

Effects 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

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

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

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

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

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

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

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

⁸School 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. The effect of these emissions is generally ignored in air quality models of fine particulate matter (PM_{2.5}) and ozone air quality. Here we quantify the effects of chlorine on PM_{2.5} and ozone across China on an annual basis by using the GEOS-Chem chemical transport model with detailed representation of gas-phase and heterogeneous chlorine chemistry. Comparison of the model to observed ClNO₂, 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. We find that anthropogenic chlorine emissions increase total PM_{2.5} by as much as 3.2 μg m⁻³ on an annual mean basis through the formation of ammonium chloride when ammonia is in excess. The nitrate component of PM_{2.5} decreases by up to 1.5 μg m⁻³ because ClNO₂ formation competes with N₂O₅ hydrolysis. Annual mean surface ozone increases by up to 1.7 ppb, mainly from ClNO₂ chemistry, while reactivities of volatile organic compounds increase by up to 48% for ethane. Our results suggest that a sufficient representation of chlorine chemistry in air quality models can be obtained from consideration of HCl/Cl⁻ thermodynamics and ClNO₂ chemistry.

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 radicals³, 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 model³. 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 a⁻¹ in recent estimates.^{7, 8}

A number of measurements of nitryl chloride (ClNO₂) and Cl⁻ concentrations are available in China^{6, 9-14}. However, very few modeling studies of Chinese air quality have considered chlorine chemistry, and those that did mainly focused on ClNO₂ chemistry on urban/regional scales with only partial accounting of anthropogenic sources.^{5, 8, 15-18}. In polluted environments, nighttime formation of nitryl chloride (ClNO₂) followed by photolysis in the daytime returns Cl atoms and nitrogen oxide radicals (NO_x) to stimulate ozone production.¹⁹⁻²¹ Liu et al.²² added chlorine emissions from coal combustion and prescribed waste incineration to the CMAQ model and found that those emissions can cause the mean daily maximum 8 hour (MDA8) ozone concentrations in November increase by up to 2.0 ppb in East and South China. A model simulation by Li et al.¹⁷ suggests that ClNO₂ chemistry accounts for up to 7 ppb surface ozone in the Pearl River Delta (PRD) region. Qiu et al.¹⁸ compared their model results with ClNO₂ observations in the Beijing-

Tianjin-Hebei (BTH) area, and found that ClNO₂ chemistry can increase surface ozone by up to 20%.

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 observations for chlorine species. From there we quantify the effect of anthropogenic chlorine on Chinese air quality.

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 chemistry²³, and to which we have updated an updated comprehensive treatment of chlorine chemistry³. 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)²⁴ 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^{25, 26}. 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, Cl₂, Cl₂O₂, ClNO₂, ClNO₃, 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 II²⁷ as part of the H₂SO₄-HCl-HNO₃-NH₃-NVCs thermodynamic system, where NVCs stands for non-volatile cations and is treated in ISORROPIA II using Na⁺ as proxy. 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 ClNO₂ formation from nighttime heterogeneous reaction of N₂O₅ with Cl⁻ in the aerosol aqueous phase to include the effect of organic coating, as described by McDuffie et al.²⁸ We added the reaction between HOCl and dissolved SO₂ (S(IV) ≡ HSO₃⁻ + SO₃²⁻) to form SO₄²⁻ aerosol.^{29, 30} We also now include in the model the reactive uptake of HCl on natural dust, limited by dust alkalinity³¹. Details of these updates are described in Supporting Information A1.

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,²⁴ 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.³², 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 (CH₂Cl₂) and chloroform (CHCl₃) are emitted from industrial activities and produce Cl atoms in GEOS-Chem through photolysis and oxidation³. Anthropogenic CH₂Cl₂ emission in China was estimated to be 318 Gg a⁻¹ in 2016 in a bottom-up study by Feng et al.,³³. The total CHCl₃ emission in China was estimated to be 88 Gg a⁻¹ in 2015 based on a Bayesian inversion of surface measurements.³⁴ We include anthropogenic CH₂Cl₂ and CHCl₃ emission using these national numbers with a spatial distribution the same as anthropogenic HCl. Since both CH₂Cl₂ and CHCl₃ 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-Chem³⁵ has

an emission of 3300 Gg a⁻¹ in China in 2014; assuming 0.15% Cl by mass based on US data³⁸, this yields a Cl⁻ source of 4.9 Gg Cl⁻ a⁻¹. Previous studies^{36, 37} have suggested that anthropogenic dust may contribute to PM_{2.5} Cl⁻ concentrations in urban environments. We include these emissions using the AFCID inventory³⁸, 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.

