The impact of chlorine chemistry combined with heterogeneous N_2O_5 reactions on air quality in China

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Abstract: The heterogeneous reaction of N_2O_5 on Cl-containing aerosols (heterogeneous N_2O_5 + Cl chemistry) plays a key role in chlorine activation, NO_x recycling and consequently O_3 and $PM_{2.5}$ formation. In this study, we use the GEOS-Chem model with additional anthropogenic and biomass burning chlorine emissions combined with updated parameterizations for the heterogeneous N_2O_5 + Cl chemistry (i.e. the uptake coefficient of N_2O_5 (γ_{N2O5}) and the $ClNO_2$ yield (φ_{ClNO2})) to investigate the impacts of chlorine chemistry on air quality in China, the role of the heterogeneous N_2O_5 + Cl chemistry, as well as the sensitivity of air pollution formation to chlorine emissions and parameterizations for γ_{N2O5} and φ_{ClNO2}. The model simulations are evaluated against multiple observational datasets across China and show significant improvement in reproducing observations of particulate chloride, N_2O_5, and $ClNO_2$ when including anthropogenic chlorine emissions and updates to the parameterization of the heterogeneous N_2O_5 + Cl chemistry relative to the default model. The simulations show that total tropospheric chlorine chemistry could increase annual mean maximum daily 8-hour average (MDA8) O_3 by up to 4.5 ppbv but decrease $PM_{2.5}$ by up to 7.9 μg m^{-3} in China, 83% and 90% of which could be attributed to the effect of the heterogeneous N_2O_5 + Cl chemistry. The heterogeneous uptake of N_2O_5 on chloride-containing aerosol surfaces is an important loss pathway of N_2O_5 as well as an important source of O_3, and hence is particularly useful in elucidating the commonly seen ozone underestimations relative to observations. The importance of chlorine chemistry largely depends on both chlorine emissions and the parameterizations for the heterogeneous N_2O_5 + Cl chemistry. With the additional chlorine emissions, the simulations show that annual MDA8 O_3 in China could be increased by up to 3.5 ppbv. The corresponding effect on $PM_{2.5}$ concentrations varies largely with regions, with an increase of up to 4.5 μg m^{-3} in the North China Plain but a decrease of up to 3.7 μg m^{-3} in the Sichuan Basin. On the other hand, even with the same chlorine emissions, the effects on MDA8 O_3 and $PM_{2.5}$ in China could differ by 48% and 27%, respectively between different parameterizations.

1 Introduction

Chlorine (Cl) plays an important role in atmospheric chemistry in both the stratosphere and the troposphere, primarily via the reactions of Cl atom with various atmospheric trace gases including dimethyl sulfide, methane, and other volatile organic compounds (VOCs). The chemistry of Cl is quite similar with that of hydroxyl radicals (OH) while Cl atom reacts up to 2 orders of magnitude faster with some VOCs than OH (Atkinson et al., 2006). Studies have shown that Cl accounts for around 2.5% – 2.7% of the global CH_4 oxidation in the troposphere, and the contribution varies across regions, reaching up to 10% – 15% in Cape Verde and ~20% in east China (Lawler et al., 2011; Hossaini et al., 2016). Cl atom, therefore, is regarded as a potentially important tropospheric oxidant.

In general, Cl atom can be produced from the photo-dissociation and the oxidation of chlorinated organic species (e.g. CH_3Cl, CH_2Cl_2 and $CHCl_3$) and inorganic chlorine species (i.e. HCl and Cl_2) (Saiz-Lopez and Von Glasow, 2012; Simpson et al., 2015). Nitryl chloride ($ClNO_2$), formed through the heterogeneous reaction between dinitrogen pentoxide (N_2O_5) and chloride-containing aerosols (hereinafter referred to as the heterogeneous N_2O_5 + Cl chemistry), is found to be another important source of tropospheric Cl atoms in polluted regions (Liu et al., 2018; Haskins et al., 2019; Choi et al., 2020; Simpson et al., 2015). The heterogeneous formation of $ClNO_2$ and the subsequent photolysis can be described by reactions R1 – R4 shown below (Finlayson-Pitts et al., 1989; Osthoff et al., 2008). The net reactions of R1 (N_2O_5 hydrolysis on none-chloride-containing aerosols) and R2 (uptake of N_2O_5 on chloride-containing aerosols) could be expressed as R3, in which the $ClNO_2$ yield (i.e. φ_{ClNO2}, defined as the molar ratio of produced $ClNO_2$ to total reacted N_2O_5) represents the fraction of N_2O_5 reacting via R2.

$$N_2O_5\,(g) + H_2O\,(aq) \rightarrow 2\,HNO_3\,(aq) \quad \text{(R1)}$$

$$N_2O_5\,(g) + HCl\,(aq) \rightarrow HNO_3\,(aq) + ClNO_2\,(g) \quad \text{(R2)}$$

$$N_2O_5\,(g) + (1-\varphi)\,H_2O\,(aq) + \varphi\,HCl\,(aq) \rightarrow (2-\varphi)\,HNO_3\,(aq) + \varphi\,ClNO_2\,(g) \quad \text{(R3)}$$

$$ClNO_2\,(g) + h\nu \rightarrow Cl\,(g) + NO_2\,(g) \quad \text{(R4)}$$

Estimates based on model simulations have suggested that $ClNO_2$ provides a source of Cl atoms totaling

0.66 Tg Cl a^{-1}, with the vast majority (95%) being in the Northern Hemisphere (Sherwen et al., 2016). The relative contribution of $ClNO_2$ to global tropospheric Cl atoms is 14% on average and exhibits clear regional variations (Sherwen et al., 2016). For example, the study by Riedel et al. (2012) reported that the relative contribution is approximately 45% in Los Angeles based on a simple box model combined with local observations.

The heterogeneous formation of $ClNO_2$ also serves as a reservoir for reactive nitrogen at night. The rapid photolysis of $ClNO_2$ at daytime (R4) not only releases highly reactive Cl atom but also recycles NO_2 back to the atmosphere, which as well significantly affect the daytime photochemistry (Riedel et al., 2014). Previous global and hemispheric models found that the heterogeneous N_2O_5 + Cl chemistry could increase monthly mean values of the maximum daily 8h average (MDA8) O_3 concentrations by 1.0 – 8.0 ppbv in most Northern Hemisphere regions (Sarwar et al., 2014; Wang et al., 2019). The reaction also impacts secondary aerosol formation, mainly through the recycling of NO_x (Staudt et al., 2019; Mitroo et al., 2019). For example, Sarwar et al. (2014) estimated that $ClNO_2$ production decreases nitrate by 3.3% in winter and 0.3% in summer averaged over the entire Northern Hemisphere. The influence of the heterogeneous formation of $ClNO_2$ in China is even larger due to the polluted environment, leading to an increase in ozone concentrations by up to 7 ppbv, and a decrease in total nitrate by up to 2.35 μg m^{-3} on monthly mean basis (Li et al., 2016; Sarwar et al., 2014)

There are two key parameters that determine the uptake efficiency of N_2O_5 and production of $ClNO_2$, the aerosol uptake coefficient of N_2O_5 (γ_{N2O5}) and the ClNO2 yield (φ_{ClNO2}). The most widely used parameterization for γ_{N2O5} and φ_{ClNO2} was proposed by Bertram and Thornton (2009) (hereinafter referred to as BT09), which is based on the laboratory studies with considerations of aerosol water content, concentrations of nitrate and chloride, and specific surface area (i.e. the ratio of surface area concentrations to particle volume concentrations). However, recent field and model studies have shown that this parameterization would overestimate both γ_{N2O5} and $\varphi_{ClNO2,}$ especially in regions with high Cl levels (Mcduffie et al., 2018b; Mcduffie et al., 2018a; Xia et al., 2019; Chang et al., 2016; Hong et al., 2020; Yu et al., 2020). The discrepancies could be partly attributed to the complexity of atmospheric aerosols (e.g. mixing state and complex coating materials) in contrast to the simple proxies used in laboratory studies (Yu et al., 2020). Specifically, the suppressive effect of organic coatings is not

considered in BT09. Several parameterizations updated from BT09 have been proposed by more recent studies based on field measurements and box model studies (Yu et al., 2020; Mcduffie et al., 2018a; Mcduffie et al., 2018b; Xia et al., 2019). However, some of these previous field-based parameterizations were derived from observations under different ambient conditions which may not be applicable to the highly polluted regions in China. A full evaluation of the representativeness of different parameterizations for the heterogeneous N_2O_5 + Cl chemistry and the associated impacts on ambient air quality in China is not available yet.

In addition to the parameterization, the influence of the heterogeneous N_2O_5 + Cl chemistry is also sensitive to chlorine emissions. In early modelling studies, global tropospheric chlorine is mainly from sea salt aerosols (SSA), and most of the chlorine over continental regions in North America and Europe is dominated by the long-range transport of SSA (Wang et al., 2019; Sherwen et al., 2017). The study by Wang et al. (2019) found an addition of anthropogenic chlorine emissions in the model would result in overestimates of HCl observations in the U.S and suggested insignificant influence of anthropogenic Cl in the U.S. However, there are also studies pointing out the importance of anthropogenic chlorine emissions in China (Le Breton et al., 2018; Yang et al., 2018; Hong et al., 2020). The study by Wang et al. (2020b) suggested that anthropogenic chlorine emissions in China are more than 8 times higher than those in the U.S., and could dominate reactive chlorine in China, resulting in an increase in $PM_{2.5}$ and Ozone by up to 3.2 μg m^{-3} and 1.9 ppbv on annual mean basis, respectively. The comprehensive effects of anthropogenic chlorine on air quality as well as their sensitivities to different parameterizations for the heterogeneous N_2O_5 + Cl chemistry, however, has not been investigated in previous studies.

In this work, we use the GEOS-Chem model to investigate the impacts of chlorine chemistry including the heterogeneous N_2O_5 + Cl chemistry on air quality in China. Multiple observational data sets, including N_2O_5, $ClNO_2$, O_3, $PM_{2.5}$ and its chemical compositions from different representative sites across China, are used to assess the model performance. With comprehensive chlorine emissions as well as appropriate parameterizations for the heterogeneous N_2O_5 + Cl chemistry, our objectives are: 1) to improve the model's performance regarding the simulation of particulate chloride, $ClNO_2$, N_2O_5, $PM_{2.5}$ and O_3 concentrations; and 2) to extend the investigation on the effects of chlorine chemistry on both $PM_{2.5}$ and ozone pollution in China as well as their sensitivities to anthropogenic chlorine emissions and

the parameterizations for the heterogeneous N_2O_5 + Cl chemistry.

2 Methodology

2.1 GEOS-Chem Model

The GEOS-Chem model (version 12.9.3, http://www.geos-chem.org, DOI: 10.5281/zenodo.3974569) is driven by assimilated meteorological fields GEOS-FP from the NASA Global Modeling and Assimilation Office (GMAO) at NASA Goddard Space Flight Center. The simulation in this study was conducted in a nested-grid model with a native horizontal resolution of 0.25° × 0.3125° (latitude × longitude) and 47 vertical levels over East Asia (70° − 140° E, 15° S − 55° N). The dynamical boundary conditions were from a global simulation with a horizontal resolution of 2° × 2.5°. We initialized the model with a 1-month spin up followed by a 1-year simulation for 2018. The simulation included a detailed representation of coupled NO_x – ozone – VOCs – aerosol − halogen chemistry (Sherwen et al., 2016; Wang et al., 2019). Previous studies have demonstrated the ability of GEOS-Chem to reasonably reproduce the magnitude and seasonal variation of surface ozone and particulate matter over East Asia and China (Wang et al., 2013; Geng et al., 2015; Li et al., 2019).

2.1.1 Chlorine Chemistry

The GEOS-Chem model includes a comprehensive chlorine chemistry mechanism coupled with bromine and iodine chemistry. Full details could be found in the study of Wang et al. (2019). Briefly, the model includes 12 gas-phase inorganic chlorine species (Cl, Cl_2, Cl_2O_2, $ClNO_2$, $ClNO_3$, ClO, ClOO, OClO, BrCl, ICl, HOCl, HCl), 3 gas-phase organic chlorine (CH_3Cl, CH_2Cl_2, $CHCl_3$), and aerosol Cl^- in two size bins (fine mode with radius ⩽ 0.5 μm and coarse mode with radius > 0.5 μm). The gas-aerosol equilibrium between HCl and Cl^- is calculated with ISORROPIA II (Fountoukis and Nenes, 2007) as part of the H_2SO_4 – HCl − HNO_3 − NH_3 – non-volatile cations (NVCs) thermodynamic system, where Na^+ is used as a proxy for NVCs.

