This is the Pre-Published Version.

This document is the Accepted Manuscript version of a Published Work that appeared in final form in Environmental science and technology, copyright © 2020 American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/acs.est.0c02296.

The following publication Wang, X., Jacob, D. J., Fu, X., Wang, T., Breton, M. L., Hallquist, M., ... & Liao, H. (2020). Effects of anthropogenic chlorine on PM2. 5 and ozone air quality in China. Environmental Science & Technology, 54(16), 9908-9916.

FigurEffects of anthropogenic chlorine on $PM_{2.5}$ and ozone air quality in China

Xuan Wang [1,2], Daniel J. Jacob [2], Xiao Fu [3], Tao Wang [3], Michael Le Breton [4], Mattias Hallquist [4], Zirui Liu [5], Erin E. McDuffie [6,7], and Hong Liao [8]*

[1]School of Energy and Environment, City University of Hong Kong, Hong Kong SAR, China

[2]School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA

[3]Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong SAR, China

[4]Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden

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

[6]Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada.

[7]Department of Energy, Environment, and Chemical Engineering, Washington University in St. Louis, USA

[8]School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing, China

ABSTRACT: China has large anthropogenic chlorine emissions from agricultural fires, residential biofuel, waste incineration, coal combustion, and industrial processes. Here we quantify the effects of chlorine on fine particulate matter ($PM_{2.5}$) and ozone air quality across China by using the GEOS-Chem chemical transport model with comprehensive anthropogenic emissions and detailed representation of gas-phase and heterogeneous chlorine chemistry. Comparison of the model to observed $ClNO_2$, HCl, and particulate Cl^- concentrations shows that reactive chlorine in China is mainly anthropogenic, unlike in other continental regions where it is mostly of marine origin. The model is successful in reproducing observed concentrations and their distributions, lending confidence in the anthropogenic chlorine emission estimates and the resulting chemistry. We find that anthropogenic chlorine emissions increase total inorganic $PM_{2.5}$ by as much as 3.2 μg m^{-3} on an annual mean basis through the formation of ammonium chloride, partly compensated by a decrease of nitrate because $ClNO_2$ formation competes with N_2O_5 hydrolysis. Annual mean MDA8 surface ozone increases by up to 1.9 ppb, mainly from $ClNO_2$ chemistry, while reactivities of volatile organic compounds increase (by up to 48% for ethane). We find that a sufficient representation of chlorine chemistry in air quality models can be obtained from consideration of HCl/Cl^- thermodynamics and $ClNO_2$ chemistry, because other more complicated aspects of chlorine chemistry have a relatively minor effect.

1. Introduction

Chlorine is emitted to the atmosphere as particulate chloride (Cl^-) from sea-salt, as hydrogen chloride (HCl) from volcanoes, as HCl/Cl^- from combustion and industry, and as chlorocarbons

from the biosphere, fires, and industrial processes[1, 2] . Subsequent atmospheric reactions can lead to the production of chlorine radicals[3], with a broad range of implications for global tropospheric chemistry and air quality. We recently presented a general analysis of the role of chlorine in global tropospheric chemistry using the GEOS-Chem chemical transport model with a detailed gas-phase and heterogeneous chlorine mechanism[3]. Here we examine the more specific implications for China air quality through the effects of chlorine chemistry on ground level ozone and $PM_{2.5}$ (particulate matter smaller than 2.5 μm diameter).

A unique feature of China air pollution is the magnitude of the anthropogenic chlorine source. The global tropospheric chlorine budget is dominated by marine sources, mainly through mobilization of chloride from sea salt aerosols (SSA)[3]. Most of the chlorine in continental regions of North America and Europe is dominated by long-range transport of this marine source.[3, 4] In contrast, atmospheric measurements suggest that chlorine in China is mostly anthropogenic.[5, 6] Anthropogenic sources in China include coal combustion, waste incineration, industrial processes, and biomass burning, totaling more than 800 Gg Cl a^{-1} in recent estimates.[7, 8] For comparison, anthropogenic chlorine emission in the US is estimated to be < 100 Gg Cl a^{-1} in the 2014 National Emissions Inventory of the Environmental Protection Agency.[9]

In polluted environments, nighttime formation of nitryl chloride ($ClNO_2$) followed by photolysis in the daytime returns Cl atoms and nitrogen oxide radicals (NO_x) to stimulate ozone production.[10-13] Sarwar et al.[14] applied a hemispheric-scale model to assess the effect of $ClNO_2$ chemistry on air quality and found significant increases of ozone and decreases of nitrate $PM_{2.5}$ in China, but they did not include anthropogenic sources of chlorine (which as we will see are dominant), and they showed no model evaluation for China due to lack of $ClNO_2$ measurements in China prior to 2010. In the recent decade, a number of measurements of $ClNO_2$ and Cl^- concentrations were conducted

in China[6, 13, 15-19]. A number of China-focused model studies incorporated anthropogenic chlorine emissions and chlorine chemistry with varying degrees of complexity and found that $ClNO_2$ chemistry increases ozone in polluted regions of China by 2-7 ppb[20-25]. Most of these studies mainly have focused on $ClNO_2$ chemistry and its impacts on the atmospheric oxidative capacity and ozone concentrations. The effects of anthropogenic chlorine on $PM_{2.5}$ have not been investigated in the previous studies.

Here, we use the GEOS-Chem model in a full-year high-resolution simulation over China and the adjacent ocean, including best estimates of anthropogenic and natural chlorine emissions combined with detailed representation of chlorine chemistry. We evaluate the model with the ensemble of atmospheric chlorine observations available for China, verifying the emission inventory. From there we quantify the effect of anthropogenic chlorine on both $PM_{2.5}$ and ozone air quality in China. Our work extends previous studies in its comprehensive treatment of chlorine chemistry, full accounting of both anthropogenic and natural chlorine emissions, and detailed comparisons with observations.

2. Materials and Methods

2.1 GEOS-Chem model

We use the GEOS-Chem model version 11-02d (http://www.geos-chem.org), which includes a detailed representation of coupled ozone–NO_x– volatile organic compound (VOC)–PM–halogen chemistry[26], and to which we have included an updated comprehensive treatment of chlorine chemistry[3]. GEOS-Chem is driven by MERRA2 (the Modern-Era Retrospective analysis for Research and Applications, Version 2) assimilated meteorological fields from the NASA Global Modeling and Assimilation office (GMAO) with native horizontal resolution of 0.5°×0.625° and

72 vertical levels from the surface to the mesosphere. Our simulation is conducted at that native resolution over East Asia (60°–150°E, 10°S–55°N), with dynamical boundary conditions from a global simulation with 4°×5° resolution. The Multi-resolution Emission Inventory for China (MEIC)[27] including seasonal, weekly, and diurnal variations for 2014 is used for Chinese anthropogenic emissions other than chlorine. Chlorine emissions are described in Section 2.2. Results presented here are from a 1-year simulation for 2014 after a 3-month model spin up.

GEOS-Chem has previously been used in a number of model studies of $PM_{2.5}$ and ozone air quality in China, showing that the model provides in general a credible representation of observations[28, 29]. However, none of these studies included comprehensive representation of chlorine chemistry. Here we added to the model the detailed chlorine chemistry mechanism (fully coupled with bromine and iodine) of Wang et al.[3]. 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, and two size ranges for aerosol Cl^- (fine mode <1 μm diameter and coarse mode >1 μm diameter). Gas-aerosol equilibrium of HCl and Cl^- is calculated with ISORROPIA II [30] as part of the H_2SO_4-HCl-HNO_3-NH_3-NVCs thermodynamic system, where NVCs stands for non-volatile cations and is treated in ISORROPIA II using Na^+ as proxy. The most important heterogeneous reactions include $N_2O_5 + Cl^-$ producing $ClNO_2$, HOBr + Cl^- producing BrCl, HOI + Cl^- producing ICl, HOCl + Cl^- producing Cl_2, OH + Cl^- producing Cl_2 (two-step process), and $ClNO_2 + Cl^-$ producing Cl_2. $ClNO_2$, BrCl, ICl, and Cl_2 all go on to photolyze to produce Cl atoms.