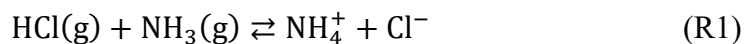
Figure 1 shows the annual HCl + Cl⁻ emissions from Chinese anthropogenic sources and Cl⁻ emissions from sea salt aerosol (SSA) as implemented in GEOS-Chem. There are two areas of high anthropogenic emissions, in the North China Plain (NCP) due to waste incineration and residential biofuel, and in Northeast 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} Cl⁻. 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 H₂SO₄-HCl-HNO₃-NH₃-NVC thermodynamic system, HCl partitions into the aqueous particulate phase through:

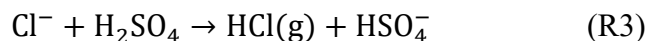


and



Since NH₃ is generally in large excess of HNO₃ in China,³⁹ equilibrium (R1) is driven to the right and uptake of HCl mostly takes place without displacement of NO₃⁻. 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 H₂SO₄ and HNO₃ produced from anthropogenic emissions of SO₂ and NO_x. This acid displacement involves (R2) and:



H₂SO₄ has a much lower vapor pressure than HCl so that (R3) fully displaces Cl⁻ if H₂SO₄ is present.⁴⁰ 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 ClNO₂ 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 ClNO₂, following standard practice^{3, 41}, because of the large diurnal variation and near-zero mixing ratios in the daytime. Again, most of ClNO₂ over China is driven by anthropogenic chlorine emissions. Values exceed 1000 ppt in inland urban areas of China, much higher than corresponding values in the US and Europe.³

We compared the model simulation for 2014 to observations collected in China for neighboring years (2012-2017), and assuming interannual differences to be a minor factor in model error. Continuous 2012-2013 observations of PM_{2.5} Cl⁻ are available from 11 sites as part of the CARE-China network⁴². The annual mean observed values are shown as circles in the middle-left panel of Figure 2. The model captures the spatial distribution of observed Cl⁻ with a correlation coefficient (R) of 0.78 and a normalized mean bias (NMB) of -12%. PM_{2.5} Cl⁻ concentrations in inland China are much higher than the corresponding concentrations in the US (mostly < 0.1 μg m⁻³).^{3, 36}

Figure 3 shows absolute maximum and mean nighttime maximum ClNO₂ mixing ratios from several field studies, and compares to the modeled values during the measurement months. Measurement locations are indicated in Figure 2. The model successfully simulates the surface ClNO₂ observations for the three sites in the Beijing-Tianjin-Hebei area (Changping, Beijing, and

Wangdu) and the mountain site (Mt. Tai) in NCP during their respective measurement periods. Ignoring the anthropogenic chlorine emissions would result in underestimates by more than a factor of 10 at these sites. In contrast, anthropogenic chlorine is relatively minor at the mountain site in Hong Kong (Mt. Tai Mo Shan), both in the model and observations, because SSA provides the dominant source of Cl^- at that site. The model overestimates anthropogenic influence at Ji'nan, for reasons that are not clear. The observations are much lower than for other surface sites in the North China Plain.

Continuous measurements of HCl , PM_{10} Cl^- (mass concentration in particles less than $1\text{ }\mu\text{m}$ diameter), and ClNO_2 were made at a semi-rural surface site at Changping (40 km northwest of Beijing urban area) during May-June 2016 by Le Breton et al.⁶ Back-trajectory analyses showed no significant marine influence in the data^{13,60}. Figure 4 compares the diurnal cycle of the observations to the model. Model concentrations at the site are almost exclusively from anthropogenic chlorine emissions. The model is consistent with the overall magnitudes observed. HCl is low at night because of dry deposition. Cl^- is low in the daytime because of ventilation. The observed nighttime peak of ClNO_2 is at 23 local time, whereas ClNO_2 in the model keeps on accumulating over the course of the night consistent with other observations in polluted areas, including another site near Beijing^{3, 13, 21, 43, 44}. The cause of the post-midnight decrease in the Changping ClNO_2 data is not clear.

In summary, the model shows general consistency with observations of Cl^- , ClNO_2 , and HCl available in China. We conclude from our comparisons that the chlorine over China is mainly anthropogenic, and that the underlying chlorine emissions and chemistry are relatively well understood.

3.3. Impact of anthropogenic chlorine emissions on PM_{2.5} in China

Figure 5 shows our simulated net impacts of anthropogenic chlorine emissions on annual mean PM_{2.5} concentrations calculated as differences between the standard simulation and a simulation without anthropogenic chlorine emissions. The largest impact is over Northeast China, where annual mean PM_{2.5} increases by 3.2 $\mu\text{g m}^{-3}$, which is 9% of the Chinese national air quality standard of 35 $\mu\text{g m}^{-3}$ and mainly contributed by biomass burning emissions. Seasonal differences of the impacts on PM_{2.5} concentrations are provided in Figure S2.