The heterogeneous uptake of N_2O_5 on aerosol surfaces leading to the production of $ClNO_2$ and HNO_3 has also been included in GEOS-Chem with the parameterizations for γ_{N2O5} and φ_{ClNO2} proposed by

McDuffie et al. (2018b; 2018a) by default (hereinafter referred to as McDuffie parameterization). McDuffie parameterization is the first field-based empirical parameterization derived from the framework proposed in multiple laboratory studies including BT09 (Anttila et al., 2006; Bertram and Thornton, 2009; Riemer et al., 2009) to account for the uptake dependence on aerosol water and nitrate concentrations as well as the resistance from an organic coating. The coefficients for McDuffie parameterization were derived from applying a box model to observations of N_2O_5, $ClNO_2$, O_3, and NO_x mixing ratios during the winter in the eastern U.S. The parameterization for γ_{N2O5} accounts for both the inorganic and organic aerosol components and can be described by Eq. 1 – 3:

$$\frac{1}{\gamma_{\mathrm{N_2O_5}}} = \frac{1}{\gamma_{\mathrm{core}}} + \frac{1}{\gamma_{\mathrm{coat}}} \quad \text{Eq. 1}$$

$$\gamma_{\mathrm{core}} = \frac{4V}{c \cdot S_{\mathrm{a}}} K_{\mathrm{H}} \times 2.14 \times 10^5 \times [\mathrm{H_2O}] \left(1 - \frac{1}{k_a \frac{[\mathrm{H_2O}]}{[\mathrm{NO_3^-}]} + 1}\right) \quad \text{Eq. 2}$$

$$\gamma_{\mathrm{coat}} = \frac{4RT\varepsilon H_{\mathrm{aq}} D_{\mathrm{aq}} R_{\mathrm{c}}}{c l R_{\mathrm{p}}} \quad \text{Eq. 3}$$

Where γ_{core} represents the reactive uptake of inorganic aerosol core and γ_{coat} represents the retardation of the organic coating; c is the average gas-phase thermal velocity of N_2O_5 (m s^{-1}), V is the total particle volume concentration (m^3 m^{-3}), S_a is the total particle surface area concentration (m^2 m^{-3}), K_H is the unitless Henry's law coefficient for N_2O_5 with a constant value of 51, $[H_2O]$ and $[NO_3^-]$ are the concentrations of aerosol liquid water content and aerosol nitrate (mol L^{-1}), respectively, and k_a is the rate constant ratio representing the competition between aerosol-phase H_2O and NO_3^- for the $H_2ONO_2^+$(aq) intermediate and is fixed at 0.04 in Eq.2; R is the ideal gas constant, T is the temperature (K), H_{aq} and D_{aq} are the aqueous Henry's law constant and aqueous-phase diffusion coefficient of N_2O_5, respectively, ε is a linear combination of relative humidity (RH) and O:C ratio (= 0.15 × O:C + 0.0016 × RH), and R_p, R_c, and l are the total particle radius, inorganic core radius and organic coating thickness, respectively (m).

φ_{ClNO2} is calculated following BT09, but is reduced by 75% based on the observations conducted in eastern U.S. and offshore in spring 2015 (i.e. the WINTER aircraft campaign) (McDuffie et al., 2018b). It could be described by Eq. 4:

$$\varphi_{\mathrm{ClNO_2}} = 0.25 \times \left(k_c \frac{[\mathrm{H_2O}]}{[\mathrm{Cl^-}]} + 1\right)^{-1} \quad \text{Eq. 4}$$

Where k_c is the rate constant ratio representing the competition between aerosol-phase H_2O and Cl^- for the $H_2ONO_2^+$(aq) intermediate and is fixed at 1/450 here, and [Cl^-] is the concentration of aerosol chloride (mol L^{-1}). For more detailed description of McDuffie parameterization, readers are referred to McDuffie et al. (2018b; 2018a). Keep it in mind that the coefficients for the parameterizations in Eq. 1 – 4 were derived to better reproduce wintertime observations in the eastern U.S. However, there are large uncertainties in both the values of the coefficients and functional form of the parameterizations, specifically related to their applicability to other regions.

Recently, Yu et al. (2020) proposed new parameterizations of γ_{N2O5} and φ_{ClNO2} based on BT09 to account for the dependence on aerosol water, nitrate, and chloride concentrations but with coefficients derived from uptake coefficients directly measured on ambient aerosol in two rural sites in China. The parameterizations of γ_{N2O5} and φ_{ClNO2} (hereinafter referred to as Yu parameterization) are described by Eq. 5 – 6, respectively:

$$\gamma_{N_2O_5} = \frac{4V}{c \cdot S_a} K_H \times 3.0 \times 10^4 \times [H_2O] \left(1 - \frac{1}{k_a \frac{[H_2O]}{[NO_3^-]} + k_b \frac{[Cl^-]}{[NO_3^-]} + 1}\right) \quad \text{Eq. 5}$$

$$\varphi_{ClNO_2} = \left(1 + k_c \frac{[H_2O]}{[Cl^-]}\right)^{-1} \quad \text{Eq. 6}$$

Where k_b is the rate constant ratio representing the competition between aerosol-phase Cl^- and NO_3^- for the $H_2ONO_2^+$(aq) intermediate and is fixed at 3.4. In contrast to McDuffie parameterization, k_a and k_c in Yu parameterization are fixed at 0.033 and 1/150, respectively.

Although both the two parameterizations are developed based on BT09, there exit significant differences of γ_{N2O5} and φ_{ClNO2} between McDuffie and Yu parameterizations. For γ_{N2O5}, McDuffie parameterization generally follows BT09 for the calculation of the uptake on inorganic aerosols (i.e. γ_{core}), but excludes the dependence on aerosol chloride so as to better reproduce observed wintertime reactive nitrogen in eastern U.S. Moreover, the parameterization accounts for the suppressive effects of the organics (i.e. γ_{coat}), which is not directly included in BT09 (Anttila et al., 2006; Riemer et al., 2009; Morgan et al., 2015). In contrast to McDuffie parameterization, Yu parameterization excludes the organic suppression but includes the chloride enhancement so as to better reproduce γ_{N2O5} observed in China (Yu et al., 2020). It is worth mentioning that the coefficients applied in the parameterization of γ_{N2O5} also differ between McDuffie and Yu parameterizations as both are fixed to reproduce the ambient observation representing

different pollution conditions. For example, k_a is equal to 0.04 in Eq. 2 but 0.033 in Eq. 5. The γ_{N2O5} in McDuffie parameterization is thus expected to be lower compared with the Yu parameterization due to the resistance from organic coating and the lack of the chloride enhancement. For φ_{ClNO2}, both the McDuffie and Yu parameterizations are based on BT09, but with different coefficients (i.e. k_c = 1/450 in Eq. 4 and 1/150 in Eq. 6). Although k_c in Eq. 4 is relatively smaller, the scaling factor of 0.25 applied in Eq. 4 ultimately results in a much smaller φ_{ClNO2} in McDuffie parameterization compared with Yu parameterization under the same condition. Again, keep it in mind that McDuffie parameterization is derived from fits to observations over the eastern U.S. (McDuffie et al., 2018a) while Yu parameterization is fitted to observations at rural locations in China (Yu et al., 2020).

In this study, we updated the parameterizations for γ_{N2O5} and φ_{ClNO2} in the heterogeneous N_2O_5 + Cl chemistry (hereinafter referred to as parameterizations for heterogeneous N_2O_5 + Cl chemistry) in the GEOS-Chem with Yu parameterization. Additional simulation cases were also performed to evaluate the representativeness of both Yu and McDuffie parameterizations regarding the simulation of N_2O_5, $ClNO_2$, O_3, $PM_{2.5}$ and its chemical compositions in China. Detailed description of the model setup for related cases is provided below in Section 2.1.3.

2.1.2 Emissions

The study uses the Hemispheric Transport of Air Pollution (HTAPv2, http://www.htap.org/) based on the emission of 2010 as a global anthropogenic inventory. This inventory is overwritten by a regional emission inventory MIX (with a horizontal resolution of 0.25° × 0.25°) over East Asia based on the emission in 2017, which is developed for the Model Inter-Comparison Study for Asia (MICS-Asia) and covers all major anthropogenic sources in 30 Asian countries and regions (Li et al., 2017). In addition, anthropogenic emissions of black carbon (BC) and organic carbon (OC) in Guangdong province, China (109° − 117° E, 20° − 26° N) are overwritten by a more recent high-resolution inventory (9 km × 9 km) described by Huang et al. (2021). Biomass burning emissions are from the Global Fire Emissions Database (GFED4) (Van et al., 2010) with a 3-hour time resolution. And the biogenic emissions of VOCs are calculated based on the Model of Emissions of Gases and Aerosols from Nature (MEGAN2.1) (Guenther et al., 2006).

Table 1 lists Cl emissions from all sources in the model. The global tropospheric chlorine by default in the model is mainly from the mobilization of Cl^- from SSA distributed over two size bins (fine and coarse modes) (Wang et al., 2019), which is computed online as the integrals of the size-dependent source function depending on wind speeds and sea surface temperatures (Jaeglé et al., 2011). During the simulation year of 2018, SSA contributes 6.5×10^4 Gg Cl^-, most of which however are distributed over the ocean due to its relatively short lifetime (~1.5 days) (Choi et al., 2020). The release of atomic Cl from organic chlorine (CH_3Cl, CH_2Cl_2 and $CHCl_3$) via the oxidation by OH and Cl is also included in the model by default. These organic chlorine gases are mainly of biogenic marine origin (Simmonds et al., 2006), with a mean tropospheric lifetime longer than 250 days (Wang et al., 2020b), and are simulated in the model by imposing fixed surface concentrations as described by Schmidt et al. (2016). Total emissions of Cl atom from CH_3Cl, CH_2Cl_2, and $CHCl_3$ are calculated to be 3.8, 2.4, and 0.70 Gg Cl a^{-1}, respectively.

Considering the importance of anthropogenic chlorine in China, we have further updated chlorine inventories in the model to account for anthropogenic HCl, Cl_2 and fine particulate Cl^-, as well as biomass burning HCl and Cl^- emissions (also shown in Table 1 and S1). For fine particulate Cl^- from both anthropogenic and biomass burning, the emissions are estimated based on $PM_{2.5}$ emissions from MIX and GFED4 inventories combined with the emission ratios of fine particulate Cl^- versus $PM_{2.5}$ for different emission sectors adopted from the study of Fu et al. (2018). Estimated Cl^- emissions from anthropogenic and biomass burning are 379 and 120 Gg, respectively, comparable to the results of 486 Gg in total for the year of 2014 by Fu et al. (2018). The anthropogenic emissions of HCl and Cl_2 are from ACEIC (Anthropogenic Chlorine Emissions Inventory for China) (Liu et al., 2018) and are estimated to be 218 and 8.9 Gg Cl in China, respectively. For HCl from biomass burning, the emission factors from Lobert et al. (1999) are used for different types of biomass provided in GFED4, and a total emission of 30 Gg Cl is obtained in China in 2018. Total implemented chlorine emission for the simulation year of 2018 is 756 Gg Cl.

Figure 1 shows the distribution of Cl emissions from the sources mentioned above. Anthropogenic and biomass burning emissions of HCl are concentrated in the Northeast Plain, North China Plain, Yangtze River Delta, and Sichuan Basin, and are up to 320 kg Cl km^{-2} a^{-1} in the Sichuan Basin. Emissions of HCl

are low in South China, mainly due to the low chlorine content of coal in these regions (Hong et al., 2020). The relative contribution of biomass burning to total HCl emissions in China is 14% on average but could become dominant in the Northeast Plain due to the discrepancies in the spatial distributions of anthropogenic and biomass burning emissions. The anthropogenic Cl_2 emissions have a similar spatial distribution to that of HCl, but are one order of magnitude lower than HCl emissions. The distribution of non-sea salt Cl^- emissions is also similar to that of HCl and Cl_2, except that non-sea salt Cl^- emissions are also high in Central China. In contrast, emissions of sea salt Cl^- (Fig. S1) are mainly distributed over the ocean, implying limited influences over inland due to rapid deposition during transport. The spatial distributions of different organic chlorine sources are similar, with maximums (~ 0.5 kg Cl km^{-2} a^{-1}) in coastal regions (Fig. S1).

2.1.3 Model setup for different simulation cases

In this study, we conducted a series of simulation cases to investigate the effects of chlorine chemistry on air quality in China, the role of $N_2O_5 - ClNO_2$ chemistry, and the associated sensitivities to chlorine emissions as well as the parameterizations for $N_2O_5 - ClNO_2$ chemistry. Detailed model setup for those cases is listed in Table 2. The Base case is the one with all updates in this study, including additional chlorine sources from anthropogenic and biomass burning emissions as well as N_2O_5 uptake and $ClNO_2$ production represented by Yu parameterization. The NoEm case is conducted with a similar setup as the Base case but only includes chlorine emissions from SSA and organic chlorine sources so as to evaluate the model improvement originated from the updated chlorine emissions through the comparison with the Base case. The McDuffie case is also performed using the McDuffie instead of Yu parameterization for γ_{N2O5} and φ_{ClNO2} while keeping others the same as the Base case so as to evaluate the discrepancies originated from different parameterizations for the heterogeneous $N_2O_5 + Cl$ chemistry.

In addition, while keeping others the same as the Base case, the NoHet case sets φ_{ClNO2} to zero (Eq.6) and removes the enhancement of N_2O_5 uptake from aerosol chloride (i.e. $[Cl^-] = 0$ in Eq. 5). The comparison between the Base and NoHet cases could thus evaluate the importance of the heterogeneous $N_2O_5 + Cl$ chemistry (i.e., the model sensitivities to a smaller gamma N_2O_5 and zero $ClNO_2$ production). Similarly, combined with three more sensitivity cases (NoChem, NoEmHet and NoAll, see details in Table 2), the study provides an overall evaluation of the importance of tropospheric chlorine chemistry

as well as its sensitivities to chlorine emissions and the parameterizations for the heterogeneous N_2O_5 + Cl chemistry in the model.

