

Effects of Anthropogenic Chlorine on PM_{2.5} and Ozone Air Quality in China

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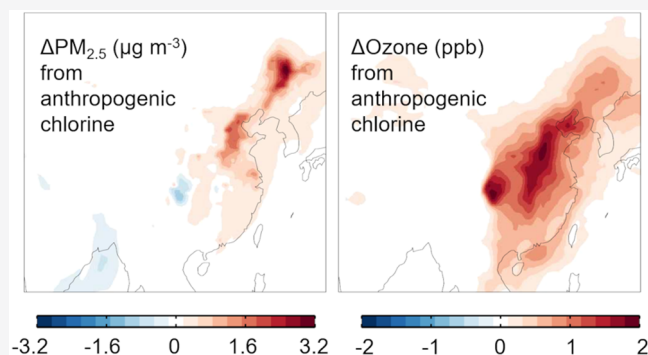


Article Recommendations



Supporting Information

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 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. 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 ClNO₂ formation competes with N₂O₅ hydrolysis. Annual mean MDA8 surface ozone increases by up to 1.9 ppb, mainly from ClNO₂ 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 ClNO₂ 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 (ClNO₂) 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 ClNO₂ 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 showed no model evaluation for China due to lack of ClNO₂ measurements in China prior to 2010. In

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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.^{51–56} 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ and ozone air quality in China. Our work extends previous studies in its comprehensive treatment of chlorine chemistry, full accounting for 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 chemistry²⁰ 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 $0.5^\circ \times 0.625^\circ$ 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 $4^\circ \times 5^\circ$ resolution. The Multiresolution Emission Inventory for China (MEIC)²¹ 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 $\text{PM}_{2.5}$ and ozone air quality in China, showing that the model provides in general a credible representation of observations.^{22,23} 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 $<1 \mu\text{m}$ diameter and coarse mode $>1 \mu\text{m}$ diameter). Gas-aerosol equilibrium of HCl and Cl^- is calculated with ISORROPIA II²⁴ as part of the H_2SO_4 – HCl – HNO_3 – NH_3 –NVCs thermodynamic system, where NVCs stands for nonvolatile cations and is treated in ISORROPIA II using Na^+ as proxy. The most important heterogeneous reactions include $\text{N}_2\text{O}_5 + \text{Cl}^-$ producing ClNO_2 , $\text{HOBr} + \text{Cl}^-$ producing BrCl , $\text{HOI} + \text{Cl}^-$ producing ICl , $\text{HOCl} + \text{Cl}^-$ producing Cl_2 , $\text{OH} + \text{Cl}^-$

producing Cl_2 (two-step process), and $\text{ClNO}_2 + \text{Cl}^-$ 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 parametrization 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.²⁵ We added the reaction between HOCl and dissolved SO_2 ($\text{S(IV)} \equiv \text{HSO}_3^- + \text{SO}_3^{2-}$) to form SO_4^{2-} aerosol.^{26,27} We also now include in the model the reactive uptake of HCl on natural dust, limited by dust alkalinity.²⁸ Details of these updates are described in Supporting Information A1.

Cl -initiated VOC oxidation can contribute to the formation of secondary organic aerosol (SOA),^{29,30} 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.^{31,32}

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 $0.1^\circ \times 0.1^\circ$. It gives total anthropogenic ($\text{HCl} + \text{fine mode } \text{Cl}^-$) 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,²¹ 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.,³³ 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.³⁴ 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.³⁵ We include anthropogenic CH_2Cl_2 and CHCl_3 emission using these national numbers with a spatial distribution the same as anthropogenic HCl . Because 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 ($>2.5 \mu\text{m}$ diameter) and not contribute to $\text{PM}_{2.5}$. Natural $\text{PM}_{2.5}$ dust in GEOS-