We find that anthropogenic chlorine has negligible effect on SO_4^{2-} concentrations in China ($< 0.1 \mu\text{g m}^{-3}$). The contribution of $\text{HOCl} + \text{S(IV)}$ to SO_2 oxidation is minimal because the main sink of HOCl is photolysis. As shown in Figure 5, anthropogenic chlorine emissions can cause annual mean surface NH_4^+ concentrations to increase by up to 1 $\mu\text{g m}^{-3}$. Since NH_3 is in excess in most areas of China,³⁹ the emitted HCl causes NH_3 transfer to NH_4^+ through reaction (R1), so that the pattern of enhanced NH_4^+ largely matches that of Cl^- concentrations. In contrast, anthropogenic chlorine emissions result in annual average NO_3^- concentrations decreases by up to 1.5 $\mu\text{g m}^{-3}$ following a similar spatial distribution as modeled ClNO_2 (Figure 2). The dominant factor for the NO_3^- decrease is not acid displacement by HCl (since NH_3 is in excess) but the increased competition of $\text{N}_2\text{O}_5 + \text{Cl}^-$ with N_2O_5 hydrolysis which is a major source of NO_3^- .⁴⁵

3.4. Impact of anthropogenic chlorine emissions on oxidants in China

Figure 6 shows the effects of anthropogenic chlorine emissions on annual mean hydroxyl radical (OH), NO_x , and ozone concentrations in surface air, calculated as differences between the standard simulation and a simulation without anthropogenic chlorine emissions. OH concentrations in surface air increase by up to 6%, mainly due to ClNO_2 chemistry^{20, 21}. Annual mean Cl atom

concentrations (not shown) increase up to 2700 cm^{-3} ; 90% of that increase is from ClNO_2 chemistry, while the remaining 10% is from $\text{HCl} + \text{OH}$ and from Cl_2 and HOCl photolysis. The latter reactions are most important in summer but even then they contribute less than 25% of the Cl atoms. The combined increases of both Cl atoms and OH enhance the annual mean reactivities of ethane, propane, higher 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 surface ozone increases by up to 1.7 ppb after including anthropogenic chlorine emissions. This is mainly because of ClNO_2 chemistry. The effect 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 extremely low.

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 $\text{PM}_{2.5}$ concentrations in China by up to $3.2\text{ }\mu\text{g m}^{-3}$ on an annual mean basis because of the condensation of $(\text{NH}_4^+, \text{Cl}^-)$ when NH_3 is in excess, as is the case generally over China. Annual mean surface OH and ozone mixing ratios increase by up to 6% and 1.7 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.

Emissions in China are presently changing rapidly in response to the governmental Clean Air Action.²⁴ 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.²⁴ No estimates are available for trends in anthropogenic chlorine emissions. Agricultural fires in China are increasingly banned out of concern for air quality⁴⁶, and coal combustion emission controls would presumably remove chlorine. On the other hand, waste incineration has increased during the 2010-2015 period.⁴⁷ 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 $\text{HCl}/(\text{HCl} + \text{PM}_{2.5} \text{ Cl}^-)$ 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 $\text{PM}_{2.5}$ concentrations in China in January and July (Figure S2); Enhancement of anthropogenic chlorine emissions on seasonal mean surface MDA6 ozone mixing ratios in China (Figure S3).

AUTHOR INFORMATION

Corresponding Author

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

Author Contributions

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Atmospheric Chemistry Program of the US National Science Foundation, by the Joint Laboratory for Air Quality and Climate (JLAQC) between Harvard and the Nanjing University for Information Science and Technology (NUIST), and by the CityU New Research Initiatives (Grant # 9610470). HCl, Cl⁻, and ClNO₂ 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). We thank Qiang Zhang’s group 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. 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.
 10. 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.
 11. 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.
 12. 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.
 13. 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.
 14. 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.
 15. 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.
 16. Mok, J.; Krotkov, N. A.; Arola, A.; Torres, O.; Jethva, H.; Andrade, M.; Labow, G.; Eck, T. F.; Li, Z.; Dickerson, R. R.; Stenchikov, G. L.; Osipov, S.; Ren, X., Impacts of brown carbon from biomass burning on surface UV and ozone photochemistry in the Amazon Basin. *Sci Rep* **2016**, *6*, 36940.
 17. 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.
 18. 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.

19. 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.

20. 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.

21. 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.

22. 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.

23. 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.

24. 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.

25. 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.