2.2 Observations

Multiple observed data sets were applied in this study to evaluate the performance of GEOS-Chem simulation, including the concentrations of chemical compositions of $PM_{2.5}$ from three representative sites, located in south (Guangzhou, 23.14° N, 113.36° E), east (Dongying, 37.82° N, 119.05° E) and north (Gucheng, 37.36° N, 115.96° E) China, respectively (Fig. S2). Concentrations of SO_4^{2-}, NO_3^-, NH_4^+, Cl^- and organic matter (OM) in $PM_{2.5}$ were measured by High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; Aerodyne Research Inc., USA, Decarlo et al. (2006)) from October 2 to November 18, 2018 (with a time resolution of 1 minute) at Guangzhou site (Chen et al., 2021b), and from March 18 to April 21, 2018 (with a 1-minute time resolution) at Dongying site. Concentrations of these species were measured by an Aerodyne Quadruple Aerosol Chemical Speciation Monitor (ACSM; Aerodyne Research Inc., USA, Ng et al. (2011)) from November 11 to December 18 in 2018, with a time resolution of 2 minutes at Gucheng site (Li et al., 2021).

Concentrations of N_2O_5 and $ClNO_2$ (with a time resolution of 1 minute) were also measured at Guangzhou site by a Chemical Ionization Mass Spectrometer (CIMS, THS Instruments Inc., Atlanta, (Kercher et al., 2009)) from September 25 to November 12 in 2018 (Ye et al., 2021). To have a thorough evaluation of the representativeness of different parameterizations for γ_{N2O5} and φ_{ClNO2}, observations of $ClNO_2$ and N_2O_5 at six more sites across China from previous studies (see Table S2 and Fig. S2) are also used in this study. It should be noted that model results sampled at those sites for comparison were simulated in the same months but different years while ignoring the uncertainties associated with the interannual variability.

In addition, we also use observed hourly data of O_3 and $PM_{2.5}$ published by the China National Environmental Monitoring Center (CNEMC, http://www.cnemc.cn/sssj/, last access on June 20, 2021) to evaluate the model's overall performance in China. The network was launched in 2013 as part of the Clean Air Action Plan and includes ~1500 stations located in 370 cities by 2018 (Fig. S2).

3 Results and discussion

3.1 Improved model performance with updated chlorine emissions and parameterizations for the heterogeneous N_2O_5 + Cl chemistry

Figure 2 shows time series of observed and simulated Cl^- concentrations at the Guangzhou, Dongying, and Gucheng sites. The observations show the lowest Cl^- concentrations at the Guangzhou site (0.55 ± 0.52 μg m^{-3}), although the site is the closest to the ocean among all three sites, while the highest concentrations (4.7 ± 3.3 μg m^{-3}) are observed at the Gucheng site, away from the sea. Moderate concentrations of Cl^- is observed at the Dongying site, around 1.1 ± 0.82 μg m^{-3}. The relatively higher concentrations observed inland again suggest the dominance of non-sea salt Cl^- in China, as mentioned before in the Introduction.

The comparison between observations and simulated results from the NoEm case shows a serious underestimate of Cl^- concentrations, with normalized mean bias (NMB) ranging from -96% to -79%, suggesting the missing of significant chlorine sources in addition to sea salt chlorine. In contrast, the Base case with updated chlorine emissions exhibits much higher Cl^- concentrations and can successfully reproduce observations, with average concentrations of 0.77 ± 0.54, 0.71 ± 0.52, and 4.5 ± 2.4 μg m^{-3} (NMB = 39%, -36% and -4.7%) at the Guangzhou, Dongying, and Gucheng sites, respectively. The increase in Cl^- concentrations in the Base case compared with the NoEm case is the most significant at the Gucheng site, by a factor of 24 (from 0.19 to 4.5 μg m^{-3} on average). The slight underestimates at the Dongying site in the Base case could be to some extent explained by the bias in GFED4, which underestimates emissions from agricultural fires due to their small size and short duration as suggested by the study of Zhang et al. (2020). In spite of that, the model with the Base case well reproduces the overall distribution of the observed particulate chloride concentrations in China. The correlation coefficients (*r*) between observed and model results at the three sites also increase from -0.05 – 0.61 in the NoEm case to 0.40 – 0.71 in the Base case. The significant improvement in the model performance again suggests sources other than SSA play a key role in Cl^- concentrations in China.

The comparison between observed and simulated N_2O_5 (Fig. 3a) shows that NMB for the NoEm case are

-58%, 150%, 108% and 25% at the Guangzhou, Wangdu, Taizhou and Mount Tai sites, respectively. In contrast, the corresponding NMB for the Base case are much smaller, -57%, 48%, 91% and 18%, respectively. The improvement in the Base case is apparent at most sites, implying that additional chlorine emissions could effectively increase the uptake coefficient of N_2O_5 in Yu parameterization. As shown in Figure S3, although the values of γ_{N2O5} between the Base and NoEm cases are similar over the ocean, the Base case has relatively higher γ_{N2O5} over China compared with the NoEm case (0.016 vs. 0.014 on annual mean basis). Little improvement is found at the Guangzhou site (-58% in the NoEm case vs. -57% in the Base case). Previous studies also found an underestimation of N_2O_5 in the Pearl River Delta, which could be partly explained by the underestimation of the sources (e.g NO_2) and/or the overestimation of the sink of N_2O_5 there (Dai et al., 2020; Li et al., 2016).

The N_2O_5 results from the McDuffie case, which uses McDuffie parameterization (a default setting in GEOS-Chem, see Section 2.1.1 and 2.1.3) instead of Yu parameterization are also shown in Fig. 3a. The NMB for the McDuffie case are -53%, 154%, 143% and 37% at the Guangzhou, Wangdu, Taizhou and Mount Tai sites, respectively. The comparison between the McDuffie and Base cases indicates that Yu parameterization can reproduce observed N_2O_5 better in China in general, while McDuffie parameterization tends to overestimate N_2O_5 concentrations. The overestimate of N_2O_5 in McDuffie parameterization suggests the potential underestimate in the corresponding γ_{N2O5}. As shown Figure S3, the value of γ_{N2O5} from the McDuffie case is much smaller than that from the Base case (0.0071 vs. 0.016 averaged over China).

The underestimate in γ_{N2O5} from the McDuffie case could to large extent be explained by the suppressive effect of organic coatings (γ_{coat}) as discussed above in Section 2.1.1. The magnitude of the organic suppression is highly dependent on many factors (e.g. organic composition, particle phase state, etc.) and thus remains poorly quantified (Griffiths et al., 2009; Gross et al., 2009; Thornton et al., 2003). Although many studies have shown that organic aerosol can suppress the N_2O_5 uptake (Anttila et al., 2006; Riemer et al., 2009), the level of organic suppression may be overpredicted in currently implemented parameterization attributed to the poorly quantified and/or unknown factors (e.g. Morgan et al. (2015)). For example, some studies found that ignoring the difference between water-soluble and water-insoluble organics may lead to an upper limit for the suppressive effect of organic coatings and consequently an

underestimate in the solubility and diffusivity of N_2O_5 in organic matter (Chang et al., 2016; Yu et al., 2020). Although the γ_{coat} in McDuffie parameterization is calculated as a function of organic aerosol O:C ratio and RH (see Eq. 2), which could increase with higher RH and higher O:C ratio, it may still overpredict the suppressive role of organic coatings in China. On the other hand, the study by Yu et al. (2020) found that excluding the organic coating best reproduced uptake coefficients observed in China. In addition, the underestimate in γ_{N2O5} in McDuffie parameterization in China could also be to some extent explained by the lack of the chloride enhancement (also discussed in Section 2.1.1). It is worth noting that the evaluation here is specific to China and the differences between Yu and McDuffie parameterizations have not been evaluated elsewhere.

For the comparison of $ClNO_2$ (Fig. 3b), we use the mean nighttime (excluding the data at local time of 10:00 – 16:00) maximum mixing ratio, as suggested by Wang et al. (2019). Observed $ClNO_2$ is high in Guangzhou (1121 pptv) and Wangdu (~ 990 pptv), followed by Changping (~ 500 pptv) and Beijing (~ 430 pptv). The lowest concentrations are obtained at Mount Tai and Mount TaiMoShan (~ 150 and 120 pptv, respectively) due to relatively clean condition at high altitude. The comparison between observed and simulated $ClNO_2$ at different sites also suggests a better model performance for the Base case with NMB in the range of -28% – 22%, compared with the NMB of -77% – -31% and -59% – -36% for the NoEm and McDuffie cases, respectively. The difference in $ClNO_2$ concentrations is mainly associated with distinct φ_{ClNO2} values among different cases. As shown in Figure S4, the value of φ_{ClNO2} is significantly higher in the Base case (0.36 averaged over China) than in the NoEm (0.14) and McDuffie (0.11) cases. The large difference between the NoEm and Base cases again emphasizes the important role of non-sea salt chlorine in the formation of $ClNO_2$. The overall underestimates in McDuffie parameterization on the other hand may suggest that the scaling factor of 0.25 applied to φ_{ClNO2} in Eq. 4 is too much for the atmospheric condition in China. More field measurements and model evaluations are required to come up with a more precise parameterization better representing φ_{ClNO2} in China.

Overall, with updated chlorine emissions and Yu parameterization for γ_{N2O5} and φ_{ClNO2}, the Base case agrees better with both the magnitude and the spatial variation of observed N_2O_5 and $ClNO_2$ in China. The differences in γ_{N2O5} and φ_{ClNO2} could also affect the ratios of $ClNO_2$ to HNO_3. As shown in Figure S5, the value of $ClNO_2/HNO_3$ is the highest from the Base case (9.8% averaged in China and up to 47%

in the Sichuan Basin on annual mean basis), followed by the McDuffie (4.7% averaged in China and up to 18% in the Sichuan Basin) and NoEm (3.1% averaged in China and up to 12% in coastal regions) cases.

To further elucidate how the model behaves in reproducing the spatial distribution of ozone and $PM_{2.5}$ through the incorporation of the additional chlorine emissions and Yu parameterization for the heterogeneous N_2O_5 + Cl chemistry, simulated MDA8 O_3 and $PM_{2.5}$ from different cases were compared with observations across China. Figure 4 shows simulated annual mean MDA8 O_3 and $PM_{2.5}$ in 2018 in China from the Base case compared with the observations from CNEMC (China National Environmental Monitoring Center, introduced in Section 2.2). The observed annual mean MDA8 O_3 and $PM_{2.5}$ are 49 ppbv and 39 μg m^{-3} respectively in 2018 in China. Model results from the Base case could generally reproduce observed spatial and seasonal variations of annual mean MDA8 O_3 and $PM_{2.5}$ concentrations, with NMB of -26% and 3.6% and *r* of 0.83 and 0.81 respectively (Fig. S6).

Table 3 also summarized the model performance on both annual and seasonal scales regarding the simulation of O_3 and $PM_{2.5}$ from different cases. For the comparison with observed MDA8 O_3, although different simulation cases show a similar range of *r*, the Base case tends to have a slightly smaller bias in general, with NMB of -26% on annual average (-49% – -5.5% on seasonal mean) vs. -28% (-54% – -5.9%) in the NoEm and -27% (-53% – -5.2%) in the McDuffie case. For the comparison with observed $PM_{2.5}$, the NMB bias from the Base case is 3.6% on annual average (-6.3% – 28% on seasonal mean). Compared with the NoEm case, there is some improvement in summer (5.0% vs. 3.9%) and winter (-7.9% vs. -4.3%) but slightly larger bias in autumn (26% vs. 28%). The McDuffie case on the other hand produces slightly higher $PM_{2.5}$ concentrations, with NMB of 5.6%. Regarding the chemical compositions of $PM_{2.5}$ (Table S3), although the model performance varies with sites and species, the Base case demonstrates better agreement with observations compared with the NoEm and McDuffie cases in general.

On the whole, the model performance is better with the additional anthropogenic and biomass burning chlorine emissions combined with Yu parameterization for the heterogeneous N_2O_5 + Cl chemistry. Therefore, the following investigation of the impacts of chlorine chemistry on air quality in China as well as their sensitivities to chlorine emissions and parameterizations for the heterogeneous N_2O_5 + Cl

chemistry is mainly based on the Base case.

3.2 Impacts of tropospheric chlorine chemistry on air quality and the role of the heterogeneous N_2O_5 + Cl chemistry

To comprehensively quantify the importance of chlorine chemistry, we conducted a sensitivity case in which all related tropospheric chlorine chemistry was turned off (NoChem, also listed in Table 2). The differences between the Base and NoChem cases (Fig. 5 and Fig. S7) could thus represent the impact of the chlorine chemistry. The comparison shows that chlorine chemistry could increase annual mean nighttime max $ClNO_2$ surface concentrations by 243 pptv averaged in China (up to 1548 pptv in the Sichuan Basin). The increase in annual mean Cl atoms is 1.7×10^3 molec cm^{-3} averaged in China (up to 7×10^3 molec cm^{-3} in coastal regions). The increased Cl atoms could react with VOCs (especially alkanes) producing more peroxy radicals, including organic peroxy radicals (RO_2) and hydroperoxyl radicals (HO_2). As shown in Figure S7 (a), the chlorine chemistry could increase annual mean HO_2 concentrations by 1.6×10^6 molec cm^{-3} averaged in China (up to 8.6×10^6 molec cm^{-3} in the coastal regions). In the presence of NO, the peroxy radicals recycle OH while oxidize NO to NO_2. The subsequent photolysis of NO_2 could further lead to more O_3 production and consequently also more OH (Osthoff et al., 2008; Riedel et al., 2014; Simpson et al., 2015). On the other hand, the recycling of NO_x back into the atmosphere associated with the photolysis of $ClNO_2$ could also lead to more O_3 production. The results here show a significant increase in surface annual mean OH (Fig. S7 (b)) and MDA8 O_3 (Fig. 5c) by 3.8×10^4 molec cm^{-3} and 1.1 ppbv respectively averaged in China (up to 1.2×10^5 molec cm^{-3} and 4.5 ppbv respectively in the Sichuan Basin). In contrast, annual mean $PM_{2.5}$ surface concentrations are decreased by 0.91 μg m^{-3} averaged in China (up to 7.9 μg m^{-3} in the Sichuan Basin), mainly due to the decrease of NO_3^- and NH_4^+ (up to 6.4 μg m^{-3} and 1.9 μg m^{-3} respectively), although SO_4^{2-} concentrations are increased slightly by up to 1.2 μg m^{-3} in the Sichuan Basin (Fig. S7).

