

1 Effects of anthropogenic chlorine on PM_{2.5} and
2 ozone air quality in China

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20 ABSTRACT: China has large anthropogenic chlorine emissions from agricultural fires, residential
21 biofuel, waste incineration, coal combustion, and industrial processes. The effect of these
22 emissions is generally ignored in air quality models of fine particulate matter (PM_{2.5}) and ozone
23 air quality. Here we the quantify the effects of chlorine on PM_{2.5} and ozone across China on an
24 annual basis by using the GEOS-Chem chemical transport model with detailed representation of
25 gas-phase and heterogeneous chlorine chemistry. Comparison of the model to observed ClNO₂,
26 HCl, and particulate Cl⁻ concentrations shows that reactive chlorine in China is mainly
27 anthropogenic, unlike in other continental regions where it is mostly of marine origin. We find that
28 anthropogenic chlorine emissions increase total PM_{2.5} by as much as 3.2 μg m⁻³ on an annual mean
29 basis through the formation of ammonium chloride when ammonia is in excess. The nitrate
30 component of PM_{2.5} decreases by up to 1.5 μg m⁻³ because ClNO₂ formation competes with N₂O₅
31 hydrolysis. Annual mean surface ozone increases by up to 1.7 ppb, mainly from ClNO₂ chemistry,
32 while reactivities of volatile organic compounds increase by up to 48% for ethane. Our results
33 suggest that a sufficient representation of chlorine chemistry in air quality models can be obtained
34 from consideration of HCl/Cl⁻ thermodynamics and ClNO₂ chemistry.

35 1. Introduction

36 Chlorine is emitted to the atmosphere as particulate chloride (Cl⁻) from sea-salt, as hydrogen
37 chloride (HCl) from volcanoes, as HCl/Cl⁻ from combustion and industry, and as chlorocarbons
38 from the biosphere, fires, and industrial processes^{1,2}. Subsequent atmospheric reactions can lead
39 to the production of chlorine radicals³, with a broad range of implications for global tropospheric

40 chemistry and air quality. We recently presented a general analysis of the role of chlorine in global
41 tropospheric chemistry using the GEOS-Chem chemical transport model³. Here we examine the
42 more specific implications for China air quality through the effects of chlorine chemistry on
43 ground level ozone and PM_{2.5} (particulate matter smaller than 2.5 μm diameter).

44 A unique feature of China air pollution is the magnitude of the anthropogenic chlorine source.
45 The global tropospheric chlorine budget is dominated by marine sources, mainly through
46 mobilization of chloride from sea salt aerosols (SSA)³. Most of the chlorine in continental regions
47 of North America and Europe is dominated by long-range transport of this marine source.^{3, 4} In
48 contrast, atmospheric measurements suggest that chlorine in China is mostly anthropogenic.^{5, 6}
49 Anthropogenic sources in China include coal combustion, waste incineration, industrial processes,
50 and biomass burning, totaling more than 800 Gg a⁻¹ in recent estimates.^{7, 8}

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

62 Tianjin-Hebei (BTH) area, and found that ClNO₂ chemistry can increase surface ozone by up to
63 20%.

64 Here, we use the GEOS-Chem model in a full-year high-resolution simulation over China and
65 the adjacent ocean, including best estimates of anthropogenic and natural chlorine emissions
66 combined with detailed representation of chlorine chemistry. We evaluate the model with the
67 ensemble of atmospheric observations for chlorine species. From there we quantify the effect of
68 anthropogenic chlorine on Chinese air quality.

69 2. Materials and Methods

70 2.1 GEOS-Chem model

71 We use the GEOS-Chem model version 11-02d (<http://www.geos-chem.org>), which includes a
72 detailed representation of coupled ozone–NO_x– volatile organic compound (VOC)–PM–halogen
73 chemistry²³, and to which we have updated an updated comprehensive treatment of chlorine
74 chemistry³. GEOS-Chem is driven by MERRA2 (the Modern-Era Retrospective analysis for
75 Research and Applications, Version 2) assimilated meteorological fields from the NASA Global
76 Modeling and Assimilation office (GMAO) with native horizontal resolution of 0.5°×0.625° and
77 72 vertical levels from the surface to the mesosphere. Our simulation is conducted at that native
78 resolution over East Asia (60°–150°E, 10°S–55°N), with dynamical boundary conditions from a
79 global simulation with 4°×5° resolution. The Multi-resolution Emission Inventory for China
80 (MEIC)²⁴ including seasonal, weekly, and diurnal variations for 2014 is used for Chinese
81 anthropogenic emissions other than chlorine. Chlorine emissions are described in Section 2.2.
82 Results presented here are from a 1-year simulation for 2014 after a 3-month model spin up.

