et al. (2017) showed that Cl₂ peaks at noon time with concentrations around 100 ppt, suggesting that the Cl₂ photolysis can be a major source of Cl•. While the contributions

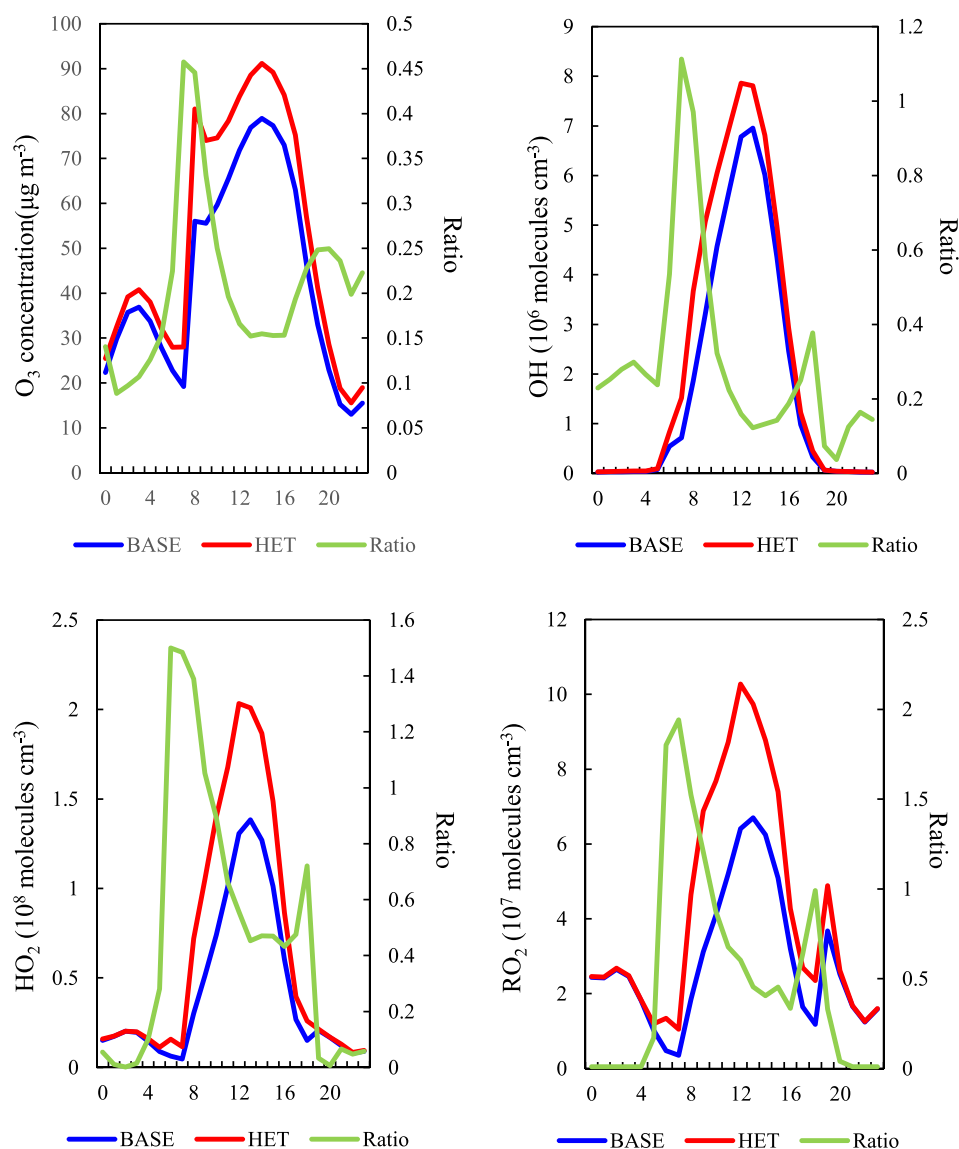


Fig. 3. Simulated averaged hourly O_3 , OH, HO_2 and RO_2 concentrations in July 2014 and the relative changes between original (BASE case) and improved CMAQ (HET case). Ratio = (HET-BASE)/BASE. The results are based on hourly concentrations at the position in the red circle in Fig. 2(j).

of $Cl\cdot$ from $ClNO_2$ and Cl_2 were estimated directly using observation data (Liu et al., 2017), previous modeling studies have not considered all heterogeneous reactions included in this study and thus could lead to more biases in their evaluation of the $Cl\cdot$ sources.