Both global and regional studies suggested that the heterogeneous N_2O_5 + Cl chemistry can enhance O_3 production through the production of Cl atoms and the recycling of NO_x (Li et al., 2016; Sarwar et al., 2014; Wang et al., 2019). Therefore, we further investigate the role that the heterogeneous N_2O_5 + Cl chemistry plays in tropospheric chlorine chemistry through the comparison between the Base and NoHet

(Fig. 6 and Fig. S8) cases. Keep it in mind that the comparison is mainly assessing the impact of $ClNO_2$ production, namely the uptake of N_2O_5 on chloride aerosol, not the general role of N_2O_5 heterogeneous chemistry. The comparison illustrates that the heterogeneous N_2O_5 + Cl chemistry could result in a significant production of $ClNO_2$, reaching 600 – 1400 pptv for annual mean nighttime max surface concentrations in the North China Plain, and up to 1546 pptv in the Sichuan Basin. The change in the surface concentrations of Cl atoms (an annual mean increase of $1 – 4 \times 10^3$ molec cm^{-3} in central and eastern China) is mainly due to the photolysis of $ClNO_2$ and accounts for 74% of total change in annual mean Cl atoms due to all tropospheric chlorine chemistry in China, which are consistent with the results from the previous study by Liu et al. (2017).

In addition to the production of Cl atoms, the $ClNO_2$ formation also affects the partitioning of NO_y from HNO_3 into more reactive forms (e.g., NO_x and $ClNO_2$) through the recycling of NO_x, and therefore of great importance in atmospheric chemistry (Bertram et al., 2013; Li et al., 2016; Wang et al., 2020a). To analyze the impact of the heterogeneous N_2O_5 + Cl chemistry on NO_y partitioning, Figure S9 shows the change in the ratios of NO_x to NO_y and NO_3^- to NO_y as the difference between the Base and NoHet cases. Since $ClNO_2$ could be treated as a reservoir for reactive nitrogen at night, we include $ClNO_2$ as part of NO_x in the calculation ($NO_x = NO + NO_2 + ClNO_2$ and $NO_y = NO + NO_2 + ClNO_2 + HNO_3 + 2 \times N_2O_5 + NO_3 + HONO + HNO_4 + NO_3^- +$ various organic nitrates). The results show that due to the $ClNO_2$ production, the ratios of NO_x to NO_y increase by 1.8% averaged in China and up to 5.4% in the Sichuan Basin, Northeast Plain and North China Plain on annual mean basis. Meanwhile, the ratios of NO_3^- to NO_y decrease by 1.1% averaged in China and up to 5.1% in the Sichuan Basin on annual mean basis.

Consequently, the annual mean MDA8 O_3 surface concentrations are increased by 1.5 – 3 ppbv in central and eastern China and up to 3.8 ppbv in the Sichuan Basin, accounting for 83% of total change in annual mean MDA8 O_3 due to all tropospheric chlorine chemistry in China. It is interesting to note that while MDA8 O_3 surface concentrations show maxima in summer and minima in winter in general, the influence of the heterogeneous N_2O_5 + Cl chemistry on O_3 concentrations exhibits a different seasonality. The increase in seasonal mean MDA8 O_3 concentrations is the largest in winter (by up to 6.5 ppbv in the Sichuan Basin) but is less than 1.5 ppbv in summer. This is because of more accumulation of N_2O_5 and $ClNO_2$ in dark conditions in long winter nights (Sarwar et al., 2014).

There also exhibits an obvious decrease in the annual mean surface concentrations of $PM_{2.5}$ attributed to the heterogeneous N_2O_5 + Cl chemistry, ranging from 1.5 to 4.5 μg m^{-3} in central and eastern China (accounting for 90% of total change in annual mean $PM_{2.5}$ due to all tropospheric chlorine chemistry in China). The decrease is more significant in autumn and winter in China, with a range of 3.5 – 5.5 μg m^{-3} in central and eastern China and being up to 11 μg m^{-3} in the Sichuan Basin. In contrast, the decrease in $PM_{2.5}$ is less than 2 μg m^{-3} in summer in China. The change in $PM_{2.5}$ is mainly due to the decrease in NO_3^- (up to 6.2 μg m^{-3} in the Sichuan Basin on annual average). In addition, NH_4^+ is also decreased by up to 1.8 μg m^{-3} in the Sichuan Basin on annual average, following the pattern of ΔNO_3^-. This is because NH_3 is in excess in most regions in China (Xu et al., 2019) and the formation of $ClNO_2$ via R2 could hinder the formation of HNO_3 and shift the partitioning between NH_3 and NH_4^+ towards NH_3. Unlike the change in NO_3^- and NH_4^+, the heterogeneous N_2O_5 + Cl chemistry increases surface SO_4^{2-} concentration slightly, which could be explained by the enhancements of atmospheric oxidation associated with the increase in Cl atoms, OH and O_3, facilitating the formation of secondary aerosols (Sarwar et al., 2014).

On the other hand, the effect of tropospheric chlorine chemistry without the heterogeneous N_2O_5 + Cl chemistry is much smaller (Fig. S10, the comparison between the NoHet and NoChem cases), leading to an increase of up to 0.7 ppbv in inland China and a decrease of 0.3 – 0.5 ppbv in coastal regions for annual mean MDA8 O_3 concentrations. The increase is probably associated with Cl atoms from photolysis of gas-phase chlorine, especially non-sea salt Cl_2 in inland China, while the decrease at coastal regions is mainly due to catalytic production of bromine and iodine radicals originated from sea-salt aerosols. The comparison demonstrates the dominance of the heterogeneous N_2O_5 + Cl chemistry in total tropospheric chlorine chemistry in China.

3.3 The effect of heterogeneous N_2O_5 + Cl chemistry in response to chlorine emissions

Since both γ_{N2O5} and φ_{ClNO2} in Yu parameterization are highly dependent on [Cl^-], the effect of the heterogeneous N_2O_5 + Cl chemistry on air quality is thus sensitive to chlorine emissions. Figure 7 shows the effects of the additional chlorine emissions from anthropogenic and biomass burring sources on annual mean surface concentrations of different species (Cl^-, Cl atom, OH, MDA8 O_3, $PM_{2.5}$ and NO_3^-) in China, calculated as the differences between the Base and the NoEm case. With the implementation of the additional chlorine emissions, the particulate Cl^- concentration increased significantly in inland

China, with the largest increase in the Sichuan Basin (4.5 μg m^{-3}) and little change in west China. The increase is in the range of 1.5 – 3.5 μg m^{-3} in the North China Plain and < 0.5 μg m^{-3} in South China. The spatial distribution of ΔCl atoms is also consistent with that of the additional chlorine emissions and ΔCl^-, showing the largest increment in the Sichuan Basin (about 4.5 – 5 × 10^3 molec cm^{-3}). There is also a moderate increase in Cl atoms in the Northeast Plain and North China Plain, with a range of 1.5 – 4 × 10^3 molec cm^{-3}. Only a minor increase of Cl atoms is found in South China (< 1 × 10^3 molec cm^{-3}).

As discussed earlier in Section 3.2, increased Cl atoms could lead to more HO_2 and OH via VOCs oxidation. Combined with increased NO_x associated with the release of NO_2 upon the photolysis of $ClNO_2$, further increases in both O_3 and OH could also be expected. The increase in OH is around 2 – 9 × 10^4 molec cm^{-3} in central and eastern China on annual mean basis. The increase in MDA8 O_3 surface concentrations ranges from 0.5 to 3 ppbv in central and eastern China and reaches up to 3.5 ppbv in the Sichuan Basin on annual average. The impacts of chlorine sources on O_3 formation also vary with seasons. Although O_3 pollution is generally severe in summer, the change in MDA8 O_3 due to the additional chlorine sources is relatively minor, with maxima of 0.7 ppbv in the Sichuan Basin and < 0.5 ppbv in most other regions averaged in summer. In contrast, the increase is most obvious in winter, with maxima of 5.2 ppbv in the Sichuan Basin on seasonal average.

The effects of the additional chlorine emissions on surface $PM_{2.5}$ concentrations are complicated. The North China Plain shows the largest increase (3 – 4.5 μg m^{-3} on annual average), mainly due to the increase in Cl^-, which could also promote the heterogeneous N_2O_5 + Cl chemistry and lead to more NO_3^- production (Chen et al., 2021a). In contrast, the Sichuan Basin exhibits both an increase (by up to 4.2 μg m^{-3}) and a decease (by up to 3.7 μg m^{-3}). The decrease of $PM_{2.5}$ in the Sichuan Basin is mainly due to the large decrease of NO_3^- there. In the Sichuan Basin, nitrate formation is dominated by the heterogeneous hydrolysis of N_2O_5 (Tian et al., 2019) while the additional Cl^- could hinder the path of N_2O_5 hydrolysis due to the competition with the path of $ClNO_2$ formation. Consequently, the additional chlorine emissions result in a decrease of NO_3^- up to 5.6 μg m^{-3} in the Sichuan Basin on annual average.

In addition, NH_4^+ concentrations could also be affected through the reaction of R5:

$$HCl\,(g) + NH_3\,(g) \rightarrow NH_4^+ + Cl^- \qquad (R5)$$

In the Northeast Plain and North China Plain where anthropogenic and biomass burning emissions of

HCl are high, the annual mean NH_4^+ surface concentrations are increased by 0.5 – 1.5 μg m^{-3} (Fig. S11 (a)). NH_4^+ concentrations are also affected by the gas-particle partitioning equilibrium, and decease as the pH value gets higher (or increase with H^+ concentrations). Therefore, the competition between the heterogeneous N_2O_5 + Cl chemistry and N_2O_5 hydrolysis could also affect the formation of NH_4^+. In other words, increased Cl^- concentrations could results in less H^+ and thus less NH_4^+. Consequently, there also exits some decrease in NH_4^+ concentrations in the Sichuan Basin associated with the large decrease in NO_3^- concentrations. In contrast, little change is found for surface SO_4^{2-} concentrations, less than 0.5 μg m^{-3} in most regions of China (Fig. S11 (b)).

It is worth mentioning that the effects of the additional chlorine emissions work mainly through the heterogeneous N_2O_5 + Cl chemistry. Without this heterogeneous chemistry, the increase of chlorine emissions shows only a minor change in Cl atoms (< 10^3 molec cm^{-3} in China, estimated as the difference between the NoHet and NoEmHet cases in Fig. S12). The impact of chlorine emissions on O_3 concentrations also weakens when the heterogeneous N_2O_5 + Cl chemistry is turned off, with an increase of 0.5 – 1 ppbv in MDA8 O_3 on annual average (vs. 0.5 – 3 ppbv mentioned above).

On the other hand, the impacts of heterogeneous N_2O_5 + Cl chemistry on air quality in inland China would be seriously underestimated if the additional anthropogenic and biomass burning chlorine sources are ignored. If only sea salt chlorine emission is included in the simulation, the increase of $ClNO_2$ surface concentrations resulted from heterogeneous N_2O_5 + Cl chemistry only occurs in coastal regions due to the heterogeneous uptake of N_2O_5 on sea salt chloride aerosols (by up to 260 pptv on annual average, indicated by the difference between the NoEm and NoEmHet cases, Fig. S13). Consequently, the increase in Cl atoms and MDA8 O_3 surface concentrations is found mainly in coastal regions. For instance, annual mean MDA8 O_3 concentrations are increased by up to 2 ppbv in coastal regions, but by less than 0.5 ppbv in inland China. In other words, the dominance of the heterogeneous N_2O_5 + Cl chemistry in the impact of chlorine chemistry on air quality in China is to large extent driven by the additional chlorine emissions.

3.4 The effect of heterogeneous N_2O_5 + Cl chemistry in response to parameterizations for γ_{N2O5} and φ_{ClNO2}

It should be noted that the impact of the heterogeneous N_2O_5 + Cl chemistry on air quality not only depends on the amount of chlorine emissions, but is also sensitive to the parameterizations for γ_{N2O5} and φ_{ClNO2}. As discussed earlier (Fig. 3a), there exists a large difference in simulated N_2O_5 between the Base and NoEm cases at the Wangdu site, implying the sensitivity of γ_{N2O5} to chlorine emissions in Yu parameterization and thus the importance of non-sea salt chlorine emissions in China. This is consistent with the dependence on chloride in Yu parameterization, which is included to better reproduce γ_{N2O5} observations in China (Yu et al., 2020). The comparison between the Base and NoHet cases (γ_{N2O5} = 0.016 and 0.014, respectively) also suggests that the heterogeneous uptake of N_2O_5 on chloride-containing aerosol surfaces in Yu parameterization is an important loss pathway of N_2O_5 and should not be ignored.