83 GEOS-Chem has previously been used in a number of model studies of PM_{2.5} and ozone air
84 quality in China, showing that the model provides in general a credible representation of
85 observations^{25, 26}. However, none of these studies included comprehensive representation of
86 chlorine chemistry. Here we added to the model the detailed chlorine chemistry mechanism (fully
87 coupled with bromine and iodine) of Wang et al.³. The model includes 12 gas-phase inorganic
88 chlorine species: Cl, Cl₂, Cl₂O₂, ClNO₂, ClNO₃, ClO, ClOO, OClO, BrCl, ICl, HOCl, HCl, and
89 two size ranges for aerosol Cl⁻ (fine mode <1 μm diameter and coarse mode >1 μm diameter). Gas-
90 aerosol equilibrium of HCl and Cl⁻ is calculated with ISORROPIA II²⁷ as part of the H₂SO₄-HCl-
91 HNO₃-NH₃-NVCs thermodynamic system, where NVCs stands for non-volatile cations and is
92 treated in ISORROPIA II using Na⁺ as proxy. We added some updates to the Wang et al.⁹
93 mechanism including Cl oxidation of toluene, monoterpenes, limonene, and methyl ethyl ketone,
94 as given in Table S1. We updated the parameterization of ClNO₂ formation from nighttime
95 heterogeneous reaction of N₂O₅ with Cl⁻ in the aerosol aqueous phase to include the effect of
96 organic coating, as described by McDuffie et al.²⁸ We added the reaction between HOCl and
97 dissolved SO₂ (S(IV) ≡ HSO₃⁻ + SO₃²⁻) to form SO₄²⁻ aerosol.^{29, 30} We also now include in the
98 model the reactive uptake of HCl on natural dust, limited by dust alkalinity³¹. Details of these
99 updates are described in Supporting Information A1.

100

101 2.2. Anthropogenic Chlorine Emissions

102 We include anthropogenic chlorine emissions from the China inventory of Fu et al.⁷ This
103 inventory was developed for 2014 with a horizontal resolution of 0.1°×0.1°. It gives total
104 anthropogenic (HCl + fine mode Cl⁻) emissions in China of 254 Gg Cl a⁻¹ from agricultural fires,
105 253 Gg Cl a⁻¹ from residential biofuel, 251 Gg Cl a⁻¹ from waste incineration, 109 Gg Cl a⁻¹ from

106 coal combustion, and 65 Gg Cl a⁻¹ from industrial processes, for a total source of 932 Gg Cl a⁻¹.
107 The inventory separates HCl (458 Gg Cl a⁻¹) and particulate Cl⁻ (486 Gg Cl a⁻¹) emissions, but the
108 cations associated with Cl⁻ emissions are not identified. We assume in our standard simulation that
109 all emissions are as HCl but also conduct a sensitivity simulation where particulate Cl⁻ is emitted
110 as such with accompanying NVCs. There is negligible difference in results, as discussed below.
111 We apply monthly, weekly, and diurnal scaling factors for coal combustion and industrial sources
112 based on the MEIC inventory,²⁴ and national mean monthly scaling factors for agricultural fires,
113 residential biofuels, and waste incineration based on Fu et al.⁷

114 We do not include any anthropogenic chlorine emissions from other countries in East Asia. The
115 only global emission inventory is that of McCulloch et al.³², built for the 1990s and found to be
116 considerably biased high relative to present-day observations and regional emission estimates.^{3,7}
117 ⁸ The effect of these emissions on China air quality would be small compared to the effect of SSA
118 chloride from the neighboring ocean.

119 Dichloromethane (CH₂Cl₂) and chloroform (CHCl₃) are emitted from industrial activities and
120 produce Cl atoms in GEOS-Chem through photolysis and oxidation³. Anthropogenic CH₂Cl₂
121 emission in China was estimated to be 318 Gg a⁻¹ in 2016 in a bottom-up study by Feng et al.,³³.
122 The total CHCl₃ emission in China was estimated to be 88 Gg a⁻¹ in 2015 based on a Bayesian
123 inversion of surface measurements.³⁴ We include anthropogenic CH₂Cl₂ and CHCl₃ emission
124 using these national numbers with a spatial distribution the same as anthropogenic HCl. Since both
125 CH₂Cl₂ and CHCl₃ have long lifetimes (> 250 days), they have negligible effect on Chinese air
126 quality and will not be discussed further.