We added some updates to the Wang et al.[9] mechanism including Cl oxidation of toluene, monoterpenes, limonene, and methyl ethyl ketone, as given in Table S1. We updated the parameterization of $ClNO_2$ formation from nighttime heterogeneous reaction of N_2O_5 with Cl^- in the aerosol aqueous phase to include the effect of organic coating, as described by McDuffie et

al.[31] We added the reaction between HOCl and dissolved SO_2 (S(IV) ≡ HSO_3^- + SO_3^{2-}) to form SO_4^{2-} aerosol.[32, 33] We also now include in the model the reactive uptake of HCl on natural dust, limited by dust alkalinity[34]. Details of these updates are described in Supporting Information A1.

Cl-initiated VOCs oxidation can contribute to the formation of secondary organic aerosol (SOA),[35, 36] but this is not considered in the model because of the large uncertainties involved. Instead, our simulation uses a simple SOA scheme which takes a fixed-yield approach to SOA formation and displays good skill in capturing observations.[37, 38]

2.2. Anthropogenic Chlorine Emissions

We include anthropogenic chlorine emissions from the China inventory of Fu et al.[7] This inventory was developed for 2014 with a horizontal resolution of 0.1°×0.1°. It gives total anthropogenic (HCl + fine mode Cl^-) emissions in China of 254 Gg Cl a^{-1} from agricultural fires, 253 Gg Cl a^{-1} from residential biofuel, 251 Gg Cl a^{-1} from waste incineration, 109 Gg Cl a^{-1} from coal combustion, and 65 Gg Cl a^{-1} from industrial processes, for a total source of 932 Gg Cl a^{-1}. The inventory separates HCl (458 Gg Cl a^{-1}) and particulate Cl^- (486 Gg Cl a^{-1}) emissions, but the cations associated with Cl^- emissions are not identified. We assume in our standard simulation that all emissions are as HCl but also conduct a sensitivity simulation where particulate Cl^- is emitted as such with accompanying NVCs. There is negligible difference in results, as discussed below. We apply monthly, weekly, and diurnal scaling factors for coal combustion and industrial sources based on the MEIC inventory,[27] and national mean monthly scaling factors for agricultural fires, residential biofuels, and waste incineration based on Fu et al.[7]

We do not include any anthropogenic chlorine emissions from other countries in East Asia. The only global emission inventory is that of McCulloch et al.[39], built for the 1990s and found to be

considerably biased high relative to present-day observations and regional emission estimates.[3, 7, 8] The effect of these emissions on China air quality would be small compared to the effect of SSA chloride from the neighboring ocean.

Dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) are emitted from industrial activities and produce Cl atoms in GEOS-Chem through photolysis and oxidation[3]. Anthropogenic CH_2Cl_2 emission in China was estimated to be 318 Gg a^{-1} in 2016 in a bottom-up study by Feng et al.,[40]. The total $CHCl_3$ emission in China was estimated to be 88 Gg a^{-1} in 2015 based on a Bayesian inversion of surface measurements.[41] We include anthropogenic CH_2Cl_2 and $CHCl_3$ emission using these national numbers with a spatial distribution the same as anthropogenic HCl. Since both CH_2Cl_2 and $CHCl_3$ have long lifetimes (> 250 days), they have negligible effect on Chinese air quality and will not be discussed further.

Dust is an additional source of particulate chloride but most of this would be present in coarse particles (>2.5 μm diameter) and not contribute to $PM_{2.5}$. Natural $PM_{2.5}$ dust in GEOS-Chem[42] has an emission of 3300 Gg a^{-1} in China in 2014; assuming 0.15% Cl by mass based on US data,[43] this yields a Cl^- source of 4.9 Gg Cl^- a^{-1}. Previous studies[44, 45] have suggested that anthropogenic dust may contribute to $PM_{2.5}$ Cl^- concentrations in urban environments. We include these emissions using the AFCID inventory[46], again assuming that the dust is 0.15% Cl by mass. The resulting emission in China is 7.9 Gg Cl a^{-1}. These dust emissions are very small compared to the anthropogenic chlorine emission from combustion.

Figure 1 shows the annual HCl + Cl^- emissions from Chinese anthropogenic sources and Cl^- emissions from sea salt aerosol (SSA) as implemented in GEOS-Chem. There are two areas of high anthropogenic emissions, in the North China Plain (NCP) due to waste incineration and residential biofuel, and in Northeast China due to agricultural fires and residential biofuel. The

SSA source over the ocean is much larger than the anthropogenic source over land (note difference in scales in Figure 1), and can contribute to $PM_{2.5}$ Cl^- over land both by direct transport and (for coarse SSA) by displacement to HCl and subsequent re-condensation to $PM_{2.5}$ [3]. However, the SSA influence over land is also limited by rapid deposition during transport. The GEOS-Chem simulation allows quantification of these effects.

3. Results and Discussion

3.1. Anthropogenic chlorine over China

Figure 2 shows our simulated annual mean distributions of HCl and $PM_{2.5}$ Cl^- concentrations in surface air. Concentrations over China are mainly from anthropogenic chlorine emissions, despite the much larger SSA emissions off-shore. Natural dust contributes 3-10% of $PM_{2.5}$ Cl^- in North China in spring, and less in other regions and seasons. Annual mean HCl mixing ratios range from 100 to 400 ppt over most of eastern China. In the H_2SO_4-HCl-HNO_3-NH_3-NVC thermodynamic system, HCl partitions into the aqueous particulate phase through:

$$HCl(g) + NH_3(g) \rightleftarrows NH_4^+ + Cl^- \quad \text{(R1)}$$

and

$$HCl(g) + NO_3^- \rightleftarrows Cl^- + HNO_3(g) \quad \text{(R2)}$$

Since NH_3 is generally in large excess in China,[47] equilibrium (R1) is driven to the right and uptake of HCl mostly takes place without displacement of NO_3^-. Figure S1 shows the HCl/(HCl + $PM_{2.5}$ Cl^-) molar ratio over China in different seasons. On average, 66% of the emitted HCl is partitioned into the particulate phase. That fraction is larger in winter and lower in summer, mainly reflecting temperature differences.

Even without considering anthropogenic chlorine emissions, anthropogenic HCl can be formed through acid displacement of SSA Cl^- by H_2SO_4 and HNO_3 produced from anthropogenic emissions of. SO_2 and NO_x. This acid displacement involves (R2) and:

$$Cl^- + H_2SO_4 \rightarrow HCl(g) + HSO_4^- \qquad (R3)$$

H_2SO_4 has a much lower vapor pressure than HCl so that (R3) fully displaces Cl^- if H_2SO_4 is present.[48] To investigate this effect we conducted two sensitivity model simulations, one without anthropogenic chlorine emissions but with anthropogenic non-chlorine emissions, and the other without any anthropogenic emissions. The difference between the two isolates the chlorine displaced from SSA Cl^- by non-chlorine anthropogenic emissions, and this is shown in the right panel of Figure 2. Acid displacement requires a deficit of ammonia and thus mainly takes place offshore. The resulting HCl can then be transported back onshore and contribute to $PM_{2.5}$ Cl^- and chlorine chemistry inland. We find that the effect is relatively small and mainly limited to southeastern coastal China. We examined the sensitivity of our results to the speciation of anthropogenic ($HCl + Cl^-$) emission by conducting a sensitivity simulation in which emission of Cl^- is with NVCs as associated cations (instead of HCl in the standard simulation). On average, adding the NVCs emission changes the simulated annual mean HCl and Cl^- concentrations by -2% and +1% respectively.