Unlike Yu parameterization, N_2O_5 concentrations have little dependence on chlorine emissions in McDuffie parameterization (Fig. 3a). This insensitivity to chlorine emissions could be expected from Eq. 2 where the dependence on aerosol chloride is not included so as to better reproduce wintertime reactive nitrogen observations in the eastern U.S. The little dependence of γ_{N2O5} on concentrations of Cl^- together with the lower value of φ_{ClNO2} make the results from the McDuffie case less sensitive to chlorine emissions, producing less $ClNO_2$ and Cl atoms compared with the Base case (with Yu parameterization) although with the same emission. Consequently, the McDuffie case produces less O_3, with annual mean surface concentrations of MDA8 O_3 lower by 0.47 ppbv averaged in China (by up to 2 ppbv in the Sichuan Basin), but results in more $PM_{2.5}$ (0.63 μg m^{-3} averaged in China and up to 4.7 μg m^{-3} in the Sichuan Basin on annual mean basis mainly due to changes in NO_3^-) (Fig. 8). In other words, compared to the Base case with Yu parameterization, the impacts of chlorine emissions on annual MDA8 O_3 and $PM_{2.5}$ in the McDuffie case has been decreased by 48% and 27% respectively averaged in China. Therefore, even with the same amounts of chlorine emissions, the impacts of the heterogeneous N_2O_5 + Cl chemistry on air quality vary significantly with different parameterizations.

4 Conclusions

Considering the importance of chlorine chemistry in modulating the O_3 and $PM_{2.5}$ as well as the previously ignored chlorine emission from anthropogenic and biomass burning, we updated the GOES-Chem model in this study with comprehensive chlorine emissions and a new parameterization based on the study of Yu et al. (2020) for the heterogeneous N_2O_5 + Cl chemistry, followed by the extensive evaluation of model performance. Through the utilization of a large number of observational datasets, we found a substantial improvement has been achieved by the additional chlorine emissions, with NMB decreasing from -96% – -79% to -36% – 39% for Cl^- simulation. The comparison with observed N_2O_5 and $ClNO_2$ also indicates better model performance with Yu parameterization while γ_{N2O5} and φ_{ClNO2} are underestimated in McDuffie parameterization (a default setting in GEOS-Chem), resulting in larger model bias. The simulation of O_3 and $PM_{2.5}$ also agrees better with observations in general in the Base case (with the additional chlorine emissions and Yu parameterization) than the others.

Total tropospheric chlorine chemistry could increase Cl atoms by up to 7×10^3 molec cm^{-3}, and leads to an increase of up to 4.5 ppbv in MDA8 O_3 but a decrease of up to 7.9 μg m^{-3} in $PM_{2.5}$ concentrations on an annual mean basis in China. The decrease in $PM_{2.5}$ is mainly associated with the decrease in NO_3^- and NH_4^+, by up to 6.4 and 1.9 μg m^{-3}, respectively. The results also indicate that the heterogeneous N_2O_5 + Cl chemistry dominate the impact of chlorine chemistry, accounting for 83% and 90% of total change in O_3 and $PM_{2.5}$ concentrations. In other words, the chlorine chemistry without the heterogeneous N_2O_5 + Cl chemistry has a minor effect on annual mean MDA8 O_3 (less than 0.7 ppbv) and $PM_{2.5}$ (less than 1.5 μg m^{-3}) concentrations in China. This mechanism is particularly useful in elucidating the commonly seen O_3 underestimations relative to observations (e.g. (Ma et al. (2019))).

The effect of the heterogeneous N_2O_5 + Cl chemistry is sensitive to chlorine emissions. With the additional anthropogenic and biomass burning sources, simulated $PM_{2.5}$ concentrations are increased by up to 4.5 μg m^{-3} in the North China Plain but decreased by up to 3.7 μg m^{-3} in the Sichuan Basin on an annual basis. The latter is mainly driven by the decrease of NO_3^- due to the competition between the formation of $ClNO_2$ and HNO_3 upon the uptake of N_2O_5 on aerosol surfaces. The additional emissions also increase Cl atoms and OH in China associated with the photolysis of $ClNO_2$, consequently leading

to an increase of annual mean MDA8 O_3 concentrations by up to 3.5 ppbv. In contrast, the significance of the heterogeneous N_2O_5 + Cl chemistry especially over inland China would be severely underestimated if only sea salt chlorine is considered, with only a slight increase in MDA8 O_3 (< 0.5 ppbv) and a minor decrease in $PM_{2.5}$ (< 1.5 μg m^{-3}) in inland China.

Moreover, we found the importance of chlorine chemistry not only depends on the amount of emissions, but is also sensitive to the parameterizations for the heterogeneous N_2O_5 + Cl chemistry. Although with the same emission, the effects on MDA8 O_3 and $PM_{2.5}$ in China from the McDuffie case are lower compared to the results with Yu parameterization: differing by 48% and 27% in the annual average, respectively.

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Competing interests.

The authors declare that they have no conflict of interest.

Data and Code availability

The data used in this study is available upon request from Qiaoqiao Wang (qwang@jnu.edu.cn). The revised codes for different simulations could be downloaded via https://zenodo.org/record/5957287#.YfyNMppBxPZ

References

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the Reactive Uptake of Gaseous Compounds by Organic-Coated Aqueous Aerosols: Theoretical Analysis and Application to the Heterogeneous Hydrolysis of N2O5, The Journal of Physical Chemistry A, 110, 10435-10443, 10.1021/jp062403c, 2006.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 10.5194/acp-6-3625-2006, 2006.

Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmospheric Chemistry & Physics Discussions, 9, 191-198, 2009.

Bertram, T. H., Perring, A. E., Wooldridge, P. J., Dibb, J., Avery, M. A., and Cohen, R. C.: On the export of reactive nitrogen from Asia: NO_x partitioning and effects on ozone, Atmos. Chem. Phys., 13, 4617-4630, 10.5194/acp-13-4617-2013, 2013.

Chang, W. L., Brown, S. S., Stutz, J., Middlebrook, A. M., Bahreini, R., Wagner, N. L., Dubé, W. P., Pollack, I. B., Ryerson, T. B., and Riemer, N.: Evaluating N2O5 heterogeneous hydrolysis parameterizations for CalNex 2010, J. Geophys. Res.: Atmos., 121, 5051-5070, https://doi.org/10.1002/2015JD024737, 2016.

Chen, C., Zhang, H., Yan, W., Wu, N., Zhang, Q., and He, K.: Aerosol water content enhancement leads to changes in the major formation mechanisms of nitrate and secondary organic aerosols in winter over the North China Plain, Environ. Pollut., 287, 117625, https://doi.org/10.1016/j.envpol.2021.117625, 2021a.

Chen, W., Ye, Y., Hu, W., Zhou, H., Pan, T., Wang, Y., Song, W., Song, Q., Ye, C., Wang, C., Wang, B., Huang, S., Yuan, B., Zhu, M., Lian, X., Zhang, G., Bi, X., Jiang, F., Liu, J., Canonaco, F., Prevot, A. S. H., Shao, M., and Wang, X.: Real-Time Characterization of Aerosol Compositions, Sources, and Aging Processes in Guangzhou During PRIDE-GBA 2018 Campaign, J. Geophys. Res.: Atmos., 126, e2021JD035114, https://doi.org/10.1029/2021JD035114, 2021b.

Choi, M. S., Qiu, X., Zhang, J., Wang, S., Li, X., Sun, Y., Chen, J., and Ying, Q.: Study of Secondary Organic Aerosol Formation from Chlorine Radical-Initiated Oxidation of Volatile Organic Compounds in a Polluted Atmosphere Using a 3D Chemical Transport Model, Environ. Sci. Technol., 54, 13409-13418, 10.1021/acs.est.0c02958, 2020.

Dai, J., Liu, Y., Wang, P., Fu, X., Xia, M., and Wang, T.: The impact of sea-salt chloride on ozone through heterogeneous reaction with N2O5 in a coastal region of south China, Atmos. Environ., 236, 117604, https://doi.org/10.1016/j.atmosenv.2020.117604, 2020.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, Anal. Chem., 78, 8281-8289, 10.1021/ac061249n, 2006.

Finlayson-Pitts, B. J., Ezell, M. J., and Pitts, J. N. J.: Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N2O5 and ClONO2, Cheminform, 20, 241-244, 1989.

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 10.5194/acp-7-4639-2007, 2007.

Fu, X., Wang, T., Wang, S., Zhang, L., Cai, S., Xing, J., and Hao, J.: Anthropogenic Emissions of Hydrogen Chloride and Fine Particulate Chloride in China, Environ. Sci. Technol., 52, 1644, 2018.

Geng, G., Zhang, Q., Martin, R. V., Van Donkelaar, A., Huo, H., Che, H., Lin, J., and He, K.: Estimating long-term PM2.5 concentrations in China using satellite-based aerosol optical depth and a chemical transport model, Remote Sens. Environ., 166, 262-270, 2015.

Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive Uptake of N2O5 by Aerosols Containing Dicarboxylic Acids. Effect of Particle Phase, Composition, and Nitrate Content, The Journal of Physical Chemistry A, 113, 5082-5090, 10.1021/jp8096814, 2009.

Gross, S., Iannone, R., Xiao, S., and Bertram, A. K.: Reactive uptake studies of NO3 and N2O5 on alkenoic acid, alkanoate, and polyalcohol substrates to probe nighttime aerosol chemistry, PCCP, 11, 7792-7803, 10.1039/B904741G, 2009.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, 10.5194/acp-6-3181-2006, 2006.

Haskins, J. D., Lee, B. H., Lopez-Hilifiker, F. D., Peng, Q., Jaeglé, L., Reeves, J. M., Schroder, J. C., Campuzano-Jost, P., Fibiger, D., McDuffie, E. E., Jiménez, J. L., Brown, S. S., and Thornton, J. A.: Observational Constraints on the Formation of Cl2 From the Reactive Uptake of ClNO2 on Aerosols in the Polluted Marine Boundary Layer, J. Geophys. Res.: Atmos., 124, 8851-8869, https://doi.org/10.1029/2019JD030627, 2019.

Hong, Y., Liu, Y., Chen, X., Fan, Q., Chen, C., Chen, X., and Wang, M.: The role of anthropogenic

chlorine emission in surface ozone formation during different seasons over eastern China, Sci. Total Environ., 723, 137697, https://doi.org/10.1016/j.scitotenv.2020.137697, 2020.

Hossaini, R., Chipperfield, M. P., Saiz-Lopez, A., Fernandez, R., Monks, S., Feng, W., Brauer, P., and von Glasow, R.: A global model of tropospheric chlorine chemistry: Organic versus inorganic sources and impact on methane oxidation, J. Geophys. Res.: Atmos., 121, 14,271-214,297, https://doi.org/10.1002/2016JD025756, 2016.

Huang, Z., Zhong, Z., Sha, Q., Xu, Y., Zhang, Z., Wu, L., Wang, Y., Zhang, L., Cui, X., Tang, M., Shi, B., Zheng, C., Li, Z., Hu, M., Bi, L., Zheng, J., and Yan, M.: An updated model-ready emission inventory for Guangdong Province by incorporating big data and mapping onto multiple chemical mechanisms, Sci. Total Environ., 769, 144535, https://doi.org/10.1016/j.scitotenv.2020.144535, 2021.

Jaeglé, L., Quinn, P. K., Bates, T. S., Alexander, B., and Lin, J. T.: Global distribution of sea salt aerosols: new constraints from in situ and remote sensing observations, Atmos. Chem. Phys., 11, 3137-3157, 10.5194/acp-11-3137-2011, 2011.

Kercher, J. P., Riedel, T. P., and Thornton, J. A.: Chlorine activation by N2O5: simultaneous, in situ detection of ClNO2 and N2O5 by chemical ionization mass spectrometry, Atmospheric Measurement Techniques Discussions, 2009.

Lawler, M. J., Sander, R., Carpenter, L. J., Lee, J. D., and Saltzman, E. S.: HOCl and Cl2 observations in marine air, Atmos. Chem. Phys., 11, 8115-8144, 10.5194/acp-11-7617-2011, 2011.

Le Breton, M., Hallquist, Å. M., Pathak, R. K., Simpson, D., Wang, Y., Johansson, J., Zheng, J., Yang, Y., Shang, D., Wang, H., Liu, Q., Chan, C., Wang, T., Bannan, T. J., Priestley, M., Percival, C. J., Shallcross, D. E., Lu, K., Guo, S., Hu, M., and Hallquist, M.: Chlorine oxidation of VOCs at a semi-rural site in Beijing: Significant chlorine liberation from ClNO2 and subsequent gas and particle phase Cl-VOC production, Atmos. Chem. Phys., 18, 13013-13030, 10.5194/acp-18-13013-2018, 2018.

Li, G., Su, H., Ma, N., Tao, J., Kuang, Y., Wang, Q., Hong, J., Zhang, Y., Kuhn, U., Zhang, S., Pan, X., Lu, N., Tang, M., Zheng, G., Wang, Z., Gao, Y., Cheng, P., Xu, W., Zhou, G., Zhao, C., Yuan, B., Shao, M., Ding, A., Zhang, Q., Fu, P., Sun, Y., Pöschl, U., and Cheng, Y.: Multiphase chemistry experiment in Fogs and Aerosols in the North China Plain (McFAN): integrated analysis and intensive winter campaign 2018, Faraday Discuss., 226, 207-222, 10.1039/D0FD00099J, 2021.