127 Dust is an additional source of particulate chloride but most of this would be present in coarse
128 particles (>2.5 μm diameter) and not contribute to PM_{2.5}. Natural PM_{2.5} dust in GEOS-Chem³⁵ has

129 an emission of 3300 Gg a⁻¹ in China in 2014; assuming 0.15% Cl by mass based on US data³⁸, this
130 yields a Cl⁻ source of 4.9 Gg Cl⁻ a⁻¹. Previous studies^{36, 37} have suggested that anthropogenic dust
131 may contribute to PM_{2.5} Cl⁻ concentrations in urban environments. We include these emissions
132 using the AFCID inventory³⁸, again assuming that the dust is 0.15% Cl by mass. The resulting
133 emission in China is 7.9 Gg Cl⁻ a⁻¹. These dust emissions are very small compared to the
134 anthropogenic chlorine emission from combustion.

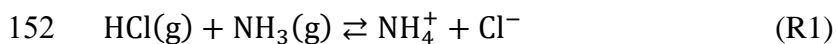
135 Figure 1 shows the annual HCl + Cl⁻ emissions from Chinese anthropogenic sources and Cl⁻
136 emissions from sea salt aerosol (SSA) as implemented in GEOS-Chem. There are two areas of
137 high anthropogenic emissions, in the North China Plain (NCP) due to waste incineration and
138 residential biofuel, and in Northeast China due to agricultural fires and residential biofuel. The
139 SSA source over the ocean is much larger than the anthropogenic source over land (note difference
140 in scales in Figure 1), and can contribute to PM_{2.5} Cl⁻ over land both by direct transport and (for
141 coarse SSA) by displacement to HCl and subsequent re-condensation to PM_{2.5}³. However, the
142 SSA influence over land is also limited by rapid deposition during transport. The GEOS-Chem
143 simulation allows quantification of these effects.

144 3. Results and Discussion

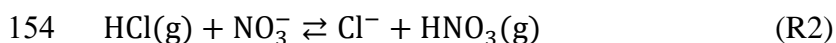
145 3.1. Anthropogenic chlorine over China

146 Figure 2 shows our simulated annual mean distributions of HCl and PM_{2.5} Cl⁻ concentrations in
147 surface air. Concentrations over China are mainly from anthropogenic chlorine emissions, despite
148 the much larger SSA emissions off-shore. Natural dust contributes 3-10% of PM_{2.5} Cl⁻ in North
149 China in spring, and less in other regions and seasons. Annual mean HCl mixing ratios range from

150 100 to 400 ppt over most of eastern China. In the H₂SO₄-HCl-HNO₃-NH₃-NVC thermodynamic
151 system, HCl partitions into the aqueous particulate phase through:

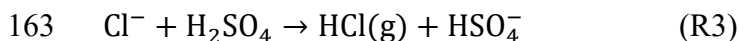


153 and



155 Since NH₃ is generally in large excess of HNO₃ in China,³⁹ equilibrium (R1) is driven to the right
156 and uptake of HCl mostly takes place without displacement of NO₃⁻. Figure S1 shows the
157 HCl/(HCl + PM_{2.5} Cl⁻) molar ratio over China in different seasons. On average, 66% of the emitted
158 HCl is partitioned into the particulate phase. That fraction is larger in winter and lower in summer,
159 mainly reflecting temperature differences.

160 Even without considering anthropogenic chlorine emissions, anthropogenic HCl can be formed
161 through acid displacement of SSA Cl⁻ by H₂SO₄ and HNO₃ produced from anthropogenic
162 emissions of SO₂ and NO_x. This acid displacement involves (R2) and:



164 H₂SO₄ has a much lower vapor pressure than HCl so that (R3) fully displaces Cl⁻ if H₂SO₄ is
165 present.⁴⁰ To investigate this effect we conducted two sensitivity model simulations, one without
166 anthropogenic chlorine emissions but with anthropogenic non-chlorine emissions, and the other
167 without any anthropogenic emissions. The difference between the two isolates the chlorine
168 displaced from SSA Cl⁻ by non-chlorine anthropogenic emissions, and this is shown in the right
169 panel of Figure 2. Acid displacement requires a deficit of ammonia and thus mainly takes place
170 offshore. The resulting HCl can then be transported back onshore and contribute to PM_{2.5} Cl⁻ and
171 chlorine chemistry inland. We find that the effect is relatively small and mainly limited to
172 southeastern coastal China. We examined the sensitivity of our results to the speciation of

173 anthropogenic (HCl + Cl⁻) emission by conducting a sensitivity simulation in which emission of
174 Cl⁻ is with NVCs as associated cations (instead of HCl in the standard simulation). On average,
175 adding the NVCs emission changes the simulated annual mean HCl and Cl⁻ concentrations by -2%
176 and +1% respectively.