26. Geng, G.; Zhang, Q.; Martin, R. V.; van Donkelaar, A.; Huo, H.; Che, H.; Lin, J.; He, K., Estimating long-term PM_{2.5} concentrations in China using satellite-based aerosol optical depth and a chemical transport model. *Remote Sensing of Environment* **2015**, 166, 262-270.

27. Fountoukis, C.; Nenes, A., ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K⁺–Ca²⁺–Mg²⁺–NH₄⁺–Na⁺–SO₄²⁻–NO₃⁻–Cl⁻–H₂O aerosols. *Atmos. Chem. Phys.* **2007**, 7 (17), 4639-4659.

28. 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.

29. Liu, T.; Abbatt, J. P. D., An experimental assessment of the importance of S (IV) oxidation by hypohalous acids in the marine atmosphere. *Geophysical Research Letters* n/a (n/a), e2019GL086465.
30. 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.
31. 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.
32. 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.
33. 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.
34. 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* **2018**.
35. 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.
36. Sarwar, G.; Simon, H.; Bhawe, 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.
37. 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 PM_{2.5} Chemical Compositions in Fourteen Chinese Cities. *Journal of the Air & Waste Management Association* **2012**, *62* (10), 1214-1226.
38. 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.
39. 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.
40. 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.
41. 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.
42. 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 PM_{2.5} 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.

43. 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 N_2O_5 and ClNO_2 in summer in urban Beijing, China. *Atmospheric Chemistry and Physics* **2018**, *18* (16), 11581-11597.

44. Faxon, C.; Bean, J.; Ruiz, L., Inland Concentrations of Cl_2 and ClNO_2 in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity. *Atmosphere* **2015**, *6* (10), 1487-1506.

45. Shah, V.; Jacob, D. J.; Li, K.; Silvern, R. F.; Zhai, S.; Liu, M.; Lin, J.; Zhang, Q., Effect of changing NO_x lifetime on the seasonality and long-term trends of satellite-observed tropospheric NO_2 columns over China. *Atmos. Chem. Phys.* **2020**, *20* (3), 1483-1495.

46. 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.

47. 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.

48. 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 ClNO_2 and subsequent gas- and particle-phase Cl–VOC production. *Atmospheric Chemistry and Physics* **2018**, *18* (17), 13013-13030.

49. 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_2O_5 and ClNO_2 at a polluted urban surface site in North China: High N_2O_5 uptake coefficients and low ClNO_2 product yields. *Atmospheric Environment* **2017**, *156*, 125-134.

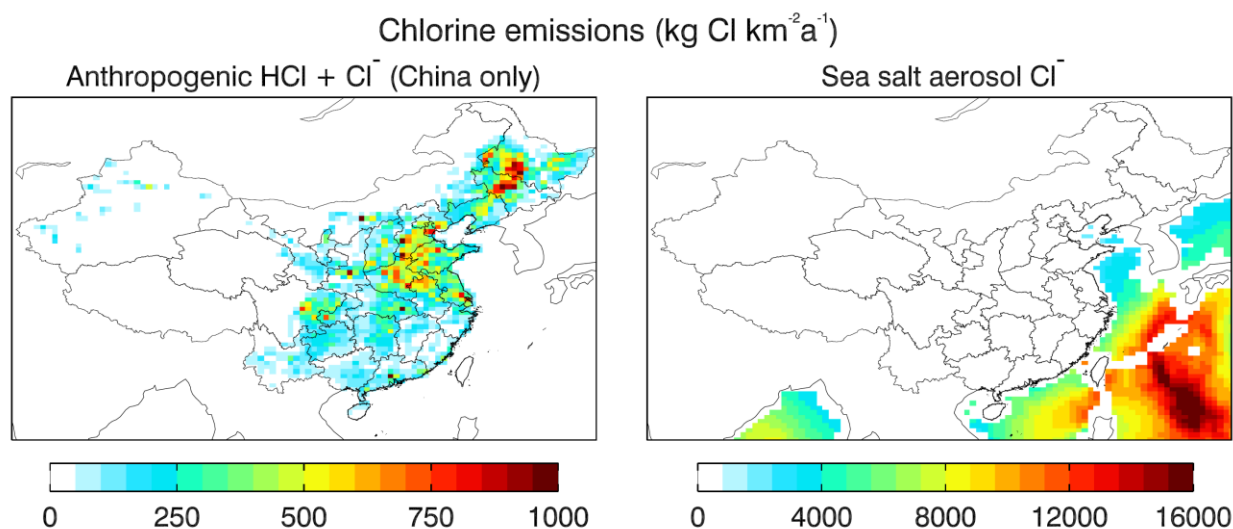


Figure 1. Annual chlorine emissions from Chinese anthropogenic sources (left) and from sea salt aerosol (right). Values are for 2014. Anthropogenic emissions are from the ($\text{HCl} + \text{Cl}^-$) inventory of Fu et al.⁷ including contributions from agricultural fires, residential biofuels, waste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