A zero-out method, which deactivates the heterogeneous reactions one at a time, is used to quantify the contributions to $Cl\cdot$ from the photolysis of Cl_2 (from heterogeneous uptakes of O_3 , OH, HOCl, $ClNO_2$, and $ClONO_2$), $ClNO_2$ (from heterogeneous uptake of N_2O_5) and $ClNO$ (from heterogeneous uptake of NO_2). The difference between a specific zero-out case and the HET case is considered as the contributions from the heterogeneous reaction that is turned off in the simulation. The non-linearity of these heterogeneous reactions on Cl_2 and $Cl\cdot$ is rather small. The sum of the contribution of each chemical reaction to $Cl\cdot$ using the zero-out method is generally equal to the total concentrations predicted by the HET case, with a relative difference of approximately 5%.

Fig. 4 shows that both the photolysis of $ClNO_2$ and Cl_2 are important contributors (42.4% and 57.6%, respectively) to atmospheric $Cl\cdot$ in the early morning hours from 5:00 to 8:00 but the photolysis of Cl_2 is the only significant source of $Cl\cdot$ after 10:00. This is because $ClNO_2$ production from N_2O_5 uptake mainly occurs at night and there is no

significant continuous source of $ClNO_2$ in the daytime due to low N_2O_5 concentrations. In contrast, Cl_2 forms continually because of excess O_3 . These results indicate that 3D CTM modeling studies without the O_3 heterogeneous reaction with PCl likely underestimated the atmospheric $Cl\cdot$ as well as OH, HO_2 , and RO_2 . It is worth mentioning that Cl_2 from the heterogeneous uptake of $ClNO_2$ is negligible because the pH of the particle seldom goes below 2 (Fig. S3), which is the acidity required for R9 to occur. The predicted high aerosol pH also agrees with a few field studies (Pan et al., 2018; Guo et al., 2017).

The contributions to Cl_2 from heterogeneous production of O_3 , OH, $ClNO_2$, $ClONO_2$, and HOCl on PCl are also quantified in July 2014. The heterogeneous reactions of O_3 (R4) are the most important source of Cl_2 (81%). The reactions of OH (R5–6, 6.4%) and $ClONO_2$ (R7, 7.4%) also have significant contributions. In general, heterogeneous reactions of $ClNO_2$ and HOCl have only small additional contributions to Cl_2 (2.2% and 3%, reactively). The photolysis of $ClNO_2$ from R3 is only important during the early morning hours (40%) but has almost negligible contributions during daytime hours (see Fig. 4). Since these additional reactions lead to significantly higher Cl_2 concentrations, previous works without these reactions likely significantly underestimated the $Cl\cdot$ and thus the impact

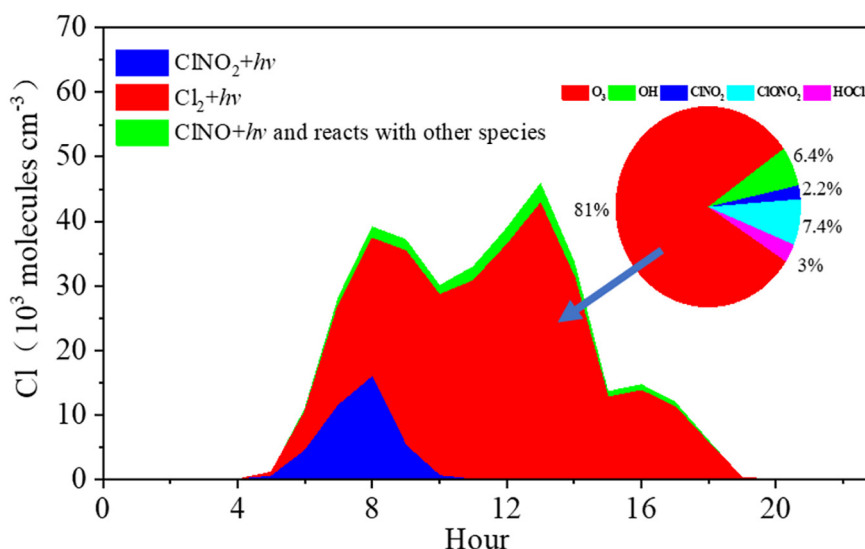


Fig. 4. Quantifications of hourly chlorine radical from the photolysis of Cl_2 , ClNO_2 and ClNO , and from other gaseous species at Wangdu. The contributions of heterogeneous reactions of O_3 , OH , ClNO_2 , ClONO_2 and HOCl to predicted Cl_2 concentrations are shown as the inset pie chart. The results are based on hourly concentrations at Wangdu in July 2014 for the HET case.

of chlorine on the oxidation of VOCs and the formation of RO_2 and HO_2 radicals from these reactions. As recent chamber studies showed that oxidation of VOCs by Cl could also be a potential source of secondary organic aerosol (Wang and Ruiz, 2017), neglecting these reactions could lead to underestimation of the contribution of Cl on SOA formation in the regional CTMs.