177 Figure 2 also shows the annual mean value of the nighttime maximum ClNO₂ mixing ratio in
178 surface air, and the contributions from anthropogenic chlorine and other (mainly NO_x) emissions.
179 We use the mean nighttime maximum mixing ratio as concentration metric for ClNO₂, following
180 standard practice^{3, 41}, because of the large diurnal variation and near-zero mixing ratios in the
181 daytime. Again, most of ClNO₂ over China is driven by anthropogenic chlorine emissions. Values
182 exceed 1000 ppt in inland urban areas of China, much higher than corresponding values in the US
183 and Europe.³

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

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

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

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

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

218

219 3.3. Impact of anthropogenic chlorine emissions on PM_{2.5} in China

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

226 We find that anthropogenic chlorine has negligible effect on SO_4^{2-} concentrations in China (<
227 0.1 $\mu\text{g m}^{-3}$). The contribution of HOCl + S(IV) to SO_2 oxidation is minimal because the main sink
228 of HOCl is photolysis. As shown in Figure 5, anthropogenic chlorine emissions can cause annual
229 mean surface NH_4^+ concentrations to increase by up to 1 $\mu\text{g m}^{-3}$. Since NH_3 is in excess in most
230 areas of China,³⁹ the emitted HCl causes NH_3 transfer to NH_4^+ through reaction (R1), so that the
231 pattern of enhanced NH_4^+ largely matches that of Cl^- concentrations. In contrast, anthropogenic
232 chlorine emissions result in annual average NO_3^- concentrations decreases by up to 1.5 $\mu\text{g m}^{-3}$
233 following a similar spatial distribution as modeled ClNO₂ (Figure 2). The dominant factor for the
234 NO_3^- decrease is not acid displacement by HCl (since NH_3 is in excess) but the increased
235 competition of $\text{N}_2\text{O}_5 + \text{Cl}^-$ with N_2O_5 hydrolysis which is a major source of NO_3^- .⁴⁵

236

237 3.4. Impact of anthropogenic chlorine emissions on oxidants in China

238 Figure 6 shows the effects of anthropogenic chlorine emissions on annual mean hydroxyl radical
239 (OH), NO_x , and ozone concentrations in surface air, calculated as differences between the standard
240 simulation and a simulation without anthropogenic chlorine emissions. OH concentrations in
241 surface air increase by up to 6%, mainly due to ClNO₂ chemistry^{20, 21}. Annual mean Cl atom

242 concentrations (not shown) increase up to 2700 cm^{-3} ; 90% of that increase is from ClNO_2
243 chemistry, while the remaining 10% is from $\text{HCl} + \text{OH}$ and from Cl_2 and HOCl photolysis. The
244 latter reactions are most important in summer but even then they contribute less than 25% of the
245 Cl atoms. The combined increases of both Cl atoms and OH enhance the annual mean reactivities
246 of ethane, propane, higher alkenes, methanol, toluene, and ethanol over the North China Plain by
247 48%, 40%, 28%, 11%, 11%, and 10%, respectively. The increase of OH leads to a decrease in NO_x
248 since the principal sink of NO_x is its oxidation by OH.

249 As shown in Figure 6, annual mean surface ozone increases by up to 1.7 ppb after including
250 anthropogenic chlorine emissions. This is mainly because of ClNO_2 chemistry. The effect is most
251 important in winter (Figure S3) due to the longer night and higher chlorine emissions from
252 residential heating. Wang et al.³ showed that tropospheric chlorine drives a global decrease of
253 ozone by catalytic production of bromine radicals from sea salt aerosol, but we find that this effect
254 is negligibly small over China because bromine concentrations (mainly of marine origin) are
255 extremely low.

256 In summary, we have examined the impact of anthropogenic chlorine emissions on air quality in
257 China through model simulations with a detailed chemical mechanism. The model is generally
258 consistent with the observations available for fine particulate Cl^- , HCl , and ClNO_2 . We show that
259 the observations are dominantly contributed by anthropogenic chlorine emissions. Anthropogenic
260 chlorine increases $\text{PM}_{2.5}$ concentrations in China by up to $3.2 \mu\text{g m}^{-3}$ on an annual mean basis
261 because of the condensation of $(\text{NH}_4^+, \text{Cl}^-)$ when NH_3 is in excess, as is the case generally over
262 China. Annual mean surface OH and ozone mixing ratios increase by up to 6% and 1.7 ppb,
263 respectively, mostly driven by ClNO_2 chemistry providing an early-morning source of radicals.
264 Our results suggest that a sufficient representation of anthropogenic chlorine chemistry in air

265 quality models for China can be obtained from consideration of H₂SO₄-HCl-HNO₃-NH₃-NVCs
266 thermodynamics and ClNO₂ chemistry.