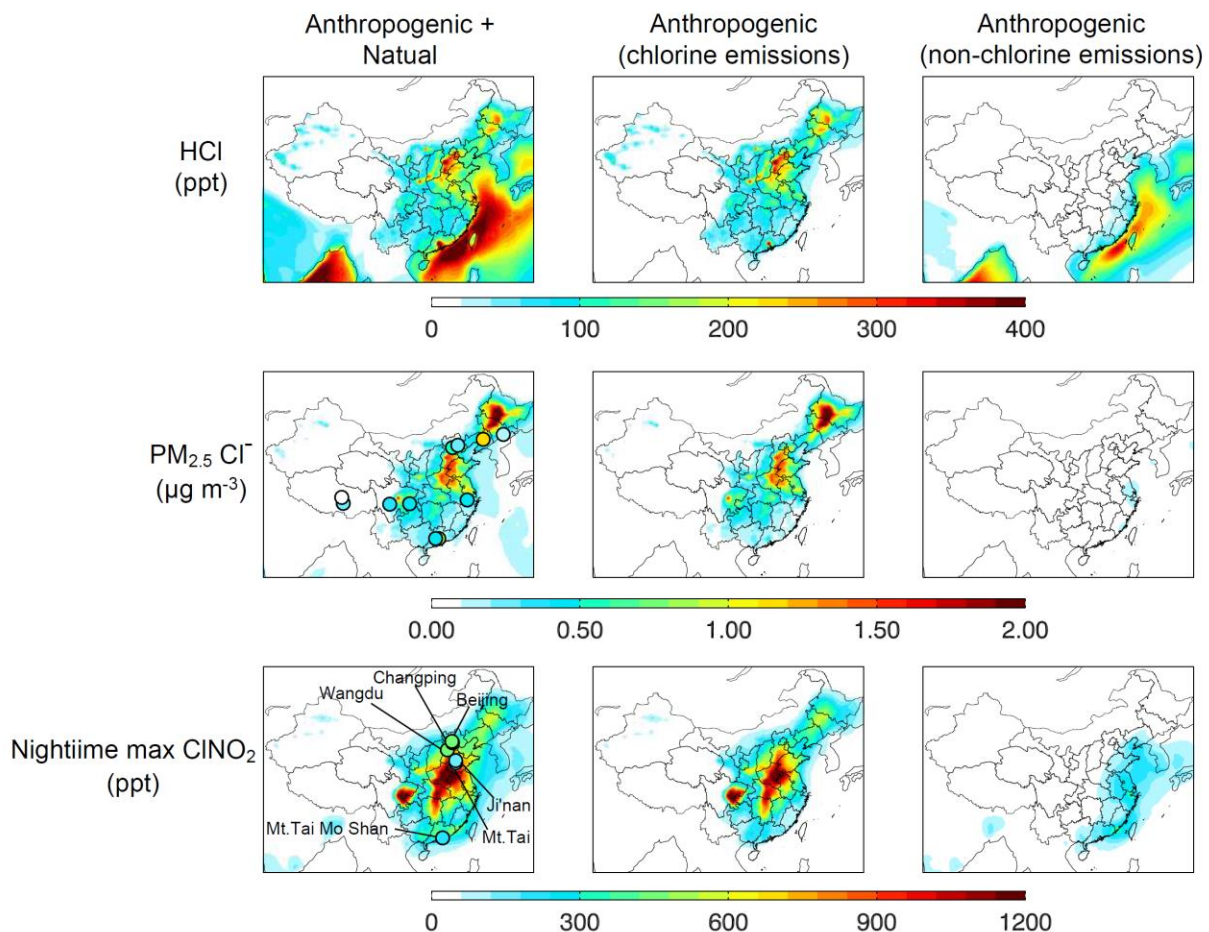