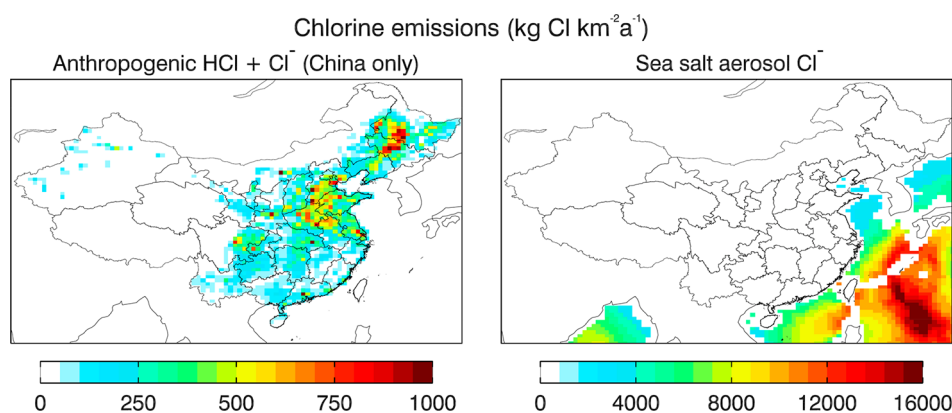


Figure 1. Annual chlorine emissions from Chinese anthropogenic sources (left) and from sea-salt aerosol (right). Values are for 2014. Anthropogenic emissions are from the (HCl + Cl⁻) inventory of Fu et al.⁷ including contributions from agricultural fires, residential biofuels, waste incineration, coal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