267 Emissions in China are presently changing rapidly in response to the governmental Clean Air
268 Action.²⁴ According to the MEIC inventory, Chinese emissions decreased by 59% for SO₂ and
269 21% for NO_x over 2013-2017, mainly due to emission controls applied to coal burning and
270 industry.²⁴ No estimates are available for trends in anthropogenic chlorine emissions. Agricultural
271 fires in China are increasingly banned out of concern for air quality⁴⁶, and coal combustion
272 emission controls would presumably remove chlorine. On the other hand, waste incineration has
273 increased during the 2010-2015 period.⁴⁷ Better understanding of trends in anthropogenic chlorine
274 emissions is needed for a comprehensive assessment of trends in China air quality.

275

276 ASSOCIATED CONTENT

277 **Supporting Information.**

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

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287 **Author Contributions**

288 **Notes**

289 The authors declare no competing financial interest.

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298

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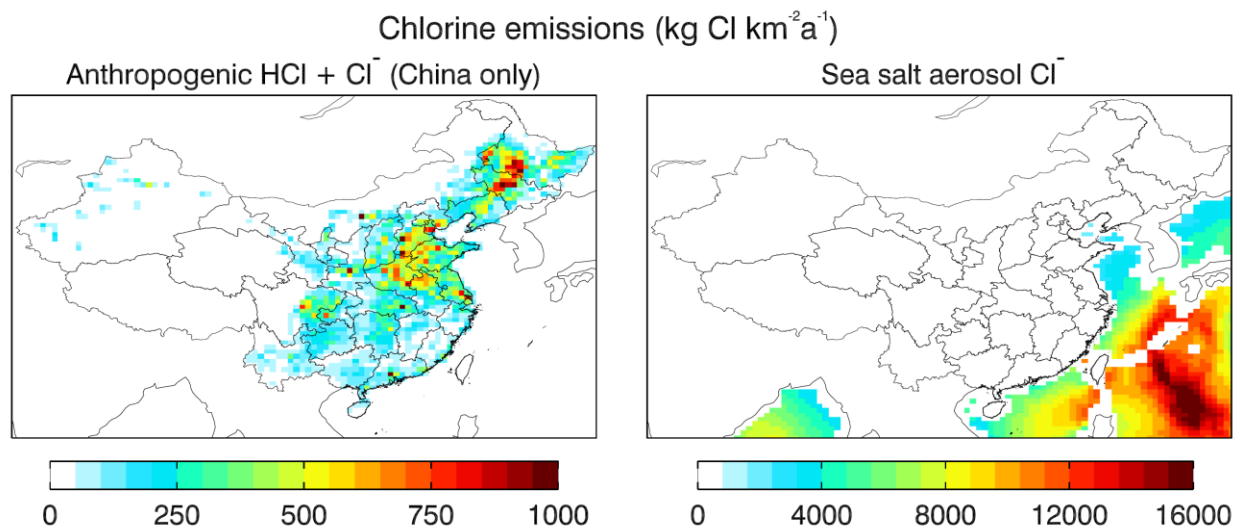
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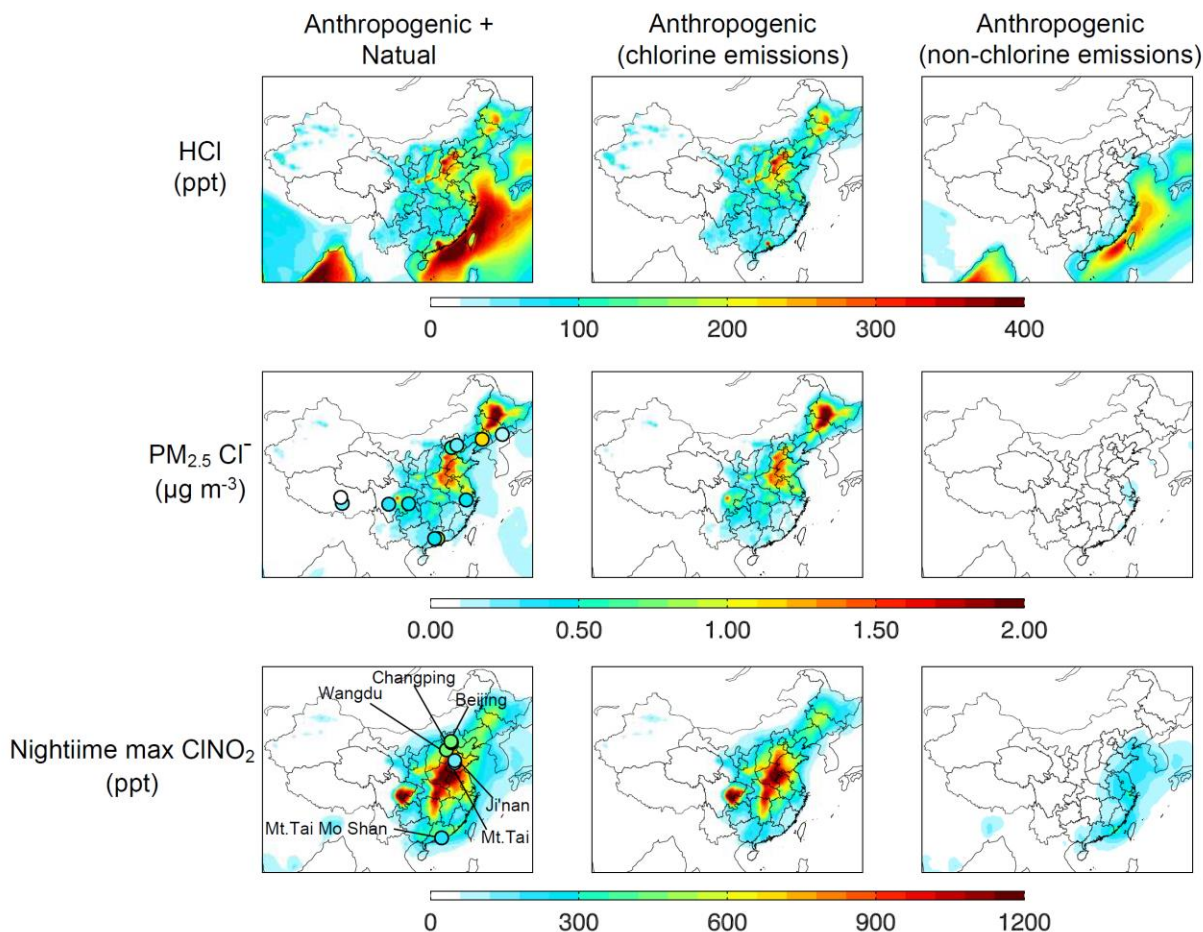
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 490 **Figure 1.** Annual chlorine emissions from Chinese anthropogenic sources (left) and from sea salt
 491 aerosol (right). Values are for 2014. Anthropogenic emissions are from the (HCl + Cl⁻) inventory
 492 of Fu et al.⁷ including contributions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