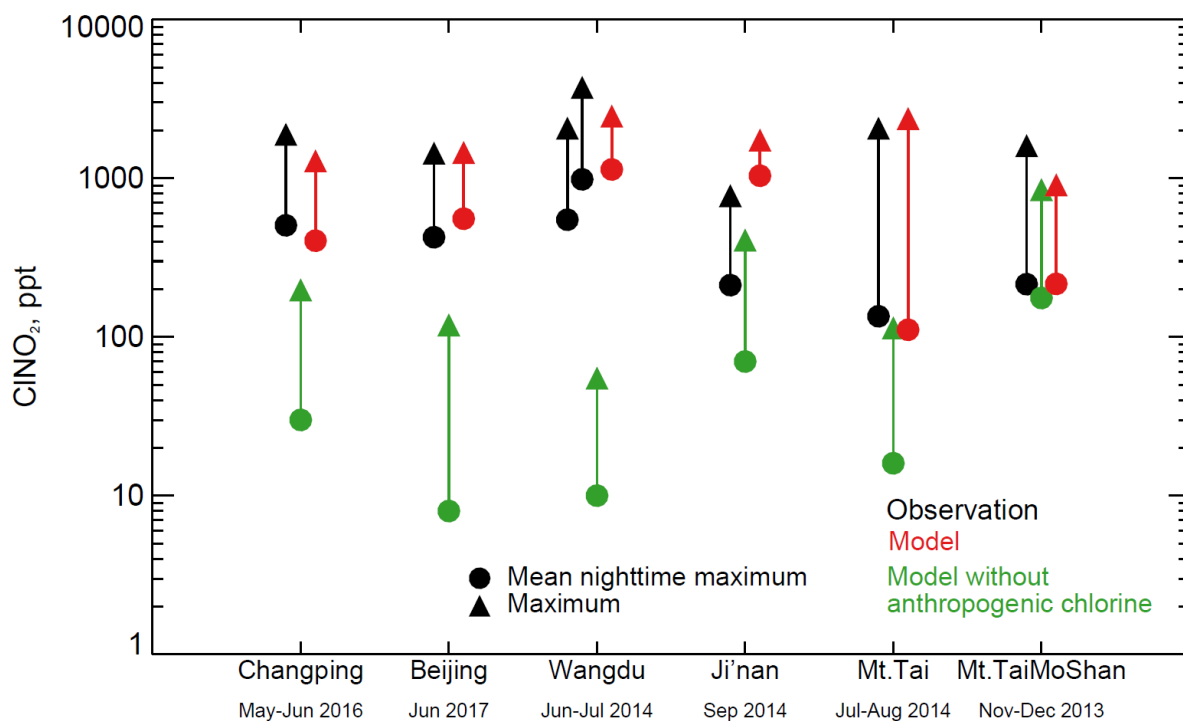