Figure 2 also shows the annual mean value of the nighttime maximum $ClNO_2$ mixing ratio in surface air, and the contributions from anthropogenic chlorine and other (mainly NO_x) emissions. We use the mean nighttime maximum mixing ratio as concentration metric for $ClNO_2$, following standard practice[3, 14], because of the large diurnal variation and near-zero mixing ratios in the daytime. Again, most of $ClNO_2$ over China is driven by anthropogenic chlorine emissions. Values

196 exceed 1000 ppt in inland urban areas of China, much higher than corresponding values in the US
197 and Europe.[3, 14]

198 We compared the model simulation for 2014 to observations collected in China for neighboring
199 years (2012-2017), and assuming interannual differences to be a minor factor in model error.
200 Continuous 2012-2013 observations of PM2.5 Cl^- are available from 11 sites as part of the CARE-
201 China network[49]. The annual mean observed values are shown as circles in the middle-left panel
202 of Figure 2. The model captures the spatial distribution of observed Cl^- with a correlation
203 coefficient (R) of 0.78 and a normalized mean bias (NMB) of -12%. $PM_{2.5}$ Cl^- concentrations in
204 inland China are much higher than the corresponding concentrations in the US (mostly < 0.1 μg
205 m^{-3}).[3, 44]

206 Figure 3 shows absolute maximum and mean nighttime maximum $ClNO_2$ mixing ratios from
207 several field studies, and compares to the modeled values during the measurement months.
208 Measurement locations are indicated in Figure 2. The model successfully simulates the surface
209 $ClNO_2$ observations for the three sites in the Beijing-Tianjin-Hebei area (Changping, Beijing, and
210 Wangdu) and the mountain site (Mt. Tai) in NCP during their respective measurement periods.
211 Ignoring the anthropogenic chlorine emissions would result in underestimates by more than a
212 factor of 10 at these sites. In contrast, anthropogenic chlorine is relatively minor at the mountain
213 site in Hong Kong (Mt. Tai Mo Shan), both in the model and observations, because SSA provides
214 the dominant source of Cl^- at that site. The model overestimates anthropogenic influence at Ji'nan,
215 for reasons that are not clear. The observations are much lower than for other surface sites in the
216 North China Plain.

217 Continuous measurements of HCl, PM_1 Cl^- (in particles less than 1 μm diameter), and $ClNO_2$
218 concentrations were made at the semi-rural surface site of Changping (40 km northwest of Beijing

219 urban area) during May-June 2016 by Le Breton et al.[6] Back-trajectory analyses showed no
220 significant marine influence in the data[13,60]. Figure 4 compares the diurnal cycle of the observations
221 to the model. Model concentrations at the site are almost exclusively from anthropogenic chlorine
222 emissions. The model is consistent with the overall magnitudes observed. HCl is low at night
223 because of dry deposition. Cl^- is low in the daytime because of ventilation. The observed nighttime
224 peak of $ClNO_2$ is at 23 local time, whereas $ClNO_2$ in the model keeps on accumulating over the
225 course of the night consistent with other observations in polluted areas, including another site near
226 Beijing.[3, 12, 18, 50, 51] The cause of the post-midnight decrease in the Changping $ClNO_2$ data is not
227 clear. Here and elsewhere in China, we find the $ClNO_2 + Cl^-$ heterogeneous sink of $ClNO_2$ to be
228 unimportant because it requires aerosol pH < 2 [52] which generally does not occur because of the
229 excess of NH_3.
230 In summary, the model shows general consistency with observations of Cl^-, $ClNO_2$, and HCl
231 available in China. We conclude from our comparisons that the chlorine over China is mainly
232 anthropogenic, and that the underlying chlorine emissions and chemistry are relatively well
233 understood.
234
235 3.3. Impact of anthropogenic chlorine emissions on inorganic $PM_{2.5}$ in China

236 Figure 5 shows our simulated net impacts of anthropogenic chlorine emissions on annual mean
237 $PM_{2.5}$ concentrations calculated as differences between the standard simulation and a simulation
238 without anthropogenic chlorine emissions. This does not account for Cl-initiated SOA formation,
239 as explained in Section 2. We find that the largest impact is over Northeast China, where annual
240 mean $PM_{2.5}$ increases by 3.2 $\mu g\ m^{-3}$ (6.5%), which is 9% of the Chinese national air quality

241 standard of 35 μg m^{-3} and mainly contributed by biomass burning emissions. Absolute and relative
242 impacts in January and July are given in Figure S2.
243 We find that anthropogenic chlorine has negligible effect on SO_4^{2-} concentrations in China (<
244 0.1 μg m^{-3}). The contribution of HOCl + S(IV) to SO_2 oxidation is minimal because the main sink
245 of HOCl is photolysis. As shown in Figure 5, anthropogenic chlorine emissions can cause annual
246 mean surface NH_4^+ concentrations to increase by up to 1 μg m^{-3}. Since NH_3 is in excess in most
247 areas of China,[47] the emitted HCl causes NH_3 transfer to NH_4^+ through reaction (R1), so that the
248 pattern of enhanced NH_4^+ largely matches that of Cl^- concentrations. In contrast, anthropogenic
249 chlorine emissions result in annual average NO_3^- concentrations decreases by up to 1.5 μg m^{-3}
250 following a similar spatial distribution as modeled $ClNO_2$ (Figure 2). The dominant factor for the
251 NO_3^- decrease is not acid displacement by HCl (since NH_3 is in excess) but the increased
252 competition of $N_2O_5 + Cl^-$ with N_2O_5 hydrolysis which is a major source of NO_3^-.[53]
253
254 3.4. Impact of anthropogenic chlorine emissions on oxidants in China

255 Figure 6 shows the effects of anthropogenic chlorine emissions on annual mean hydroxyl radical
256 (OH), NO_x, and ozone concentrations in surface air, calculated as differences between the standard
257 simulation and a simulation without anthropogenic chlorine emissions. OH concentrations in
258 surface air increase by up to 6%, mainly due to $ClNO_2$ chemistry [11, 12]. Annual mean Cl atom
259 concentrations (not shown) increase up to 2700 cm^{-3}; 90% of that increase is from $ClNO_2$
260 chemistry, while the remaining 10% is from HCl + OH and from Cl_2 and HOCl photolysis. The
261 latter reactions are most important in summer but even then they contribute less than 25% of the
262 Cl atoms. The combined increases of both Cl atoms and OH enhance the annual mean reactivities
263 of ethane, propane, $\geq C_3$ alkenes, methanol, toluene, and ethanol over the North China Plain by

48%, 40%, 28%, 11%, 11%, and 10%, respectively. The increase of OH leads to a decrease in NO_x since the principal sink of NO_x is its oxidation by OH.

As shown in Figure 6, annual mean values of maximum daily 8-hour average (MDA8) ozone concentrations increase by up to 1.9 ppb (3.2%) after including anthropogenic chlorine emissions. Seasonal effects are presented in Figure S3 and relative effects are in Figure S4. The ozone increase is mainly because of $ClNO_2$ chemistry and is most important in winter (Figure S3) due to the longer night and higher chlorine emissions from residential heating. Wang et al.[3] showed that tropospheric chlorine drives a global decrease of ozone by catalytic production of bromine radicals from sea salt aerosol, but we find that this effect is negligibly small over China because bromine concentrations (mainly of marine origin) are negligibly low.[3]

In summary, we have examined the impact of anthropogenic chlorine emissions on air quality in China through model simulations with a detailed chemical mechanism. The model is generally consistent with the observations available for fine particulate Cl^-, HCl, and $ClNO_2$. We show that the observations are dominantly contributed by anthropogenic chlorine emissions. Anthropogenic chlorine increases $PM_{2.5}$ concentrations in China by up to 3.2 μg m^{-3} on an annual mean basis because of the condensation of (NH_4^+, Cl^-) when NH_3 is in excess, as is the case generally over China. Annual mean surface OH and MDA8 ozone concentrations increase by up to 6% and 1.9 ppb, respectively, mostly driven by $ClNO_2$ chemistry providing an early-morning source of radicals. Our results suggest that a sufficient representation of anthropogenic chlorine chemistry in air quality models for China can be obtained from consideration of H_2SO_4-HCl-HNO_3-NH_3-NVCs thermodynamics and $ClNO_2$ chemistry, since other aspects of chlorine chemistry have a relatively minor effect.