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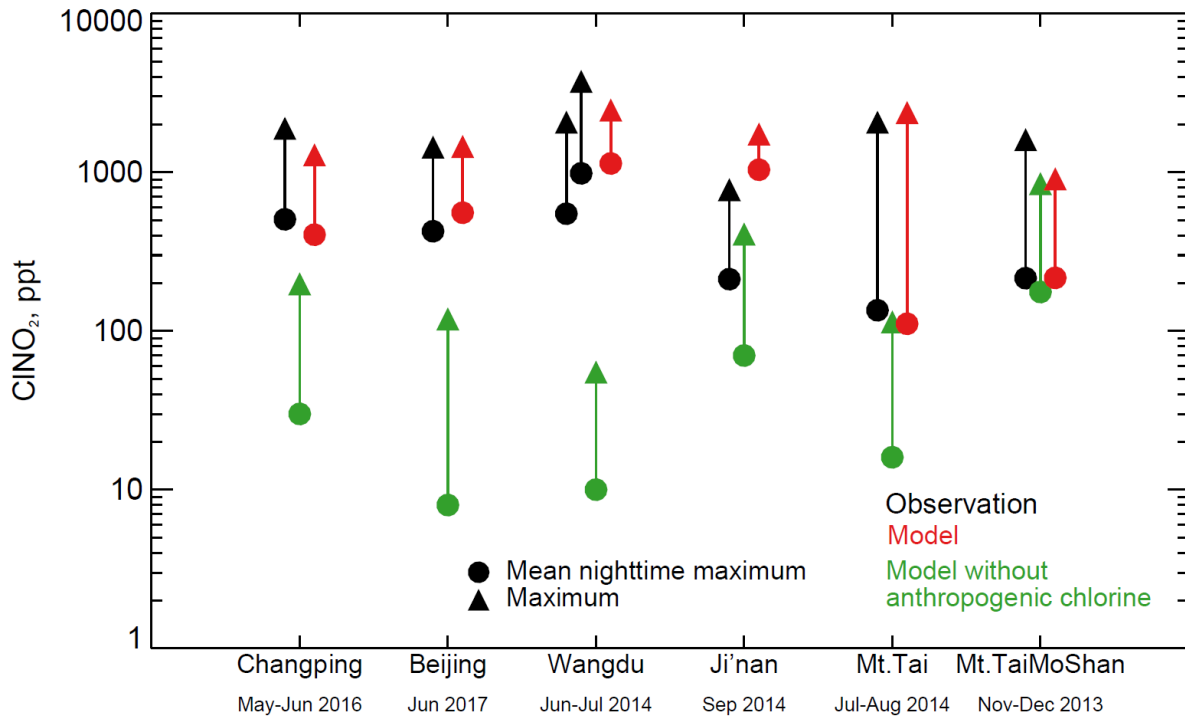
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 497 **Figure 2.** Annual mean mixing ratios of HCl, PM_{2.5} Cl⁻, and nighttime maximum ClONO₂ in surface
 498 air. The left panels show the concentrations in the standard GEOS-Chem simulation, with
 499 superimposed circles showing PM_{2.5} Cl⁻ and ClONO₂ observations discussed in the text. The middle
 500 panels show the contributions from Chinese anthropogenic chlorine emissions, as diagnosed by
 501 difference with a simulation shutting off these emissions. The right panel shows the contributions
 502 from anthropogenic non-chlorine emissions driving Cl⁻ displacement from sea-salt aerosol, as
 503 further diagnosed by difference with a simulation shutting off all Chinese anthropogenic
 504 emissions.