Figure 2. Annual mean mixing ratios of HCl, $\text{PM}_{2.5} \text{Cl}^-$, and nighttime maximum ClNO_2 in surface air. The left panels show the concentrations in the standard GEOS-Chem simulation, with superimposed circles showing $\text{PM}_{2.5} \text{Cl}^-$ and ClNO_2 observations discussed in the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

506



507

508 **Figure 3.** ClNO₂ mixing ratios measured at 6 sites in China. The maximum (triangle) and mean
509 nighttime maximum (circle) during the measurement periods are shown. Model values are sampled
510 for the measurement locations and months. Results from a sensitivity simulation without
511 anthropogenic chlorine emissions are also shown. Observations are for Changping⁴⁸, Beijing⁴³,
512 Wangdu^{13,12}; Ji'nan⁴⁹, Mountain Tai¹⁰, and Mountain Tai Mo Shan⁹. Site locations are shown in
513 Figure 2. Two measurements are available at the Wangdu site during the same time period, and
514 both values are shown here.

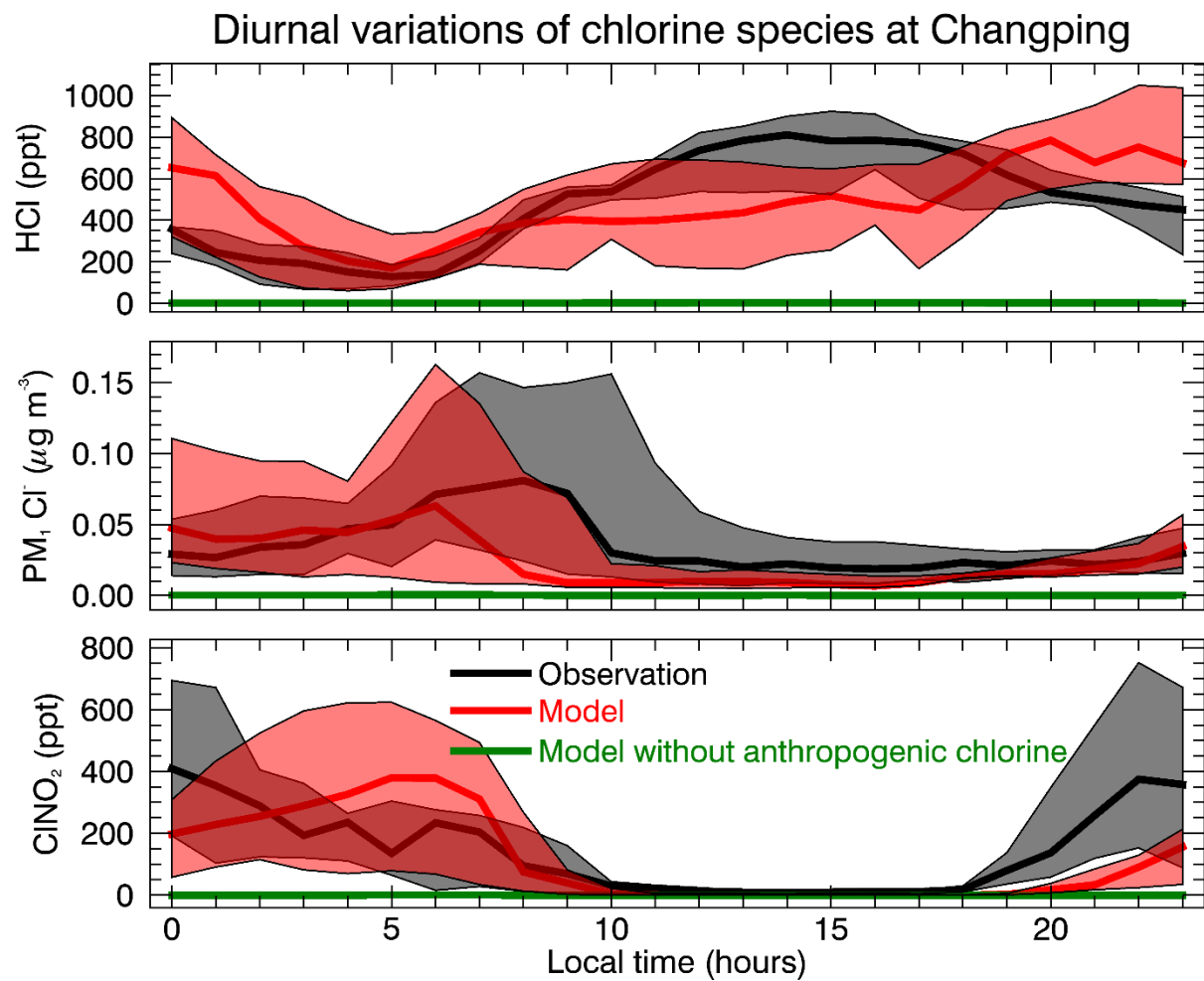


Figure 4. Diurnal variations of HCl, $\text{PM}_{10} \text{Cl}^-$, and ClNO_2 mixing ratios at Changping in May-June 2016. Model values are compared to observations from Le Breton et al.⁶ Median values are shown as solid lines and shaded regions span 25th - 75th percentiles.