Emissions in China are presently changing rapidly in response to the governmental Clean Air Action.[27] According to the MEIC inventory, Chinese emissions decreased by 59% for SO_2 and 21% for NO_x over 2013-2017, mainly due to emission controls applied to coal burning and industry.[27] No estimates are available for trends in anthropogenic chlorine emissions. Agricultural fires in China are increasingly banned out of concern for air quality[54], and coal combustion emission controls would presumably remove chlorine. On the other hand, waste incineration has increased during the 2010-2015 period.[55] Better understanding of trends in anthropogenic chlorine emissions is needed for a comprehensive assessment of trends in China air quality.

ASSOCIATED CONTENT

Supporting Information.

Updated chlorine chemistry in GEOS-Chem (A1); Bimolecular reactions between Cl atom and VOC included in model scheme (Table S1); Seasonal mean $HCl/(HCl + PM_{2.5}\ Cl^-)$ ratio in surface air over China in GEOS-Chem due to anthropogenic emissions of HCl (Figure S1); Effects of anthropogenic chlorine emissions on monthly mean surface $PM_{2.5}$ concentrations in China in January and July (Figure S2); Absolute (Figure S3) and relative (Figure S4) enhancement of anthropogenic chlorine emissions on seasonal mean surface MDA6 ozone mixing ratios in China.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xuanwang@cityu.edu.hk

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Joint Laboratory for Air Quality and Climate (JLAQC) between Harvard and the Nanjing University for Information Science and Technology (NUIST), by the Atmospheric Chemistry Program of the US National Science Foundation (Grant # 1643217), and by the City University of Hong Kong New Research Initiatives (Grant # 9610470). HCl, Cl^-, and $ClNO_2$ measurements at Changping are part of the framework research program on "Photochemical smog in China" financed by the Swedish Research Council (Grant # 639-2013-6917). X.F. and T.W. acknowledges financial support from the Hong Kong Research Grants Council (APolyU502/16, T24-504/17-N). We thank Qiang Zhang's group at Tsinghua University for providing the MEIC data.

REFERENCES

1. Saiz-Lopez, A.; von Glasow, R., Reactive halogen chemistry in the troposphere. *Chem Soc Rev* **2012,** *41* (19), 6448-72.
2. Simpson, W. R.; Brown, S. S.; Saiz-Lopez, A.; Thornton, J. A.; Glasow, R., Tropospheric halogen chemistry: sources, cycling, and impacts. *Chem Rev* **2015,** *115* (10), 4035-62.
3. 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.; Liao, H., The role of chlorine in global tropospheric chemistry. *Atmospheric Chemistry and Physics* **2019,** *19* (6), 3981-4003.
4. 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.; Bloss, W. J., Effects of halogens on European air-quality. *Faraday Discuss* **2017,** *200*, 75-100.
5. Yang, X.; Wang, T.; Xia, M.; Gao, X.; Li, Q.; Zhang, N.; Gao, Y.; Lee, S.; Wang, X.; Xue, L.; Yang, L.; Wang, W., Abundance and origin of fine particulate chloride in continental China. *Sci Total Environ* **2018,** *624*, 1041-1051.
6. 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.; 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. *Atmospheric Chemistry and Physics* **2018,** *18* (17), 13013-13030.

7. Fu, X.; Wang, T.; Wang, S.; Zhang, L.; Cai, S.; Xing, J.; Hao, J., Anthropogenic Emissions of Hydrogen Chloride and Fine Particulate Chloride in China. *Environ Sci Technol* **2018,** *52* (3), 1644-1654.
8. Brown, H.; Liu, X.; Feng, Y.; Jiang, Y.; Wu, M.; Lu, Z.; Wu, C.; Murphy, S.; Pokhrel, R., Radiative effect and climate impacts of brown carbon with the Community Atmosphere Model (CAM5). *Atmospheric Chemistry and Physics* **2018,** *18* (24), 17745-17768.
9. EPA 2014 National Emissions Inventory (NEI) Data. https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data (accessed 2020.6.18).
10. Behnke, W.; George, C.; Scheer, V.; Zetzsch, C., Production and decay of ClNO2 from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments. *Journal of Geophysical Research: Atmospheres* **1997,** *102* (D3), 3795-3804.
11. 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.; Brown, S. S., High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nature Geoscience* **2008,** *1* (5), 324-328.
12. Thornton, J. A.; Kercher, J. P.; Riedel, T. P.; Wagner, N. L.; Cozic, J.; Holloway, J. S.; Dubé, W. P.; Wolfe, G. M.; Quinn, P. K.; Middlebrook, A. M.; Alexander, B.; Brown, S. S., A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* **2010,** *464*, 271.
13. Wang, T.; Tham, Y. J.; Xue, L.; Li, Q.; Zha, Q.; Wang, Z.; Poon, S. C. N.; Dubé, W. P.; Blake, D. R.; Louie, P. K. K.; Luk, C. W. Y.; Tsui, W.; Brown, S. S., Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China. *Journal of Geophysical Research: Atmospheres* **2016,** *121* (5), 2476-2489.
14. Sarwar, G.; Simon, H.; Xing, J.; Mathur, R., Importance of tropospheric ClNO2 chemistry across the Northern Hemisphere. *Geophysical Research Letters* **2014,** *41* (11), 4050-4058.
15. Wang, Z.; Wang, W.; Tham, Y. J.; Li, Q.; Wang, H.; Wen, L.; Wang, X.; Wang, T., Fast heterogeneous N₂O₅ uptake and ClNO₂ production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain. *Atmospheric Chemistry and Physics* **2017,** *17* (20), 12361-12378.
16. Tham, Y. J.; Yan, C.; Xue, L.; Zha, Q.; Wang, X.; Wang, T., Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry. *Chinese Science Bulletin* **2014,** *59* (4), 356-359.
17. Tham, Y. J.; Wang, Z.; Li, Q.; Yun, H.; Wang, W.; Wang, X.; Xue, L.; Lu, K.; Ma, N.; Bohn, B.; Li, X.; Kecorius, S.; Größ, J.; Shao, M.; Wiedensohler, A.; Zhang, Y.; Wang, T., Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China. *Atmospheric Chemistry and Physics* **2016,** *16* (23), 14959-14977.
18. Liu, X.; Qu, H.; Huey, L. G.; Wang, Y.; Sjostedt, S.; Zeng, L.; Lu, K.; Wu, Y.; Hu, M.; Shao, M.; Zhu, T.; Zhang, Y., High Levels of Daytime Molecular Chlorine and Nitryl Chloride at a Rural Site on the North China Plain. *Environ Sci Technol* **2017,** *51* (17), 9588-9595.
19. Brown, S. S.; Dubé, W. P.; Tham, Y. J.; Zha, Q.; Xue, L.; Poon, S.; Wang, Z.; Blake, D. R.; Tsui, W.; Parrish, D. D.; Wang, T., Nighttime chemistry at a high altitude site above Hong Kong. *Journal of Geophysical Research: Atmospheres* **2016,** *121* (5), 2457-2475.