Li, K., Jacob, D. J., Liao, H., Shen, L., Zhang, Q., and Bates, K. H.: Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, P. Natl. Acad. Sci., 116, 422-427, 10.1073/pnas.1812168116, 2019.

Li, M., Zhang, Q., Kurokawa, J. I., Woo, J. H., He, K., Lu, Z., Ohara, T., Song, Y., Streets, D. G., Carmichael, G. R., Cheng, Y., Hong, C., Huo, H., Jiang, X., Kang, S., Liu, F., Su, H., and Zheng, B.: MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP, Atmos. Chem. Phys., 17, 935-963, 10.5194/acp-17-935-2017, 2017.

Li, Q., Zhang, L., Wang, T., Tham, Y. J., Ahmadov, R., Xue, L., Zhang, Q., and Zheng, J.: 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, 10.5194/acp-16-14875-2016, 2016.

Liu, X., Qu, H., Huey, L. G., Wang, Y., Sjostedt, S., Zeng, L., Lu, K., Wu, Y., Hu, M., Shao, M., Zhu, T., and Zhang, Y.: High Levels of Daytime Molecular Chlorine and Nitryl Chloride at a Rural Site on the North China Plain, Environ. Sci. Technol., 51, 9588-9595, 10.1021/acs.est.7b03039, 2017.

Liu, Y., Fan, Q., Chen, X., Zhao, J., Ling, Z., Hong, Y., Li, W., Chen, X., Wang, M., and Wei, X.: 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, 10.5194/acp-18-2709-2018, 2018.

Lobert, J. M., Keene, W. C., Logan, J. A., and Yevich, R.: Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory, J. Geophys. Res.: Atmos., 104, 8373-8389, https://doi.org/10.1029/1998JD100077, 1999.

Ma, M., Gao, Y., Wang, Y., Zhang, S., Leung, L. R., Liu, C., Wang, S., Zhao, B., Chang, X., Su, H., Zhang, T., Sheng, L., Yao, X., and Gao, H.: Substantial ozone enhancement over the North China Plain from increased biogenic emissions due to heat waves and land cover in summer 2017, Atmos. Chem. Phys., 19, 12195-12207, 10.5194/acp-19-12195-2019, 2019.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez Hilfiker, F., Lee, B. H., Jaeglé, L., Guo, H., Weber, R. J., Reeves, J. M., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Dibb, J. E., Veres, P., Ebben, C., Sparks, T. L., Wooldridge, P. J., Cohen, R. C., Campos, T., Hall, S. R., Ullmann, K., Roberts, J. M., Thornton, J. A., and Brown, S. S.: ClNO2 Yields From Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of the Current Parameterization, J. Geophys. Res.: Atmos., 123, 12,994-913,015, https://doi.org/10.1029/2018JD029358, 2018a.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., Shah, V., Jaeglé, L., Guo, H., Weber, R. J., Michael Reeves, J., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Dibb, J. E., Veres, P., Ebben, C., Sparks, T. L., Wooldridge, P. J., Cohen, R. C., Hornbrook, R. S., Apel, E. C., Campos, T., Hall, S. R., Ullmann, K., and Brown,

S. S.: Heterogeneous N2O5 Uptake During Winter: Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of Current Parameterizations, J. Geophys. Res.: Atmos., 123, 4345-4372, https://doi.org/10.1002/2018JD028336, 2018b.

Mitroo, D., Gill, T. E., Haas, S., Pratt, K. A., and Gaston, C. J.: ClNO2 Production from N2O5 Uptake on Saline Playa Dusts: New Insights into Potential Inland Sources of ClNO2, Environ. Sci. Technol., 53, 7442-7452, 2019.

Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N_2O_5 uptake: airborne regional measurements in northwestern Europe, Atmos. Chem. Phys., 15, 973-990, 10.5194/acp-15-973-2015, 2015.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Technol., 45, 780-794, 10.1080/02786826.2011.560211, 2011.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, Nat. Geosci., 1, 324-328, 10.1038/ngeo177, 2008.

Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S. M., Gilman, J., De Gouw, J., and Bon, D. M.: Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer, Environ. Sci. Technol., 46, 10463-10470, 2012.

Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler-Scharr, A., and Mentel, T. F.: Relative importance of organic coatings for the heterogeneous hydrolysis of N2O5 during summer in Europe, J. Geophys. Res.: Atmos., 114, https://doi.org/10.1029/2008JD011369, 2009.

Saiz-Lopez, A. and von Glasow, R.: Reactive halogen chemistry in the troposphere, Chem. Soc. Rev., 41, 6448-6472, 10.1039/C2CS35208G, 2012.

Sarwar, G., Simon, H., Xing, J., and Mathur, R.: Importance of tropospheric ClNO2 chemistry across the Northern Hemisphere, Geophys. Res. Lett., 2014.

Schmidt, J. A., Jacob, D. J., Horowitz, H. M., Hu, L., Sherwen, T., Evans, M. J., Liang, Q., Suleiman, R. M., Oram, D. E., Le Breton, M., Percival, C. J., Wang, S., Dix, B., and Volkamer, R.: Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, J. Geophys. Res.: Atmos., 121, 11,819-811,835, https://doi.org/10.1002/2015JD024229, 2016.

Sherwen, T., Evans, M. J., Sommariva, R., Hollis, L. D. J., Ball, S. M., Monks, P. S., Reed, C., Carpenter, L. J., Lee, J. D., Forster, G., Bandy, B., Reeves, C. E., and Bloss, W. J.: Effects of halogens on European air-quality, Faraday Discuss., 200, 75-100, 10.1039/C7FD00026J, 2017.

Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., Jacob, D. J., Dix, B., Koenig, T. K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S., and Ordóñez, C.: Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem, Atmos. Chem. Phys., 16, 12239-12271, 10.5194/acp-16-12239-2016, 2016.

Simmonds, P. G., Manning, A. J., Cunnold, D. M., McCulloch, A., O'Doherty, S., Derwent, R. G., Krummel, P. B., Fraser, P. J., Dunse, B., Porter, L. W., Wang, R. H. J., Greally, B. R., Miller, B. R., Salameh, P., Weiss, R. F., and Prinn, R. G.: Global trends, seasonal cycles, and European emissions of dichloromethane, trichloroethene, and tetrachloroethene from the AGAGE observations at Mace Head, Ireland, and Cape Grim, Tasmania, J. Geophys. Res.: Atmos., 111, https://doi.org/10.1029/2006JD007082, 2006.

Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chem. Rev., 115, 4035-4062, 10.1021/cr5006638, 2015.

Staudt, S., Gord, J. R., Karimova, N. V., McDuffie, E. E., Brown, S. S., Gerber, R. B., Nathanson, G. M., and Bertram, T. H.: Sulfate and Carboxylate Suppress the Formation of ClNO2 at Atmospheric Interfaces, ACS Earth and Space Chemistry, 3, 1987-1997, 10.1021/acsearthspacechem.9b00177, 2019.

Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N2O5 hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size, PCCP, 5, 4593-4603, 10.1039/B307498F, 2003.

Tian, M., Liu, Y., Yang, F., Zhang, L., Peng, C., Chen, Y., Shi, G., Wang, H., Luo, B., Jiang, C., Li, B., Takeda, N., and Koizumi, K.: Increasing importance of nitrate formation for heavy aerosol pollution in two megacities in Sichuan Basin, southwest China, Environ. Pollut., 250, 898-905, https://doi.org/10.1016/j.envpol.2019.04.098, 2019.

Van, d. W., G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., Defries, R. S., Jin, Y., and Van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmos. Chem. Phys., 10, 16153-16230, 10.5194/acp-10-11707-2010, 2010.

Wang, S., Su, H., Chen, C., Tao, W., Streets, D. G., Lu, Z., Zheng, B., Carmichael, G. R., Lelieveld, J., Pöschl, U., and Cheng, Y.: Natural gas shortages during the “coal-to-gas” transition in China have

caused a large redistribution of air pollution in winter 2017, P. Natl. Acad. Sci., 117, 31018-31025, 10.1073/pnas.2007513117, 2020a.

Wang, X., Jacob, D. J., Fu, X., Wang, T., and Liao, H.: Effects of Anthropogenic Chlorine on PM 2.5 and Ozone Air Quality in China, Environ. Sci. Technol., 54, 9908-9916, 2020b.

Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., Alexander, B., Sherwen, T., Evans, M. J., Lee, B. H., Haskins, J. D., Lopez-Hilfiker, F. D., Thornton, J. A., Huey, G. L., and Liao, H.: The role of chlorine in global tropospheric chemistry, Atmos. Chem. Phys., 19, 3981-4003, 10.5194/acp-19-3981-2019, 2019.

Wang, Y., Shen, L., Wu, S., Mickley, L., He, J., and Hao, J.: Sensitivity of surface ozone over China to 2000–2050 global changes of climate and emissions, Atmos. Environ., 75, 374-382, 2013.

Xia, M., Wang, W., Wang, Z., Gao, J., Li, H., Liang, Y., Yu, C., Zhang, Y., Wang, P., Zhang, Y., Bi, F., Cheng, X., and Wang, T.: Heterogeneous Uptake of N2O5 in Sand Dust and Urban Aerosols Observed during the Dry Season in Beijing, Atmosphere, 10, 204, 2019.

Xu, Z., Liu, M., Zhang, M., Song, Y., Wang, S., Zhang, L., Xu, T., Wang, T., Yan, C., Zhou, T., Sun, Y., Pan, Y., Hu, M., Zheng, M., and Zhu, T.: High efficiency of livestock ammonia emission controls in alleviating particulate nitrate during a severe winter haze episode in northern China, Atmos. Chem. Phys., 19, 5605-5613, 10.5194/acp-19-5605-2019, 2019.

Yang, X., Wang, T., Xia, M., Gao, X., Li, Q., Zhang, N., Gao, Y., Lee, S., Wang, X., Xue, L., Yang, L., and Wang, W.: Abundance and origin of fine particulate chloride in continental China, Sci. Total Environ., 624, 1041-1051, https://doi.org/10.1016/j.scitotenv.2017.12.205, 2018.

Ye, C., Yuan, B., Lin, Y., Wang, Z., Hu, W., Li, T., Chen, W., Wu, C., Wang, C., Huang, S., Qi, J., Wang, B., Wang, C., Song, W., Wang, X., Zheng, E., Krechmer, J. E., Ye, P., Zhang, Z., Wang, X., Worsnop, D. R., and Shao, M.: Chemical characterization of oxygenated organic compounds in the gas phase and particle phase using iodide CIMS with FIGAERO in urban air, Atmos. Chem. Phys., 21, 8455-8478, 10.5194/acp-21-8455-2021, 2021.

Yu, C., Wang, Z., Xia, M., Fu, X., Wang, W., Tham, Y. J., Chen, T., Zheng, P., Li, H., Shan, Y., Wang, X., Xue, L., Zhou, Y., Yue, D., Ou, Y., Gao, J., Lu, K., Brown, S. S., Zhang, Y., and Wang, T.: Heterogeneous N2O5 reactions on atmospheric aerosols at four Chinese sites: improving model representation of uptake parameters, Atmos. Chem. Phys., 20, 4367-4378, 10.5194/acp-20-4367-2020, 2020.

Zhang, T., de Jong, M. C., Wooster, M. J., Xu, W., and Wang, L.: Trends in eastern China agricultural fire emissions derived from a combination of geostationary (Himawari) and polar (VIIRS) orbiter fire radiative power products, Atmos. Chem. Phys., 20, 10687-10705, 10.5194/acp-20-10687-2020,

860 2020.