4. Discussion

4.1. Potential cause of model underpredictions and overpredictions of chlorine species

To the best knowledge of the authors, this study is the first study to compare modeled and observed Cl_2 in a polluted urban region using a 3D CTM. Simulated Cl_2 and ClNO_2 levels from the HET case are still substantially higher or lower than the observations. One of the uncertainties in the model parameters is the uptake coefficients. As N_2O_5 are important precursors of ClNO_2 , the sensitivity simulations that with the N_2O_5 parameterization from Davies et al. input are conducted, Fig. S4 shows that in both Wangdu and IAP, the alternative N_2O_5 parameterization from Davis et al. does not lead to much change in Cl_2 (neither in ClNO_2 , not shown in Fig. S4). The overprediction of Cl_2 may be associated with a very large uptake coefficient, e.g. the hypothetical value used in the present study (10^{-3} as suggested by Keene et al., 1990) have not been confirmed and is required to reproduce the observed level of Cl_2 in the ambient air.

Another important source of uncertainty is the particle surface area. The capability of the CMAQ model in predicting particle surface area (PSA) concentrations is much less studied than its ability in predicting particle mass concentrations. As there is no direct measurement of PSA at Wangdu, the predicted hourly particulate surface area at the IAP site are compared with measurements reported in Zhou et al. (2018), as shown in Fig. S5(a). The CMAQ model appears to significantly underpredicted PSA at night by a factor of 7–8 and a factor of 3–4 during the day even though the dry mass concentrations are well predicted. The CMAQ model might under-estimated the Aitken mode particles, which contributes little mass but could contribute more in surface area, or underestimate the water content of the aerosols, which can affect their size. On the other hand, the observed PSA was based on measured number size distribution and converted to wet PSA using growth factors, which may subject to large uncertainties as well. However, it is without question that PSA is underpredicted in the current study.

An additional sensitivity simulation is conducted by increasing the calculated surface area by a factor of 3 during the day (0800–2000) and a factor of 8 for the rest of the hours. This resulted in significantly higher ClNO_2 concentrations in both Wangdu and IAP (Fig. S5(b)) and improved model performance (Table S4). More studies are needed in the future to evaluate and improve the capability of the CMAQ model in predicting particle surface areas.

PCI and NO_x emission and transport can also affect the predicted Cl_2 and ClNO_2 concentrations. The NCP region has high PCI emissions and PCI in the HET case is not depleted (see Fig. S6), indicating that the PCI concentration is not a limiting factor in determining the Cl_2 , ClNO_2 , and other gaseous chlorine species. A sensitivity simulation which increases the PCI emission by a factor of 2 in the entire domain only leads to 5–10% increases in the Cl_2 and ClNO_2 concentrations. The NO_x emissions in the NCP region have been subjected to many previous studies and are relatively accurate (Cai et al., 2017). Model performance for NO_2 and other species in the NCP (see Table S2) further confirms this. Thus, it is expected that mixing and regional transport of NO_x are well captured in the model and is not a major factor that affects the accuracy of the predicted Cl_2 and ClNO_2 concentrations.

4.2. Implications

Taking the north China as an example, this work showed that the concentrations of ozone and free radicals can increase by various extents (averaged by 20%, 28%, 36% and 48% for O_3 , OH , HO_2 and RO_2 for some regions in southern BTH area) due to inclusion of seven heterogeneous reactions that generate reactive chlorine species, proving that chlorine heterogeneous chemistry has a significant impact on atmospheric ozone and free radical formation. In particular, the inclusion of several of these heterogeneous reactions on chlorinated particles that generate Cl_2 , especially the one with O_3 , can explain the observed Cl_2 concentrations and the strong correlation between elevated O_3 and Cl_2 concentrations in the field. These results suggest that previous 3D modeling studies without these reactions were likely significantly underestimated the Cl radical concentrations and thus the impact of chlorine on the oxidation of VOCs and the formation of RO_2 and HO_2 radicals from these reactions. Box model simulations constrained by observations should also be reexamined to assess the impact of these additional reactions.

In addition, recent chamber studies showed that oxidation of VOCs by Cl could also be a potential source of secondary organic

aerosol (Wang and Ruiz, 2017), neglecting these reactions could lead to underestimation of the contribution of Cl on SOA formation in the regional CTMs. Our study also suggests that the on-going NO_x emission controls in the NCP region with a goal to reduce both O₃ and secondary nitrate can also have the co-benefit of reducing the formation Cl• from ClNO₂ and Cl₂, which may also lead to lower secondary organic aerosol formation and thus the control of summertime PM_{2.5} in the region.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.133580>.

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