20. Zhang, L.; Li, Q.; Wang, T.; Ahmadov, R.; Zhang, Q.; Li, M.; Lv, M., Combined impacts of nitrous acid and nitryl chloride on lower-tropospheric ozone: new module development in WRF-Chem and application to China. *Atmospheric Chemistry and Physics* **2017,** *17* (16), 9733-9750.
21. Li, Q.; Zhang, L.; Wang, T.; Tham, Y. J.; Ahmadov, R.; Xue, L.; Zhang, Q.; 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. *Atmospheric Chemistry and Physics* **2016,** *16* (23), 14875-14890.
22. Qiu, X.; Ying, Q.; Wang, S.; Duan, L.; Wang, Y.; Lu, K.; Wang, P.; Xing, J.; Zheng, M.; Zhao, M.; Zheng, H.; Zhang, Y.; Hao, J., Significant impact of heterogeneous reactions of reactive chlorine species on summertime atmospheric ozone and free-radical formation in north China. *Sci Total Environ* **2019,** *693*, 133580.
23. Liu, Y.; Fan, Q.; Chen, X.; Zhao, J.; Ling, Z.; Hong, Y.; Li, W.; Chen, X.; Wang, M.; Wei, X., Modeling the impact of chlorine emissions from coal combustion and prescribed waste incineration on tropospheric ozone formation in China. *Atmospheric Chemistry and Physics* **2018,** *18* (4), 2709-2724.
24. Li, Q.; Badia, A.; Wang, T.; Sarwar, G.; Fu, X.; Zhang, L.; Zhang, Q.; Fung, J.; Cuevas, C. A.; Wang, S.; Zhou, B.; Saiz-Lopez, A., Potential Effect of Halogens on Atmospheric Oxidation and Air Quality in China. *J Geophys Res Atmos* **2020,** *125* (9).
25. Dai, J.; Liu, Y.; Wang, P.; Fu, X.; Xia, M.; Wang, T., The impact of sea-salt chloride on ozone through heterogeneous reaction with N2O5 in a coastal region of south China. *Atmospheric Environment* **2020,** *236*.
26. 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.; Ordóñez, C., Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem. *Atmospheric Chemistry and Physics* **2016,** *16* (18), 12239-12271.
27. Zheng, B.; Tong, D.; Li, M.; Liu, F.; Hong, C.; Geng, G.; Li, H.; Li, X.; Peng, L.; Qi, J.; Yan, L.; Zhang, Y.; Zhao, H.; Zheng, Y.; He, K.; Zhang, Q., Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions. *Atmos. Chem. Phys.* **2018,** *18* (19), 14095-14111.
28. Li, K.; Jacob, D. J.; Liao, H.; Shen, L.; Zhang, Q.; Bates, K. H., Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China. *Proceedings of the National Academy of Sciences* **2019,** *116* (2), 422-427.
29. Geng, G.; Zhang, Q.; Martin, R. V.; van Donkelaar, A.; Huo, H.; Che, H.; Lin, J.; He, K., Estimating long-term PM2.5 concentrations in China using satellite-based aerosol optical depth and a chemical transport model. *Remote Sensing of Environment* **2015,** *166*, 262-270.
30. Fountoukis, C.; Nenes, A., ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K⁺–Ca²⁺–Mg²⁺–NH₄⁺–Na⁺–SO₄^{2−}–NO₃[−]–Cl[−]–H₂O aerosols. *Atmos. Chem. Phys.* **2007,** *7* (17), 4639-4659.
31. 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.; Brown, S. S., Heterogeneous N2O5 Uptake During Winter: Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of Current Parameterizations. *Journal of Geophysical Research: Atmospheres* **2018,** *123* (8), 4345-4372.
32. Liu, T. Y.; Abbatt, J. P. D., An Experimental Assessment of the Importance of S(IV) Oxidation by Hypohalous Acids in the Marine Atmosphere. *Geophysical Research Letters* **2020,** *47* (4), e2019GL086465.
33. Fogelman, K. D.; Walker, D. M.; Margerum, D. W., Nonmetal redox kinetics: hypochlorite and hypochlorous acid reactions with sulfite. *Inorganic Chemistry* **1989,** *28* (6), 986-993.
34. Fairlie, T. D.; Jacob, D. J.; Dibb, J. E.; Alexander, B.; Avery, M. A.; van Donkelaar, A.; Zhang, L., Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes. *Atmospheric Chemistry and Physics* **2010,** *10* (8), 3999-4012.
35. Wang, D. S.; Ruiz, L. H., Secondary organic aerosol from chlorine-initiated oxidation of isoprene. *Atmospheric Chemistry and Physics* **2017,** *17* (22), 13491-13508.
36. Dhulipala, S. V.; Bhandari, S.; Hildebrandt Ruiz, L., Formation of oxidized organic compounds from Cl-initiated oxidation of toluene. *Atmospheric Environment* **2019,** *199*, 265-273.
37. Pai, S. J.; Heald, C. L.; Pierce, J. R.; Farina, S. C.; Marais, E. A.; Jimenez, J. L.; Campuzano-Jost, P.; Nault, B. A.; Middlebrook, A. M.; Coe, H.; Shilling, J. E.; Bahreini, R.; Dingle, J. H.; Vu, K., An evaluation of global organic aerosol schemes using airborne observations. *Atmos. Chem. Phys.* **2020,** *20* (5), 2637-2665.
38. Kim, P. S.; Jacob, D. J.; Fisher, J. A.; Travis, K.; Yu, K.; Zhu, L.; Yantosca, R. M.; Sulprizio, M. P.; Jimenez, J. L.; Campuzano-Jost, P.; Froyd, K. D.; Liao, J.; Hair, J. W.; Fenn, M. A.; Butler, C. F.; Wagner, N. L.; Gordon, T. D.; Welti, A.; Wennberg, P. O.; Crounse, J. D.; St. Clair, J. M.; Teng, A. P.; Millet, D. B.; Schwarz, J. P.; Markovic, M. Z.; Perring, A. E., Sources, seasonality, and trends of southeast US aerosol: an integrated analysis of surface, aircraft, and satellite observations with the GEOS-Chem chemical transport model. *Atmos. Chem. Phys.* **2015,** *15* (18), 10411-10433.
39. McCulloch, A.; Aucott, M. L.; Benkovitz, C. M.; Graedel, T. E.; Kleiman, G.; Midgley, P. M.; Li, Y.-F., Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research: Atmospheres* **1999,** *104* (D7), 8391-8403.
40. Feng, Y.; Bie, P.; Wang, Z.; Wang, L.; Zhang, J., Bottom-up anthropogenic dichloromethane emission estimates from China for the period 2005–2016 and predictions of future emissions. *Atmospheric Environment* **2018,** *186*, 241-247.
41. Fang, X.; Park, S.; Saito, T.; Tunnicliffe, R.; Ganesan, A. L.; Rigby, M.; Li, S.; Yokouchi, Y.; Fraser, P. J.; Harth, C. M.; Krummel, P. B.; Mühle, J.; O'Doherty, S.; Salameh, P. K.; Simmonds, P. G.; Weiss, R. F.; Young, D.; Lunt, M. F.; Manning, A. J.; Gressent, A.; Prinn, R. G., Rapid increase in ozone-depleting chloroform emissions from China. *Nature Geoscience* **2019,** *12* (2), 89-93.
42. Ridley, D. A.; Heald, C. L.; Kok, J. F.; Zhao, C., An observationally constrained estimate of global dust aerosol optical depth. *Atmos. Chem. Phys.* **2016,** *16* (23), 15097-15117.
43. Reff, A.; Bhave, P. V.; Simon, H.; Pace, T. G.; Pouliot, G. A.; Mobley, J. D.; Houyoux, M., Emissions Inventory of PM2.5 Trace Elements across the United States. *Environmental Science & Technology* **2009,** *43* (15), 5790-5796.