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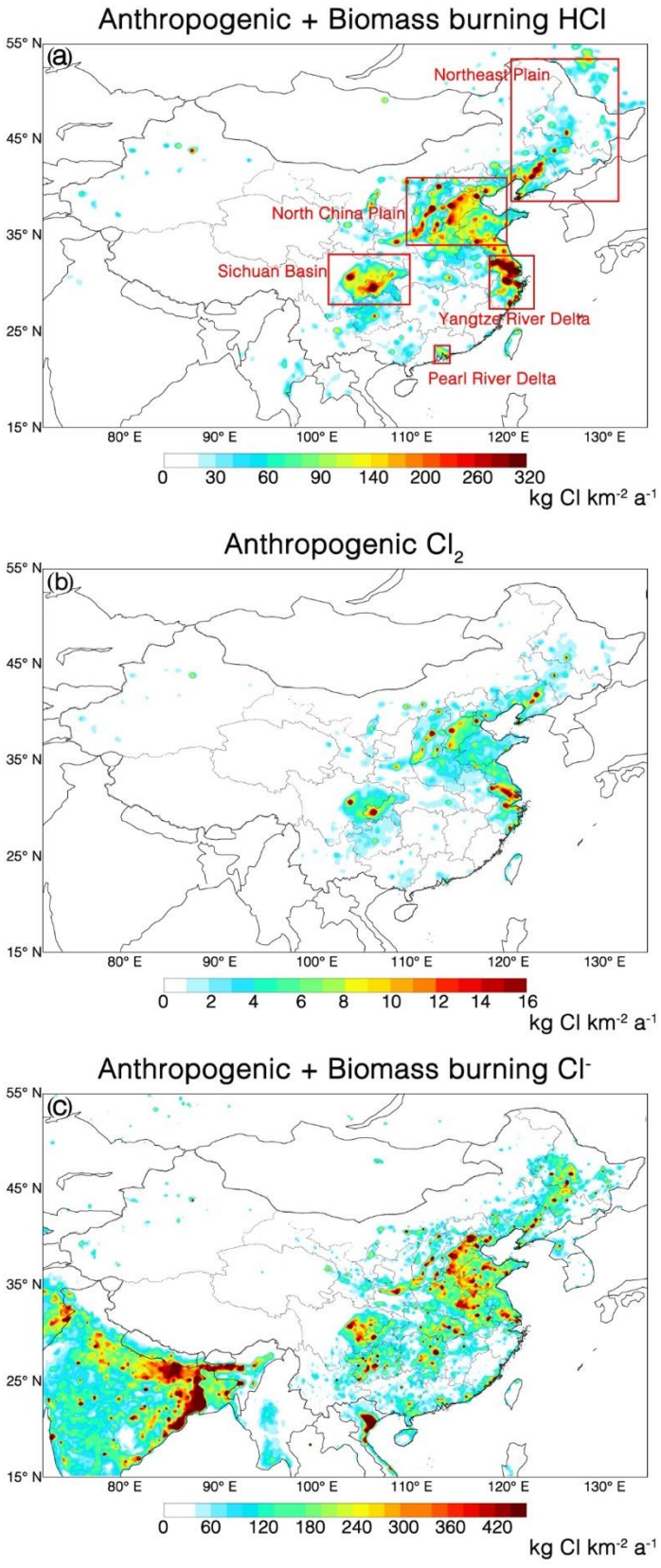


862

863 **Figure 1. Annual emissions of (a) HCl, (b) Cl_2, (c) non-sea salt Cl^-. Locations of the Northeast Plain, North**

China Plain, Yangtze River Delta, Pearl River Delta and Sichuan Basin are highlighted by red boxes in (a).

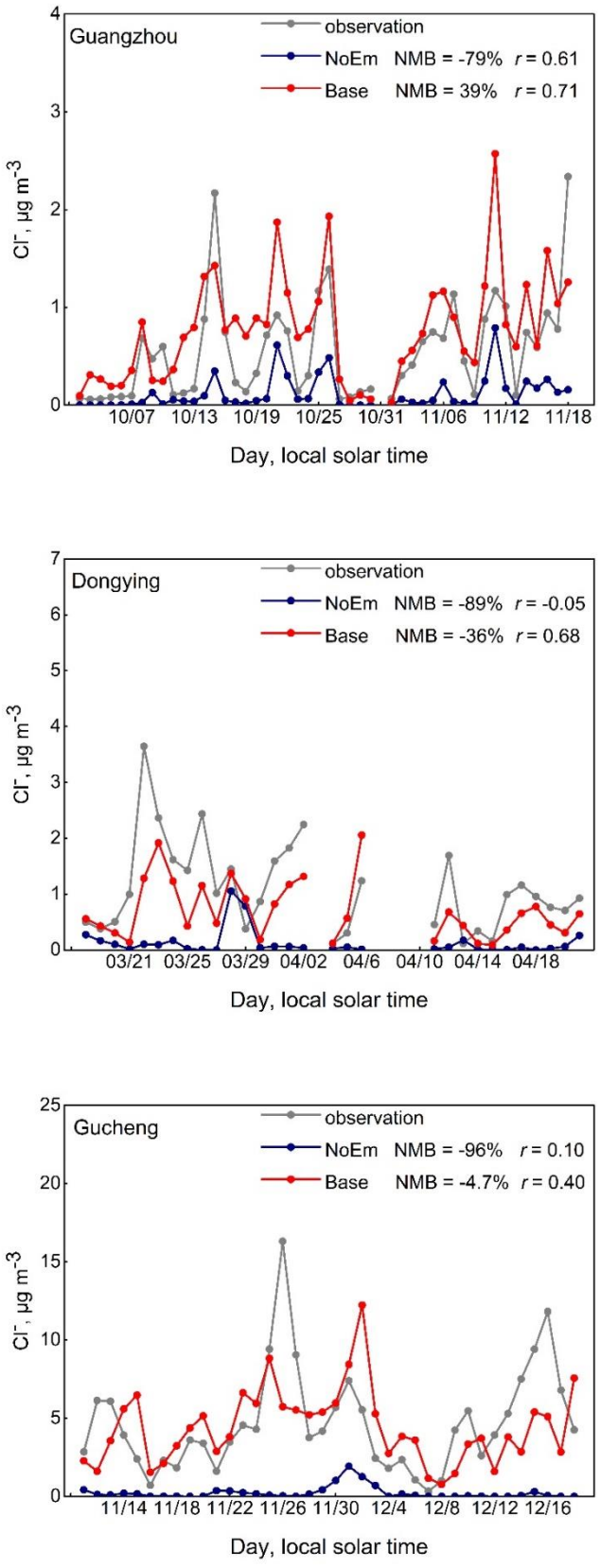


Figure 2. Time series of simulated and observed particulate Cl^- concentrations at the Guangzhou, Dongying and Gucheng sites.

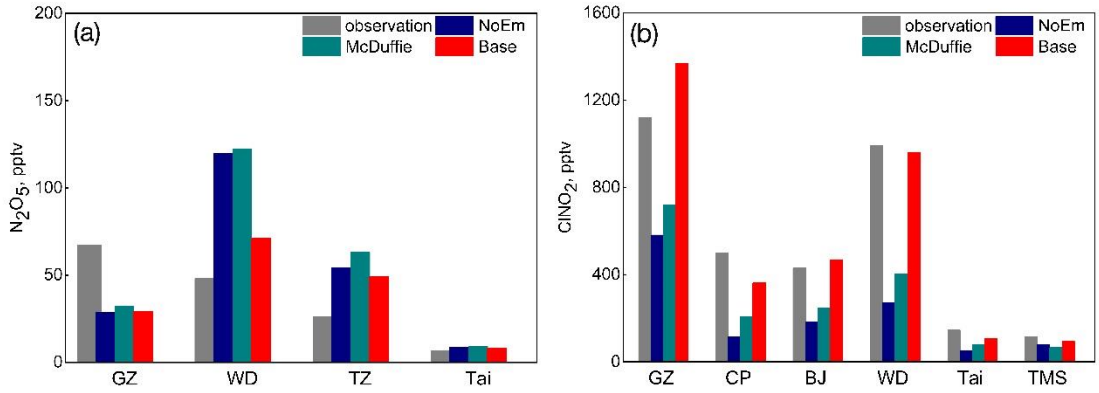


Figure 3. Comparison of observed and simulated (a) averaged N_2O_5 concentrations and (b) mean nighttime maximum mixing ratio of $ClNO_2$ concentrations at different sites. The simulation definitions are provided in Table 2. GZ: Guangzhou; WD: Wangdu; TZ: Taizhou; Tai: Mount Tai; CP: Changping; BJ: Beijing; TMS: Mount TaiMoShan

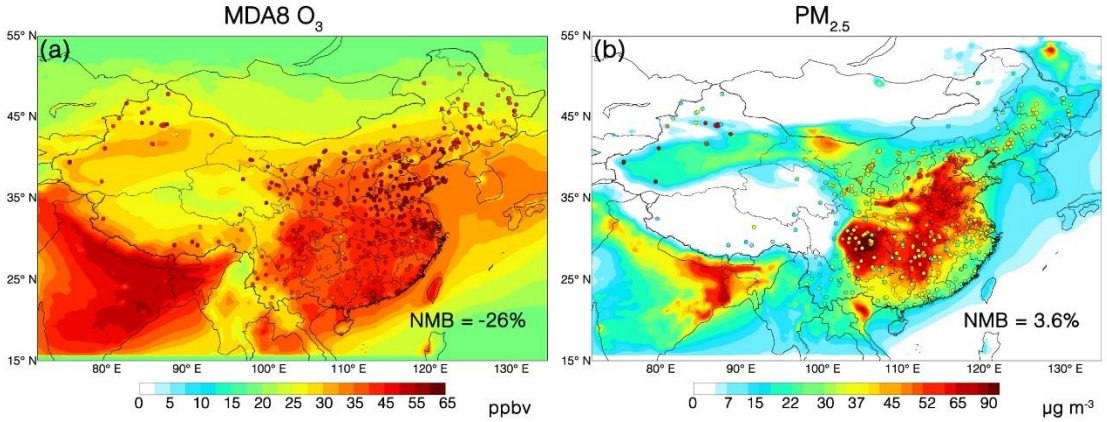
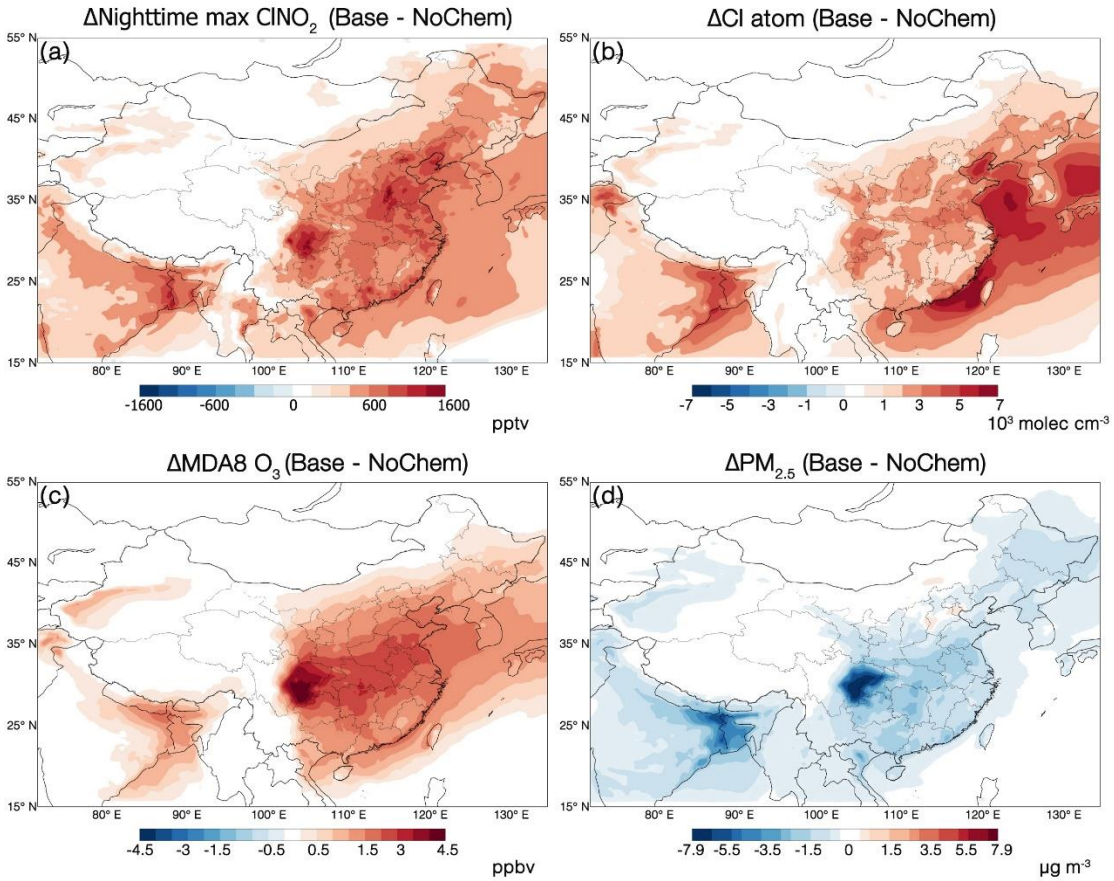


Figure 4. Annual mean surface concentrations of (a) MDA8 O_3 and (b) $PM_{2.5}$ over China in 2018. GEOS-Chem model values from the Base case are shown as contours. Observations from China National Environmental Monitoring Center (CNEMC) are shown as circles.