Change in PM_{2.5} from anthropogenic chlorine emissions

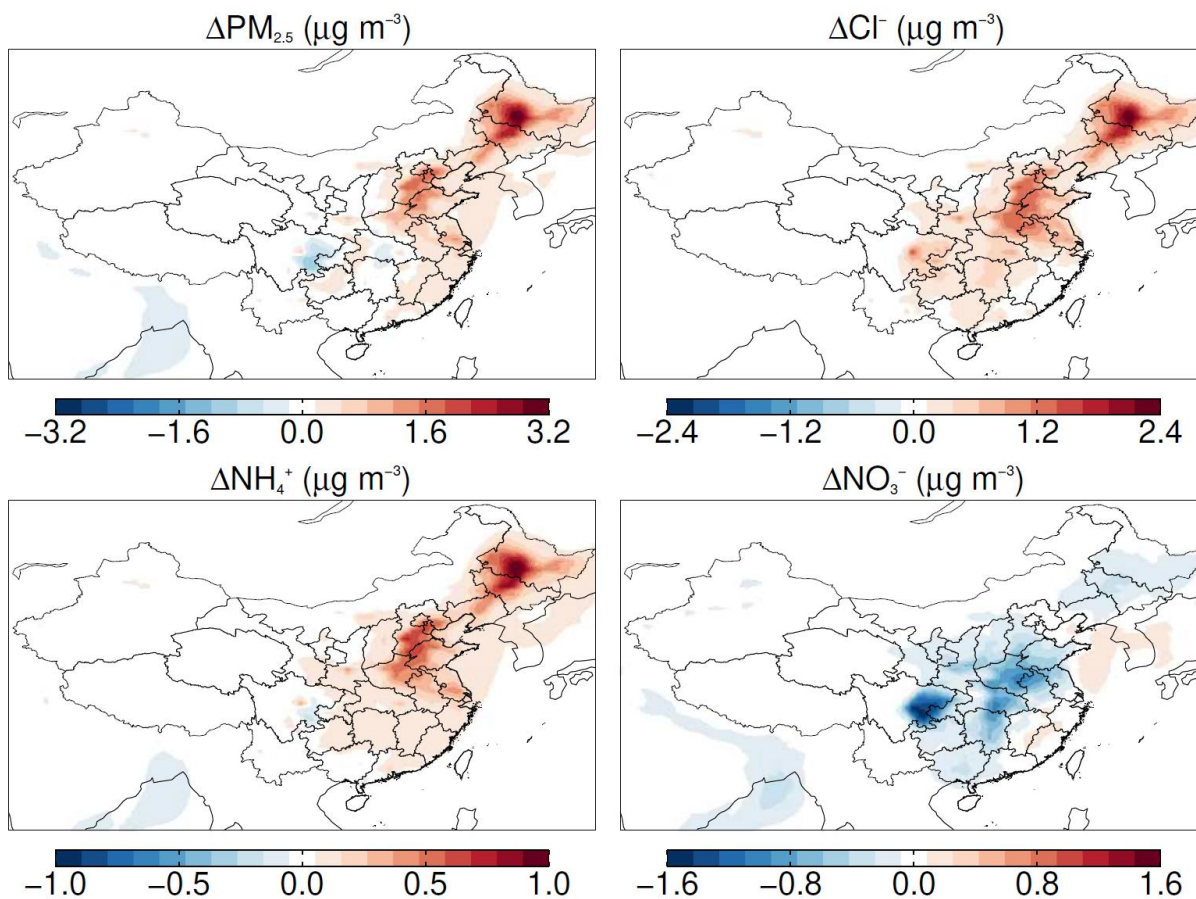


Figure 5. Effect of anthropogenic chlorine emissions on annual mean concentrations of PM_{2.5} and selected components in surface air in China. Values are obtained by difference between our standard GEOS-Chem simulation and a sensitivity simulation with anthropogenic chlorine emissions shut off. Note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

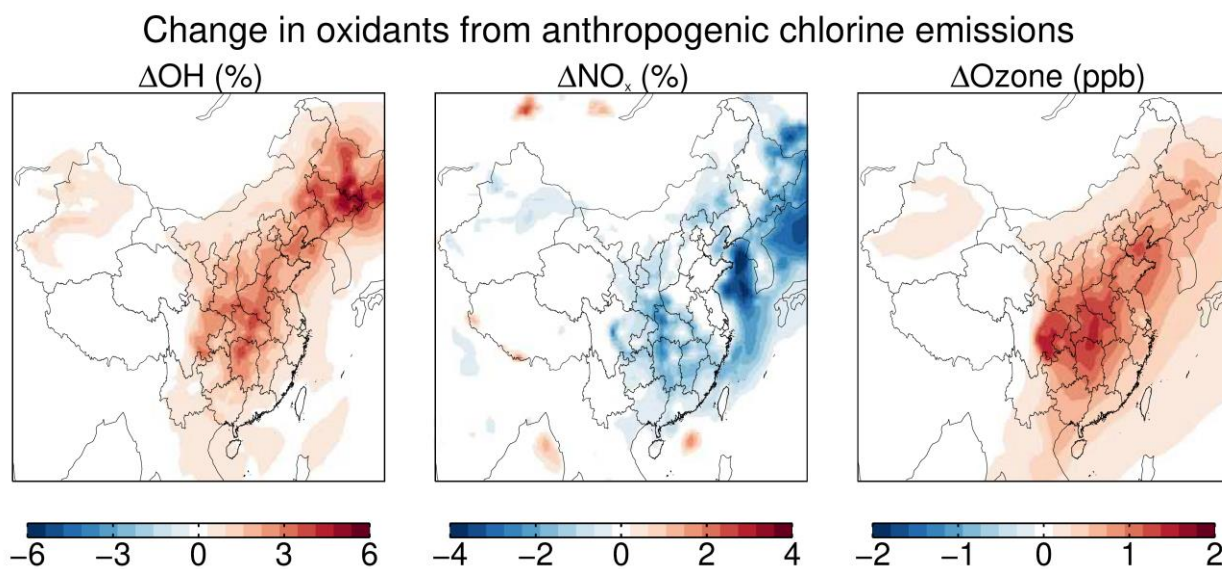


Figure 6. Effect of anthropogenic chlorine emissions on annual mean concentrations of OH, NO_x, and ozone in surface air in China. Values are obtained by difference between our standard GEOS-Chem simulation and a sensitivity simulation with anthropogenic chlorine emissions shut off. Note differences in units and scales between panels.