44. Sarwar, G.; Simon, H.; Bhave, P.; Yarwood, G., Examining the impact of heterogeneous nitryl chloride production on air quality across the United States. *Atmospheric Chemistry and Physics* **2012,** *12* (14), 6455-6473.
45. Cao, J.-J.; Shen, Z.-X.; Chow, J. C.; Watson, J. G.; Lee, S.-C.; Tie, X.-X.; Ho, K.-F.; Wang, G.-H.; Han, Y.-M., Winter and Summer PM2.5 Chemical Compositions in Fourteen Chinese Cities. *Journal of the Air & Waste Management Association* **2012,** *62* (10), 1214-1226.
46. Philip, S.; Martin, R. V.; Snider, G.; Weagle, C. L.; van Donkelaar, A.; Brauer, M.; Henze, D. K.; Klimont, Z.; Venkataraman, C.; Guttikunda, S. K.; Zhang, Q., Anthropogenic fugitive, combustion and industrial dust is a significant, underrepresented fine particulate matter source in global atmospheric models. *Environmental Research Letters* **2017,** *12* (4), 044018.
47. 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.; 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.* **2019,** *19* (8), 5605-5613.
48. Jacob, D. J.; Waldman, J. M.; Munger, J. W.; Hoffmann, M. R., Chemical composition of fogwater collected along the California coast. *Environmental Science & Technology* **1985,** *19* (8), 730-736.
49. Liu, Z.; Gao, W.; Yu, Y.; Hu, B.; Xin, J.; Sun, Y.; Wang, L.; Wang, G.; Bi, X.; Zhang, G.; Xu, H.; Cong, Z.; He, J.; Xu, J.; Wang, Y., Characteristics of PM2.5 mass concentrations and chemical species in urban and background areas of China: emerging results from the CARE-China network. *Atmospheric Chemistry and Physics* **2018,** *18* (12), 8849-8871.
50. Zhou, W.; Zhao, J.; Ouyang, B.; Mehra, A.; Xu, W.; Wang, Y.; Bannan, T. J.; Worrall, S. D.; Priestley, M.; Bacak, A.; Chen, Q.; Xie, C.; Wang, Q.; Wang, J.; Du, W.; Zhang, Y.; Ge, X.; Ye, P.; Lee, J. D.; Fu, P.; Wang, Z.; Worsnop, D.; Jones, R.; Percival, C. J.; Coe, H.; Sun, Y., Production of N₂O₅ and ClNO₂ in summer in urban Beijing, China. *Atmospheric Chemistry and Physics* **2018,** *18* (16), 11581-11597.
51. Faxon, C.; Bean, J.; Ruiz, L., Inland Concentrations of Cl2 and ClNO2 in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity. *Atmosphere* **2015,** *6* (10), 1487-1506.
52. Roberts, J. M.; Osthoff, H. D.; Brown, S. S.; Ravishankara, A. R., N₂O₅ Oxidizes Chloride to Cl₂ in Acidic Atmospheric Aerosol. *Science* **2008,** *321* (5892), 1059-1059.
53. Shah, V.; Jacob, D. J.; Li, K.; Silvern, R. F.; Zhai, S.; Liu, M.; Lin, J.; Zhang, Q., Effect of changing NOx lifetime on the seasonality and long-term trends of satellite-observed tropospheric NO2 columns over China. *Atmos. Chem. Phys.* **2020,** *20* (3), 1483-1495.
54. Shen, L.; Jacob, D. J.; Zhu, L.; Zhang, Q.; Zheng, B.; Sulprizio, M. P.; Li, K.; De Smedt, I.; González Abad, G.; Cao, H.; Fu, T.-M.; Liao, H., The 2005–2016 Trends of Formaldehyde Columns Over China Observed by Satellites: Increasing Anthropogenic Emissions of Volatile Organic Compounds and Decreasing Agricultural Fire Emissions. *Geophysical Research Letters* **2019,** *46* (8), 4468-4475.
55. Zhou, Q.; Yang, J.; Liu, M.; Liu, Y.; Sarnat, S.; Bi, J., Toxicological Risk by Inhalation Exposure of Air Pollution Emitted from China's Municipal Solid Waste Incineration. *Environ Sci Technol* **2018,** *52* (20), 11490-11499.
56. 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.; 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. *Atmospheric Chemistry and Physics* **2018,** *18* (17), 13013-13030.

57. Wang, X.; Wang, H.; Xue, L.; Wang, T.; Wang, L.; Gu, R.; Wang, W.; Tham, Y. J.; Wang, Z.; Yang, L.; Chen, J.; Wang, W., Observations of N 2 O 5 and ClNO 2 at a polluted urban surface site in North China: High N 2 O 5 uptake coefficients and low ClNO 2 product yields. *Atmospheric Environment* **2017,** *156*, 125-134.

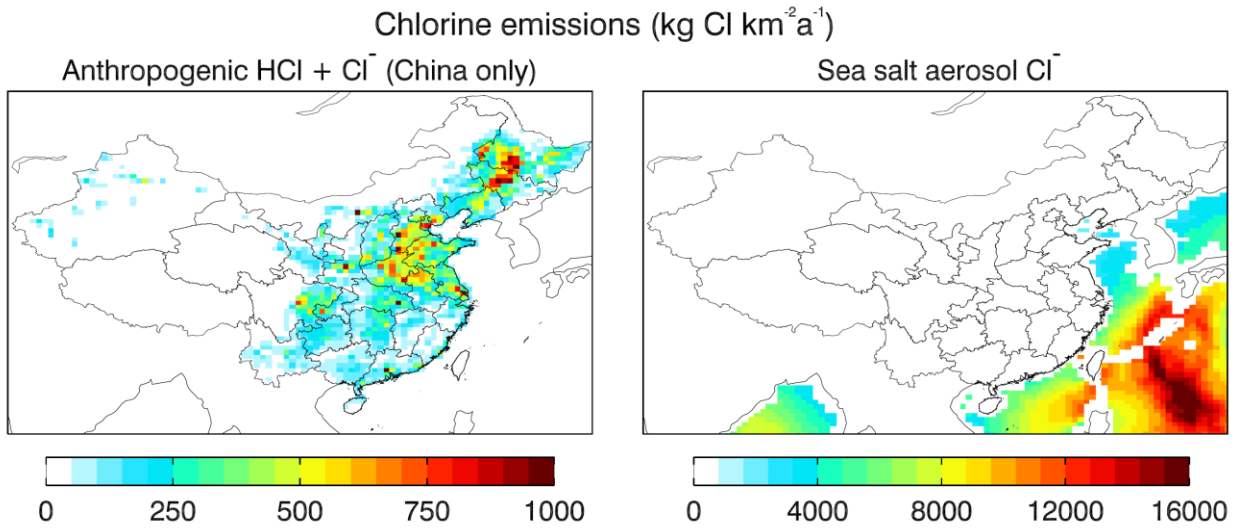
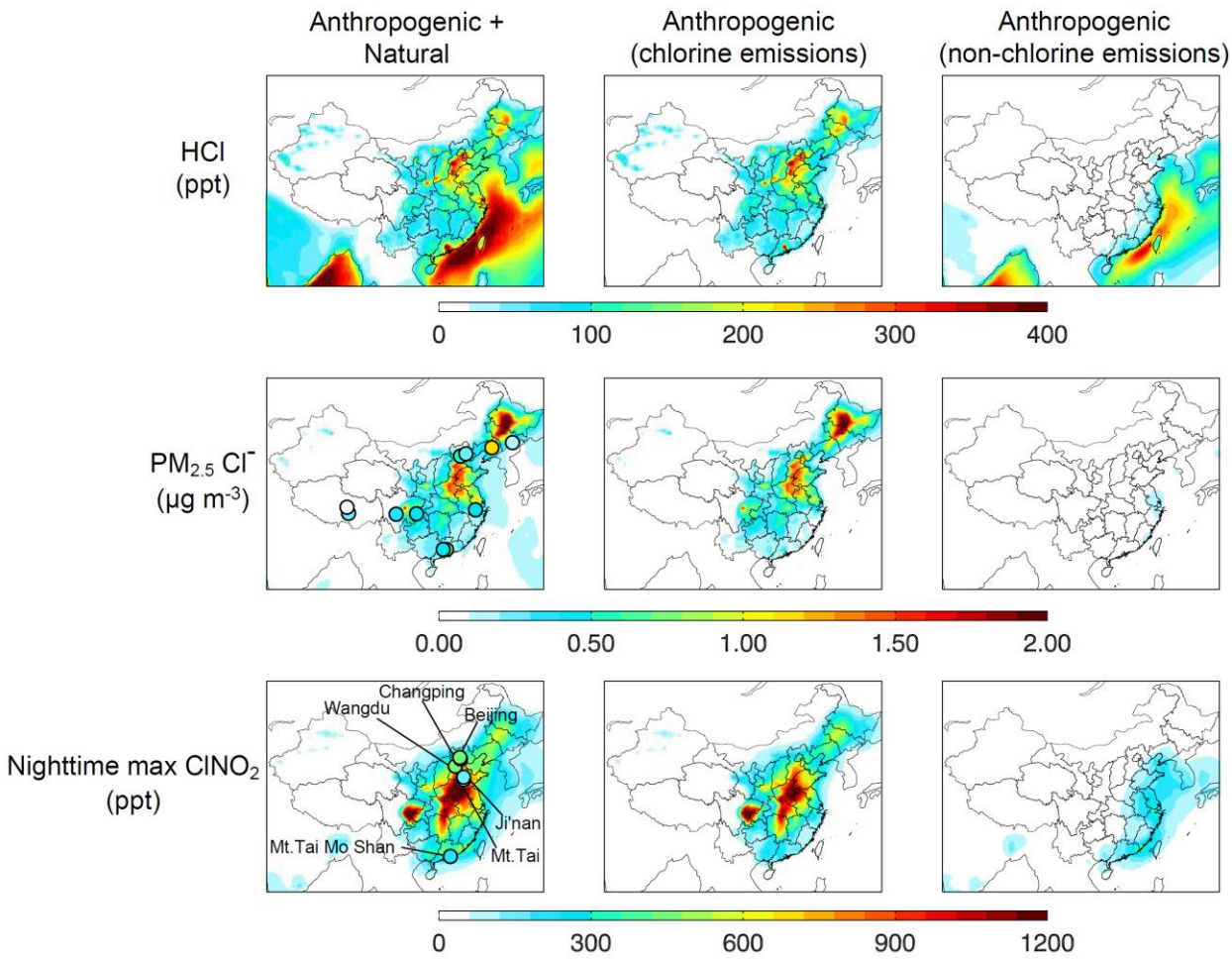