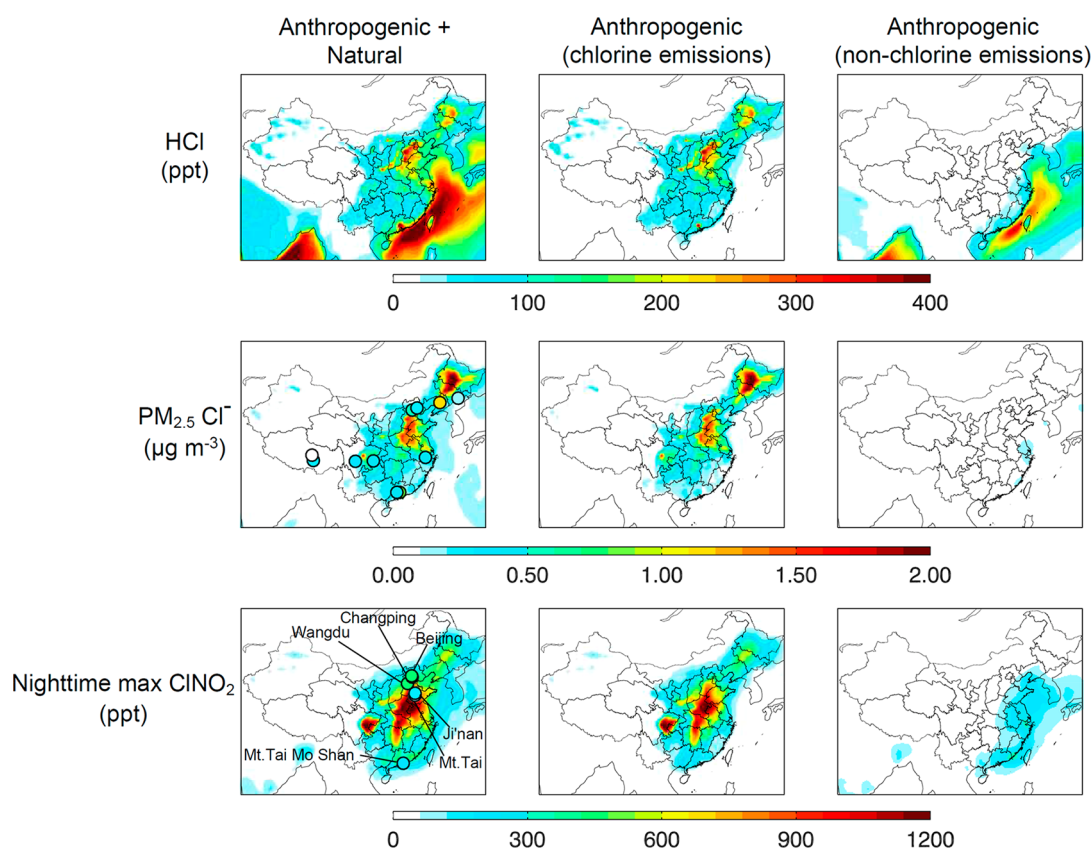


Figure 2. Annual mean concentrations of HCl, PM_{2.5} Cl⁻, and nighttime maximum ClNO₂ in surface air. The left panels show the concentrations in the standard GEOS-Chem simulation, with superimposed circles showing PM_{2.5} Cl⁻ and ClNO₂ observations discussed in the text. The middle panels show the 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 nonchlorine emissions driving Cl⁻ displacement from sea-salt aerosol, as further diagnosed by difference with a simulation shutting off all Chinese anthropogenic emissions.

Chem³⁶ has an emission of 3300 Gg a⁻¹ in China in 2014, assuming 0.15% Cl by mass based on US data,⁵⁸ this yields a Cl⁻ source of 4.9 Gg Cl⁻a⁻¹. Previous studies^{37,38} have suggested that anthropogenic dust may contribute to PM_{2.5}Cl⁻ concentrations in urban environments. We include these emissions using the AFCID inventory,³⁹ 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

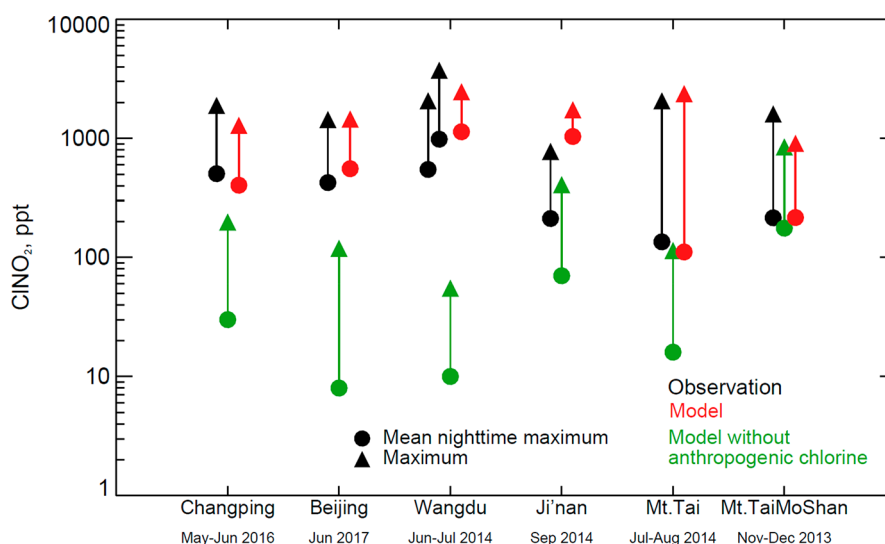
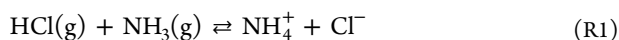


Figure 3. ClNO_2 mixing ratios measured at six sites in China. The maximum (triangle) and mean nighttime maximum (circle) during the measurement periods are shown. Model values are sampled for the measurement locations and months. Results from a sensitivity simulation without anthropogenic chlorine emissions are also shown. Observations are for Changping,⁴⁹ Beijing,⁴³ Wangdu,^{18,17} Ji'nan,⁵⁰ 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.

and subsequent recondensation to $\text{PM}_{2.5}$.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 $\text{PM}_{2.5}\text{Cl}^-$ 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 $\text{PM}_{2.5}\text{Cl}^-$ 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 $\text{H}_2\text{SO}_4\text{--HCl--HNO}_3\text{--NH}_3\text{--NVC}$ thermodynamic system, HCl partitions into the aqueous particulate phase through:

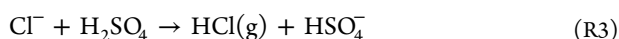


and



Because NH_3 is generally in large excess in China,⁴⁰ equilibrium (R1) is driven to the right and uptake of HCl mostly takes place without displacement of NO_3^- . Figure S1 shows the $\text{HCl}/(\text{HCl} + \text{PM}_{2.5}\text{Cl}^-)$ 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:



H_2SO_4 has a vapor pressure much lower than that of HCl so that (R3) fully displaces Cl^- if H_2SO_4 is present.⁴¹ To investigate this effect, we conducted two sensitivity model simulations, one without anthropogenic chlorine emissions but with anthropogenic nonchlorine emissions and the other without any anthropogenic emissions. The difference between the two isolates the chlorine displaced from SSA Cl^- by nonchlorine 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 $\text{PM}_{2.5}\text{Cl}^-$ 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 ($\text{HCl} + \text{Cl}^-$) 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 NVC 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 exceed 1000 ppt in inland urban areas of China, much higher than corresponding values in the US and Europe.^{3,14}

We compared the model simulation for 2014 to observations collected in China for neighboring years (2012–2017) and assumed interannual differences to be a minor factor in model error. Continuous 2012–2013 observations of $\text{PM}_{2.5}\text{Cl}^-$ are available from 11 sites as part of the CARE-China network.⁴² 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% . $\text{PM}_{2.5}\text{Cl}^-$ concentrations in inland China are much higher than the corresponding concentrations in the US (mostly $<0.1 \mu\text{g m}^{-3}$).^{3,37}

Figure 3 shows absolute maximum and mean nighttime maximum ClNO_2 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 ClNO_2 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, $\text{PM}_1 \text{Cl}^-$ (in particles less than $1 \mu\text{m}$ diameter), and ClNO_2 concentrations were made at the semirural surface site of 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.⁵⁷ Figure 4 compares the diurnal

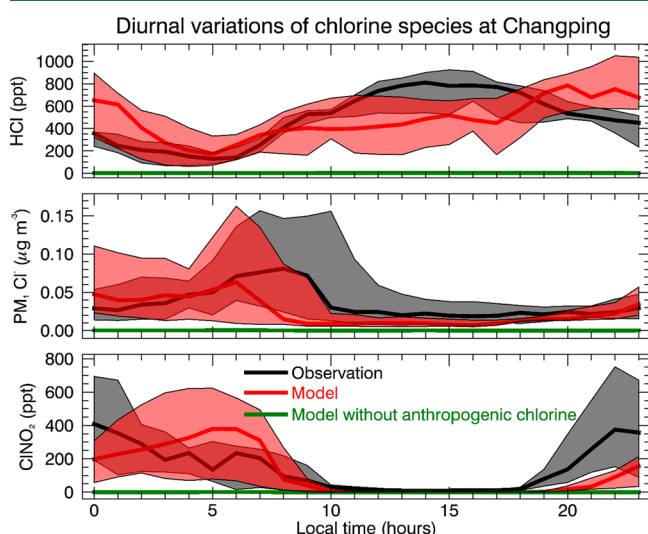


Figure 4. Diurnal variations of HCl, $\text{PM}_1 \text{Cl}^-$, and ClNO_2 concentrations at Changping in May–June 2016. Model values are compared to observations from Le Breton et al.⁶ Median values are shown as solid lines and shaded regions span 25th to 75th percentiles.

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.^{3,12,18,43,44} The cause of the postmidnight decrease in the Changping ClNO_2 data is not clear. Here and elsewhere in China we find the $\text{ClNO}_2 + \text{Cl}^-$

heterogeneous sink of ClNO_2 to be unimportant because it requires aerosol $\text{pH} < 2$ ⁴⁵ which generally does not occur because of the excess of NH_3 .

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.