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882 **Figure 5. Effects of chlorine chemistry on annual mean surface concentrations of (a) nighttime max $ClNO_2$,**
883 **(b) Cl atom, (c) MDA8 O_3 and (d) $PM_{2.5}$ in China, estimated as the differences between the Base and**
884 **NoChem cases.**

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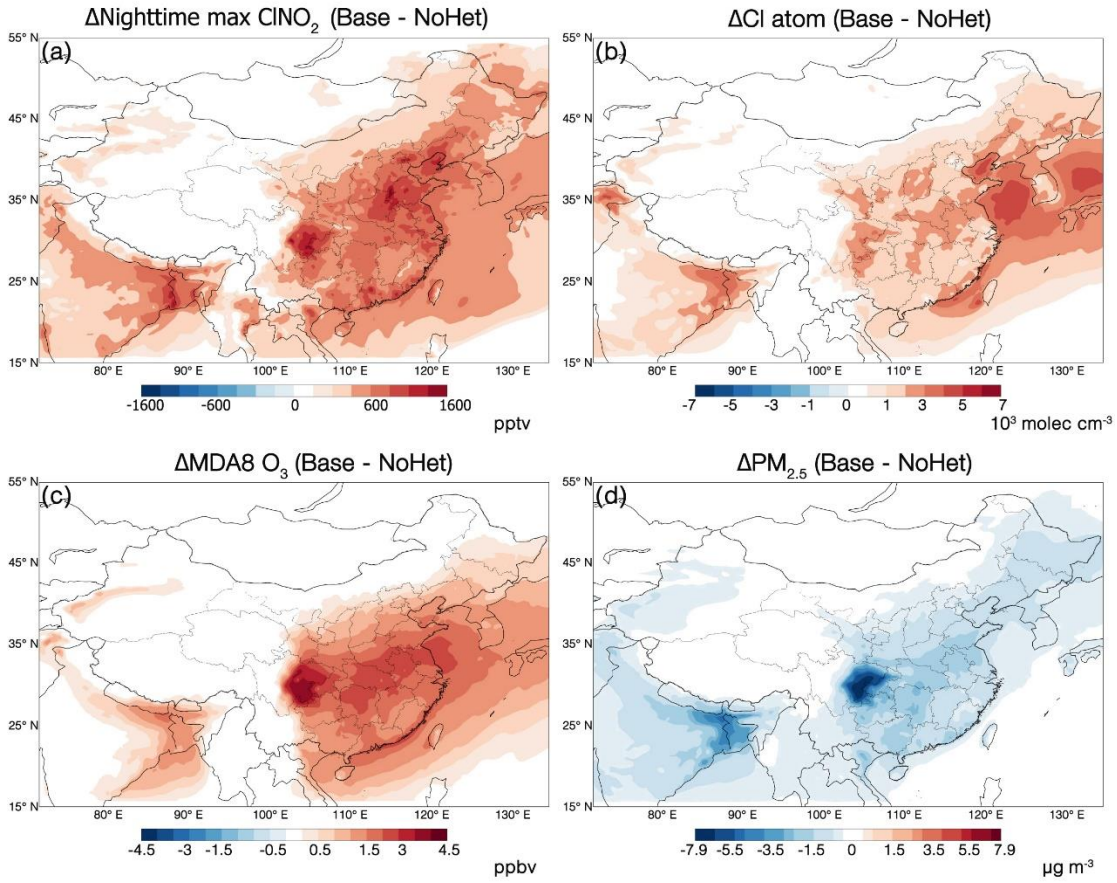

886

887 **Figure 6. Effects of the heterogeneous N_2O_5 + Cl chemistry on annual mean surface concentrations of (a)**
888 **nighttime max $ClNO_2$, (b) Cl atom, (c) MDA8 O_3 and (d) $PM_{2.5}$ in China, estimated as the differences**
889 **between the Base and NoHet cases.**

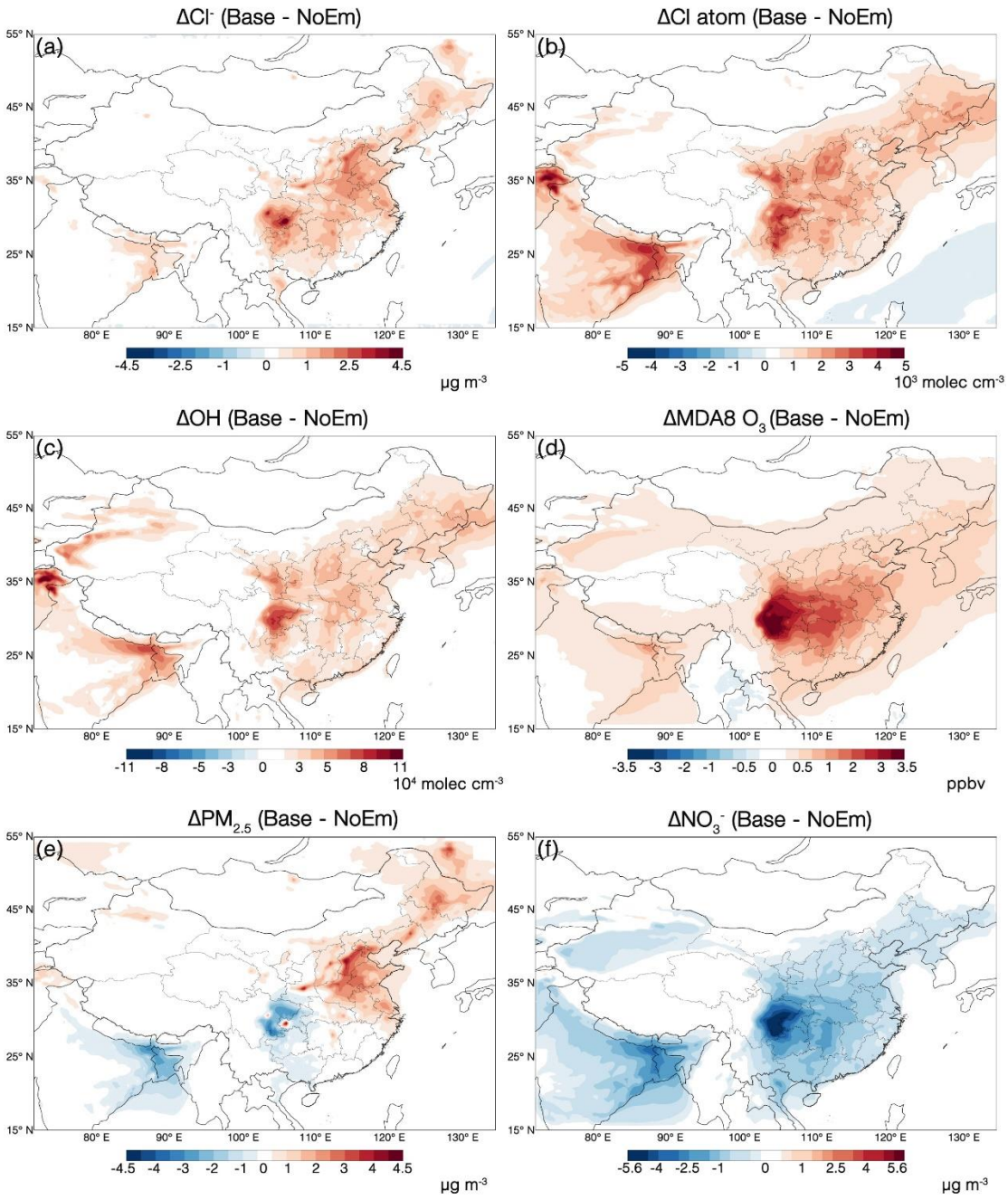

Figure 7. Effects of anthropogenic and biomass burning chlorine emissions on annual mean surface concentrations of (a) Cl^-, (b) Cl atom, (c) OH, (d) MDA8 O_3, (e) $PM_{2.5}$ and (f) NO_3^- in China, estimated as the differences between the Base and NoEm cases.

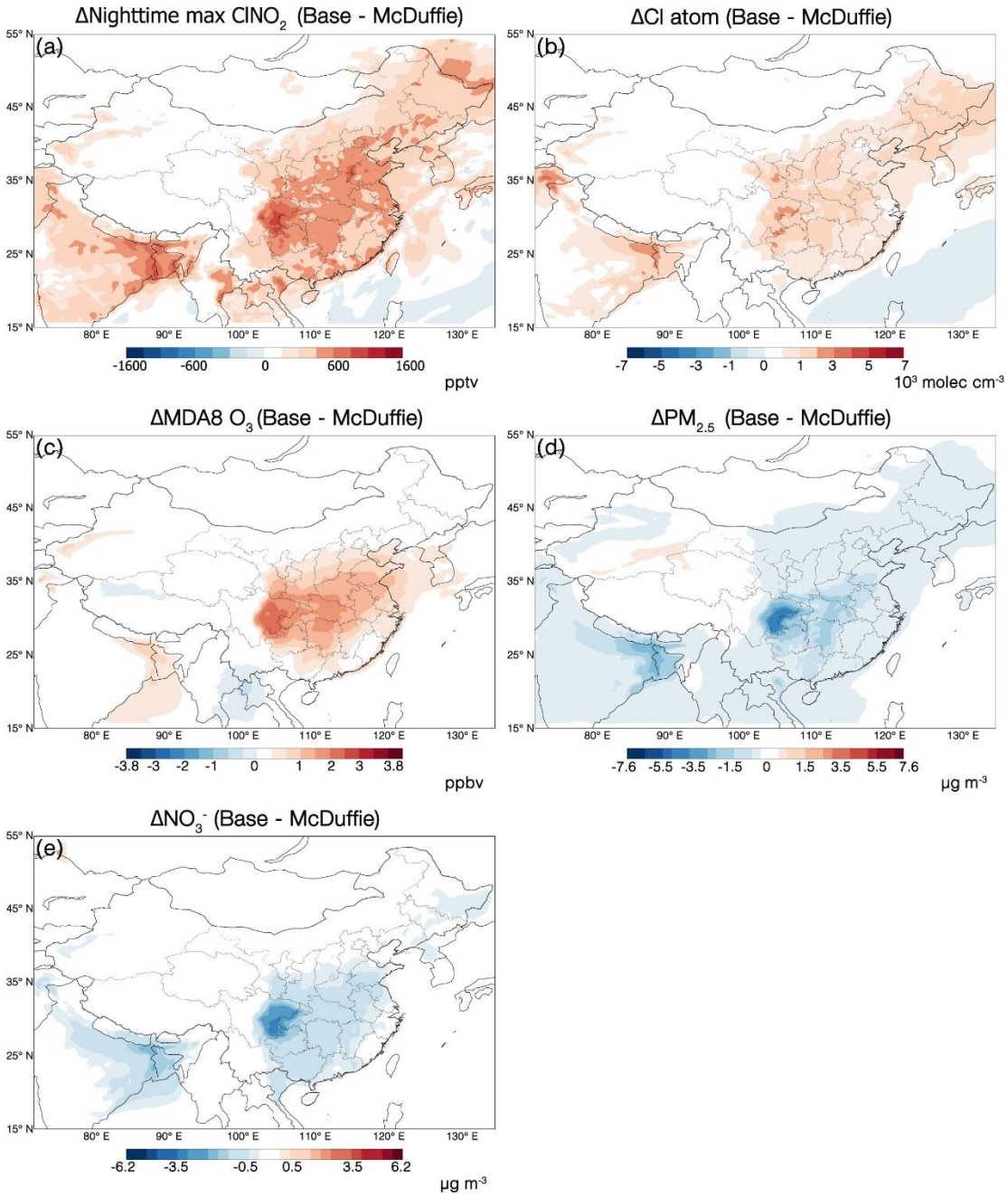

Figure 8. Effects of different parameterizations on annual mean surface concentrations of (a) nighttime max $ClNO_2$, (b) Cl atom, (c) MDA8 O_3, (d) $PM_{2.5}$, and (e) NO_3^- in China, estimated as the differences between the Base and McDuffie cases.

907 **Table 1. Chlorine emissions in China in the model.**

Sources	By default (Gg Cl a^{-1})	Updated in this study (Gg Cl a^{-1})
Sea salt Cl^-	6.5×10^4	6.5×10^4
Anthropogenic HCl	0	218
Biomass burning HCl	0	30
Anthropogenic Cl_2	0	8.9
Anthropogenic Cl^-	0	379
Biomass burning Cl^-	0	120
CH_3Cl[a]	3.8	3.8
CH_2Cl_2[a]	2.4	2.4
$CHCl_3$[a]	0.70	0.70

908 [a]: Sources are shown in terms of the chemical release (e.g. +Cl, +OH, +hν)

909

910 **Table 2. Model setup of all simulation cases**

Cases	N_2O_5 uptake (γ_{N2O5})	$ClNO_2$ production (φ_{ClNO2})	Other tropospheric chlorine chemistry	Anthropogenic and biomass burning inorganic chlorine emissions
Base	Yu et al. (2020)	Yu et al. (2020)	Full	Yes
McDuffie	McDuffie et al. (2018a, 2018b)	McDuffie et al. (2018a, 2018b)	Full	Yes
NoEm	Yu et al. (2020)	Yu et al. (2020)	Full	None
NoHet	Yu et al. (2020) but with $[Cl^-] = 0$	None	Full	Yes
NoChem	Yu et al. (2020) but with $[Cl^-] = 0$	None	None	Yes
NoEmHet	Yu et al. (2020) but with $[Cl^-] = 0$	None	Full	None
NoAll	Yu et al. (2020) but with $[Cl^-] = 0$	None	None	None

911

912 **Table 3. Normalized mean bias (NMB) and correlation coefficients (*r*) between observed and simulated**
913 **MDA8 O_3 and $PM_{2.5}$ concentrations during 2018 in China**

Species	Time	Base		McDuffie		NoEm	
		NMB	*r*	NMB	*r*	NMB	*r*
MDA8 O_3	Annual	-26%	0.83	-27%	0.83	-28%	0.82
	MAM[a]	-35%	0.87	-36%	0.87	-36%	0.87
	JJA[b]	-5.5%	0.50	-5.2%	0.48	-5.9%	0.48
	SON[c]	-24%	0.79	-26%	0.78	-28%	0.76
	DJF[d]	-49%	0.81	-53%	0.80	-54%	0.80
$PM_{2.5}$	Annual	3.6%	0.81	5.6%	0.81	2.3%	0.80
	MAM	-6.3%	0.52	-4.9%	0.53	-6.2%	0.52
	JJA	3.9%	0.70	4.6%	0.70	5.0%	0.70
	SON	28%	0.79	32%	0.80	26%	0.79
	DJF	-4.3%	0.82	-2.6%	0.82	-7.9%	0.82

914 [a]: March, April, and May (Spring)

915 [b]: June, July, and August (Summer)

916 [c]: September, October, and November (Autumn)

917 [d]: December, January, and February (Winter)

918