Figure 1. Annual chlorine emissions from Chinese anthropogenic sources (left) and from sea salt aerosol (right). Values are for 2014. Anthropogenic emissions are from the ($HCl + Cl^-$) inventory of Fu et al.[7] including contributions from agricultural fires, residential biofuels, waste incineration, coal combustion, and industry. Note difference in scales between panels.



542

543 **Figure 2.** Annual mean concentrations of HCl, $PM_{2.5}$ Cl^-, and nighttime maximum $ClNO_2$ in
544 surface air. The left panels show the concentrations in the standard GEOS-Chem simulation, with
545 superimposed circles showing $PM_{2.5}$ Cl^- and $ClNO_2$ observations discussed in the text. The middle
546 panels show the contributions from Chinese anthropogenic chlorine emissions, as diagnosed by
547 difference with a simulation shutting off these emissions. The right panel shows the contributions
548 from anthropogenic non-chlorine emissions driving Cl^- displacement from sea-salt aerosol, as
549 further diagnosed by difference with a simulation shutting off all Chinese anthropogenic
550 emissions.

551

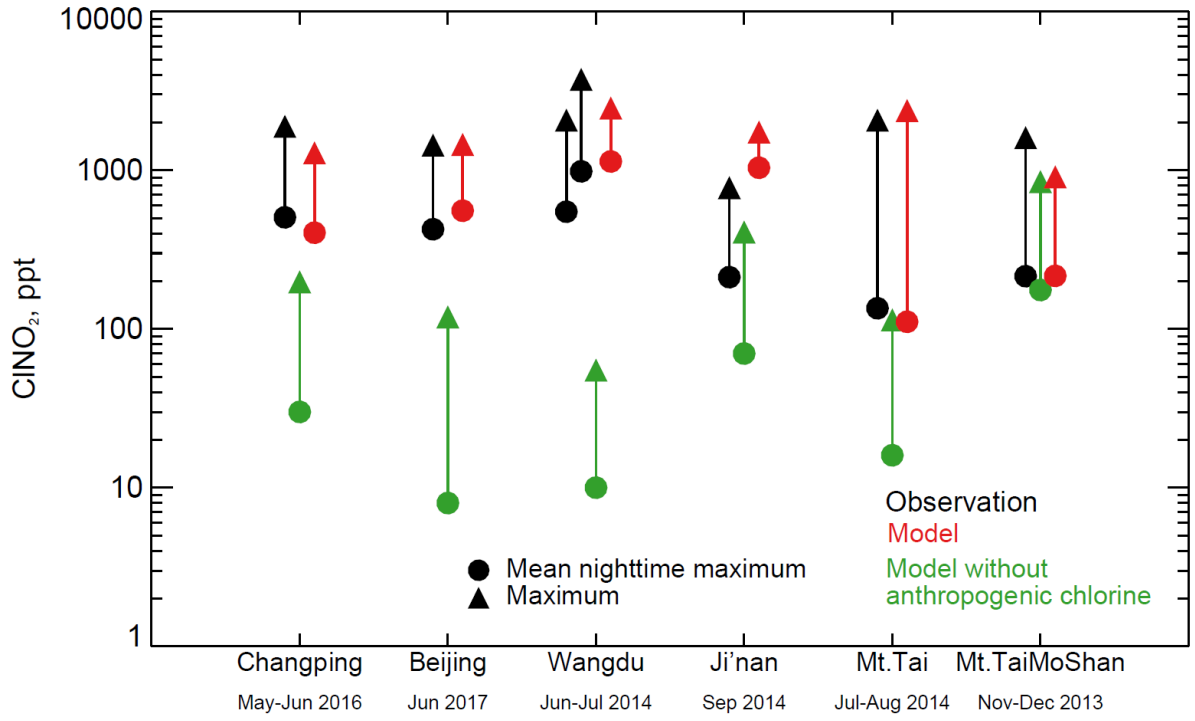
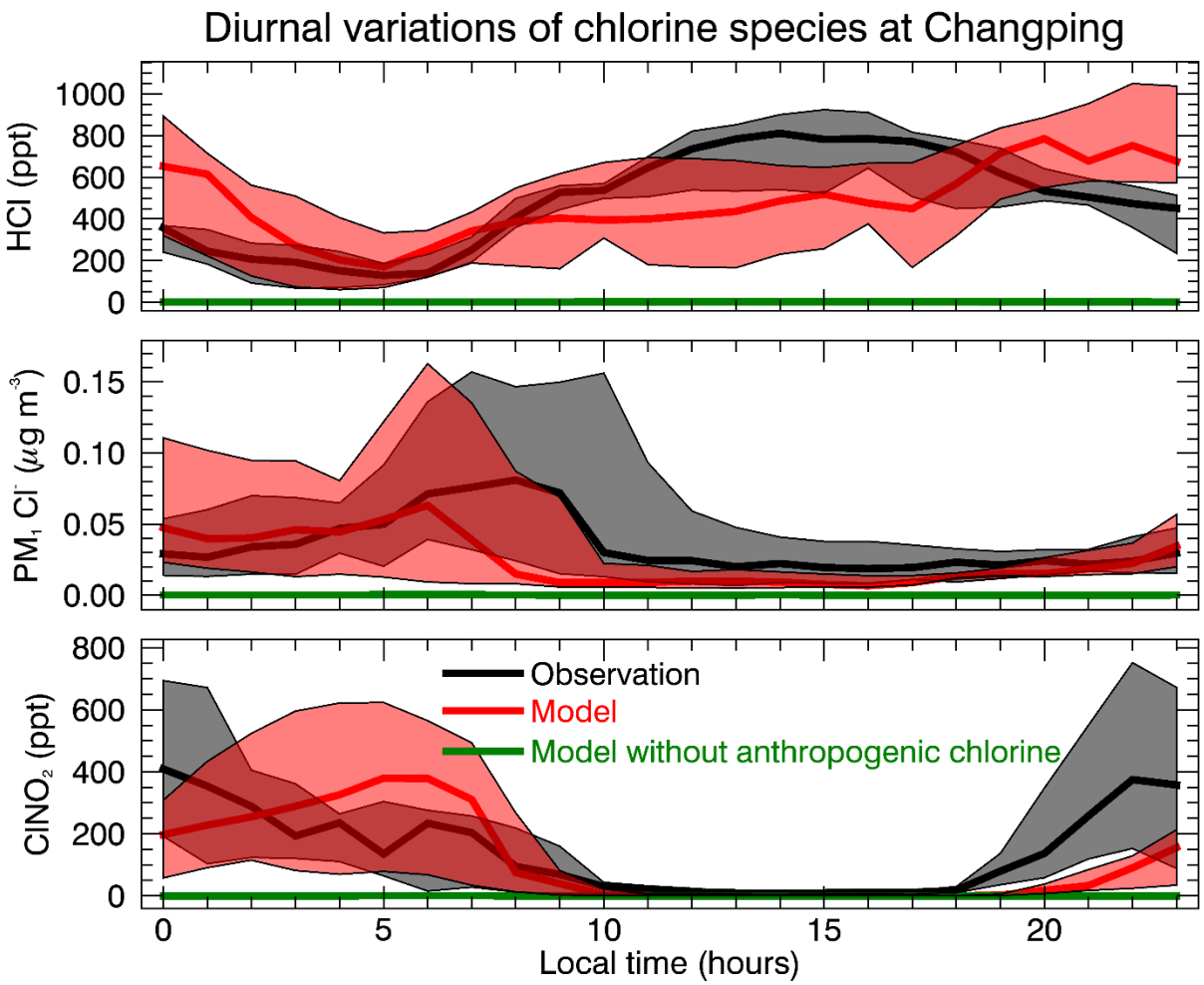


Figure 3. $ClNO_2$ mixing ratios measured at 6 sites in China. The maximum (triangle) and mean nighttime maximum (circle) during the measurement periods are shown. Model values are sampled for the measurement locations and months. Results from a sensitivity simulation without anthropogenic chlorine emissions are also shown. Observations are for Changping[56], Beijing[50], Wangdu[18,17]; Ji'nan[57], Mountain Tai[15], and Mountain Tai Mo Shan[13]. Site locations are shown in Figure 2. Two measurements are available at the Wangdu site during the same time period, and both values are shown here.