3.2. Impact of Anthropogenic Chlorine Emissions on Inorganic $\text{PM}_{2.5}$ in China.

Figure 5 shows our simulated net

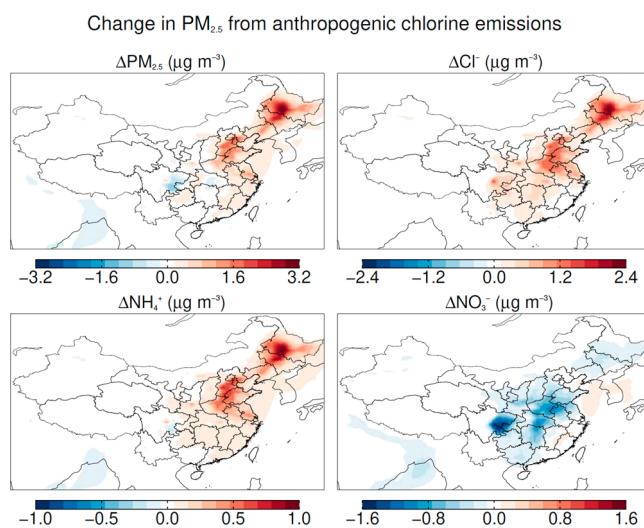


Figure 5. Effect of anthropogenic chlorine emissions on annual mean concentrations of $\text{PM}_{2.5}$ and selected components in surface air in China. Values are obtained by difference between our standard GEOS-Chem simulation and a sensitivity simulation with anthropogenic chlorine emissions shut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

impacts of anthropogenic chlorine emissions on annual mean $\text{PM}_{2.5}$ concentrations calculated as differences between the standard simulation and a simulation without anthropogenic chlorine emissions. This does not account for Cl-initiated SOA formation, as explained in section 2. We find that the largest impact is over Northeast China, where annual mean $\text{PM}_{2.5}$ increases by $3.2 \mu\text{g m}^{-3}$ (6.5%), which is 9% of the Chinese national air quality standard of $35 \mu\text{g m}^{-3}$ and mainly contributed by biomass burning emissions. Absolute and relative impacts in January and July are given in Figure S2.

We find that anthropogenic chlorine has a 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 $1 \mu\text{g m}^{-3}$. Because NH_3 is in excess in most areas of China,⁴⁰ 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 (because 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^- .⁴⁶

3.3. Impact of Anthropogenic Chlorine Emissions on Oxidants in China. Figure 6 shows the effects of

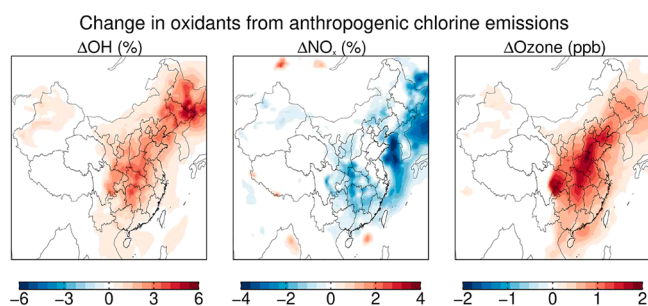


Figure 6. Effect of anthropogenic chlorine emissions on annual mean concentrations of OH, NO_x, and maximum daily 8-h average (MDA8) ozone in surface air in China. Values are obtained by the difference between our standard GEOS-Chem simulation and a sensitivity simulation with anthropogenic chlorine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

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 ClNO₂ chemistry.^{11,12} Annual mean Cl atom concentrations (not shown) increase up to 2700 cm⁻³; 90% of that increase is from ClNO₂ chemistry, while the remaining 10% is from HCl + OH and from Cl₂ 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, ≥C₃ 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 because the principal sink of NO_x is its oxidation by OH.

As shown in Figure 6, annual mean values of maximum daily 8-h 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 ClNO₂ chemistry and is most important in winter (Figure S3) due to the longer night and higher chlorine emissions from residential heating. Wang et al.⁵ 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 ClNO₂. 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 (NH₄⁺, Cl⁻) when NH₃ 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 ClNO₂ 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 H₂SO₄–HCl–HNO₃–NH₃–NVCs thermodynamics and ClNO₂ chemistry, because 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.²¹ According to the MEIC inventory, Chinese emissions decreased by 59% for SO₂ and 21% for NO_x over 2013–2017, mainly due to emission controls applied to coal burning and industry.²¹ No estimates are available for trends in anthropogenic chlorine emissions. Agricultural fires in China are increasingly banned out of concern for air quality,⁴⁷ and coal combustion emission controls would presumably remove chlorine. On the other hand, waste incineration has increased during the 2010–2015 period.⁴⁸ Better understanding of trends in anthropogenic chlorine emissions is needed for a comprehensive assessment of trends in China air quality.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c02296>.

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 (PDF)

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Notes

The authors declare no competing financial interest.

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