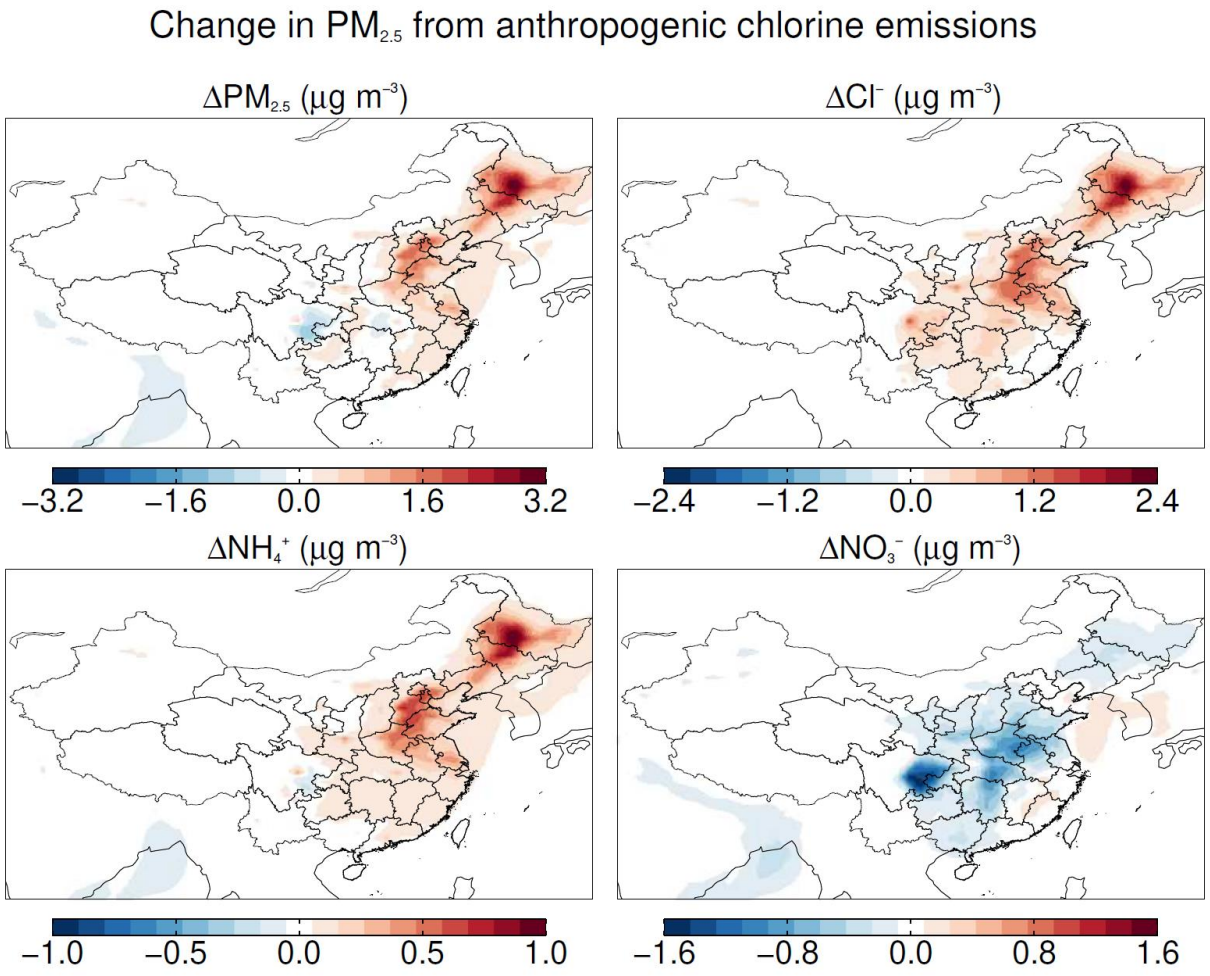
561

562 **Figure 4.** Diurnal variations of HCl, PM_1 Cl^-, and $ClNO_2$ concentrations at Changping in May-

563 June 2016. Model values are compared to observations from Le Breton et al.[6] Median values are

564 shown as solid lines and shaded regions span 25th - 75th percentiles.

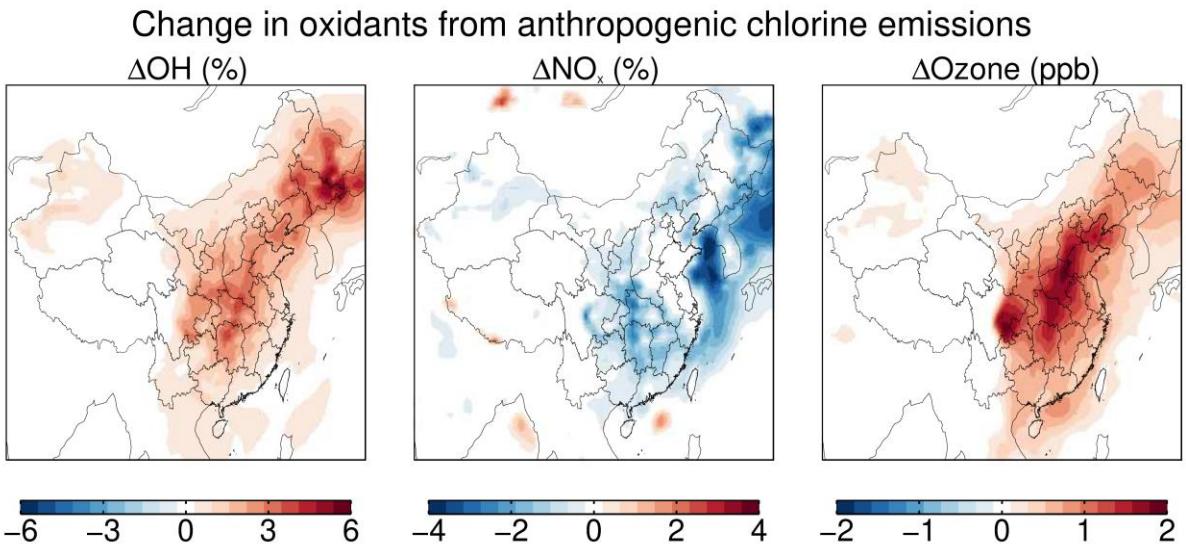
565



566

567 **Figure 5.** Effect of anthropogenic chlorine emissions on annual mean concentrations of $PM_{2.5}$ and
568 selected components in surface air in China. Values are obtained by difference between our
569 standard GEOS-Chem simulation and a sensitivity simulation with anthropogenic chlorine
570 emissions shut off. Note difference in scale between panels.

571



572

573 **Figure 6.** Effect of anthropogenic chlorine emissions on annual mean concentrations of OH, NO_x,
574 and maximum daily 8-hour average (MDA8) ozone in surface air in China. Values are obtained
575 by difference between our standard GEOS-Chem simulation and a sensitivity simulation with
576 anthropogenic chlorine emissions shut off. Note differences in units and scales between panels.