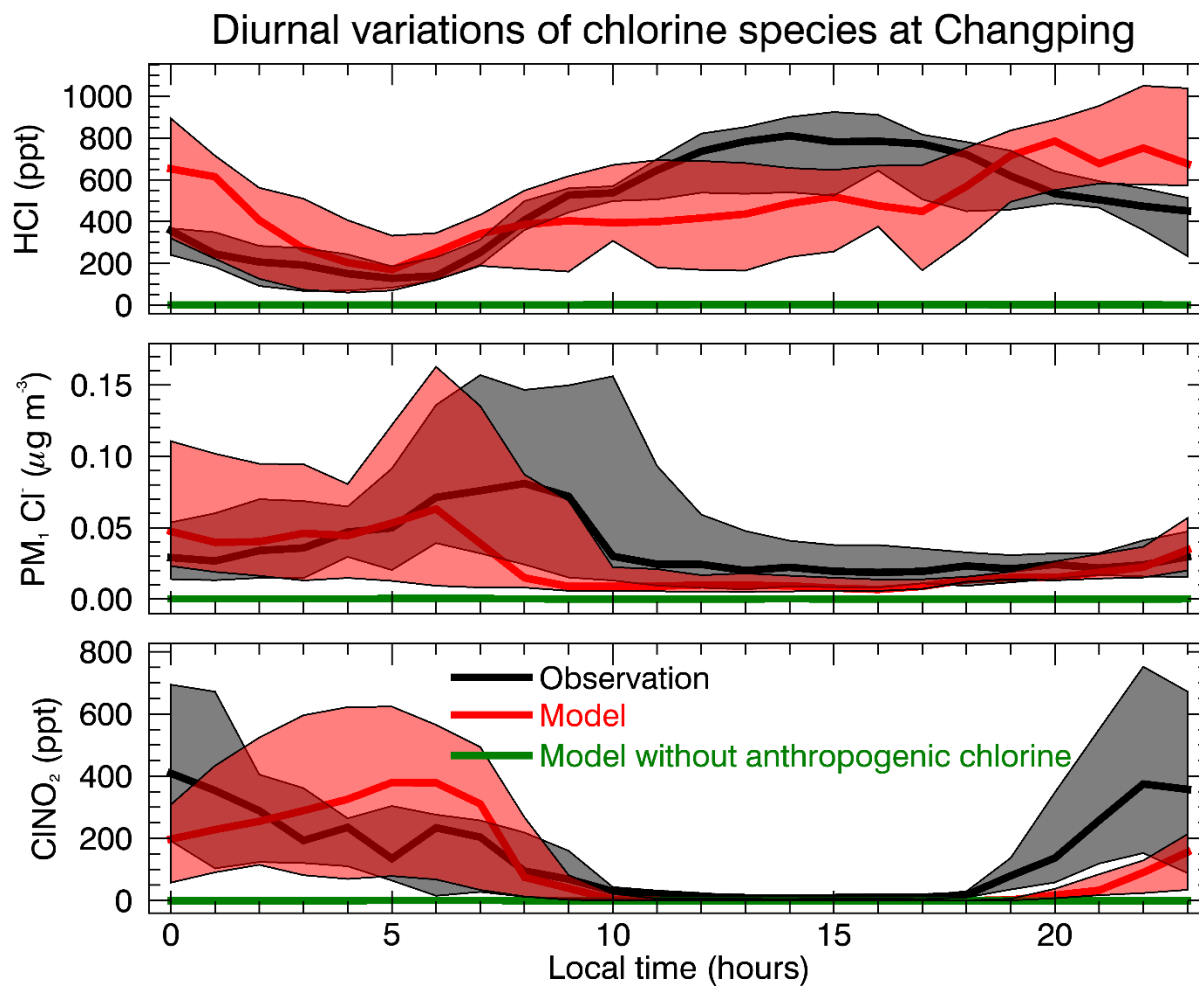
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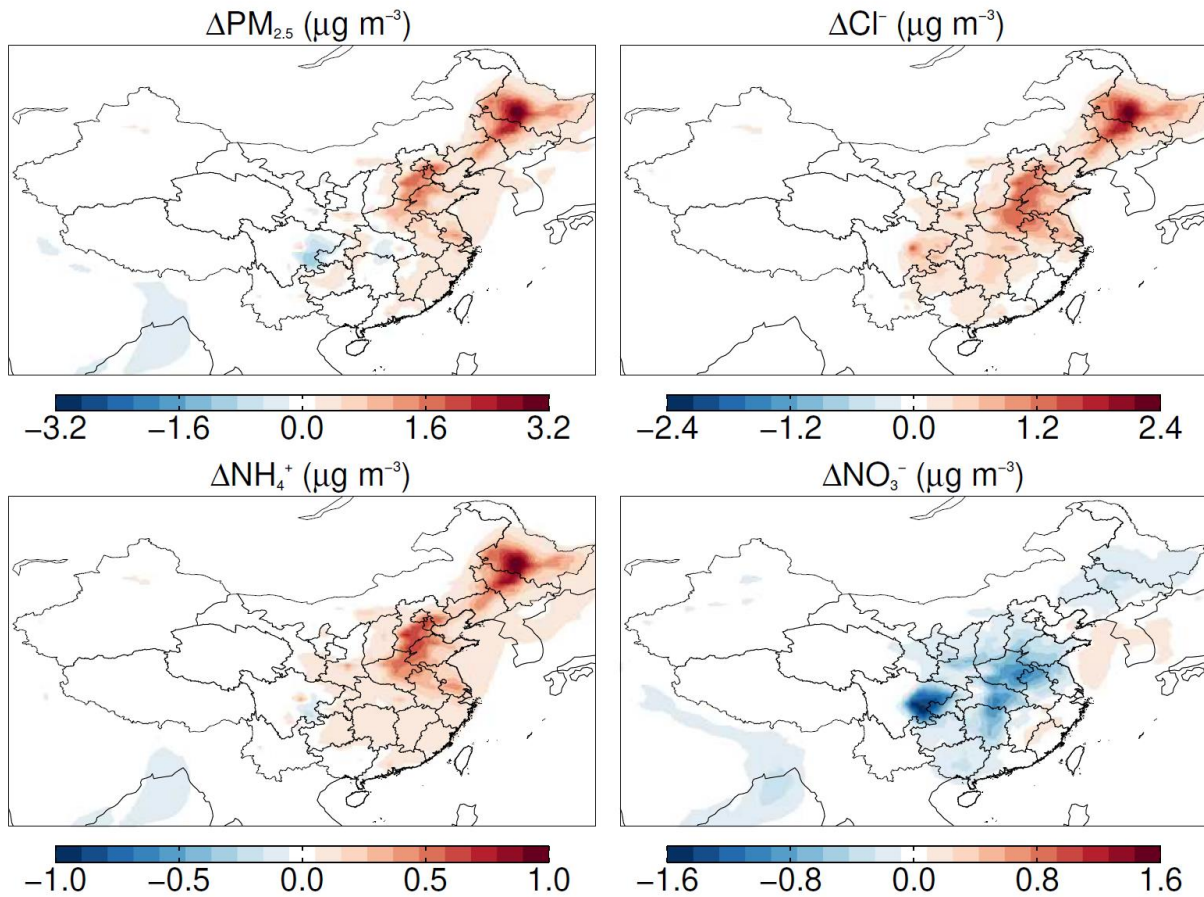
508 **Figure 3.** ClONO₂ mixing ratios measured at 6 sites in China. The maximum (triangle) and mean
509 nighttime maximum (circle) during the measurement periods are shown. Model values are sampled
510 for the measurement locations and months. Results from a sensitivity simulation without
511 anthropogenic 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.



515
 516 **Figure 4.** Diurnal variations of HCl, PM₁ Cl⁻, and ClNO₂ mixing ratios at Changping in May-June
 517 2016. Model values are compared to observations from Le Breton et al.⁶ Median values are shown
 518 as solid lines and shaded regions span 25th - 75th percentiles.

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Change in $PM_{2.5}$ from anthropogenic chlorine emissions

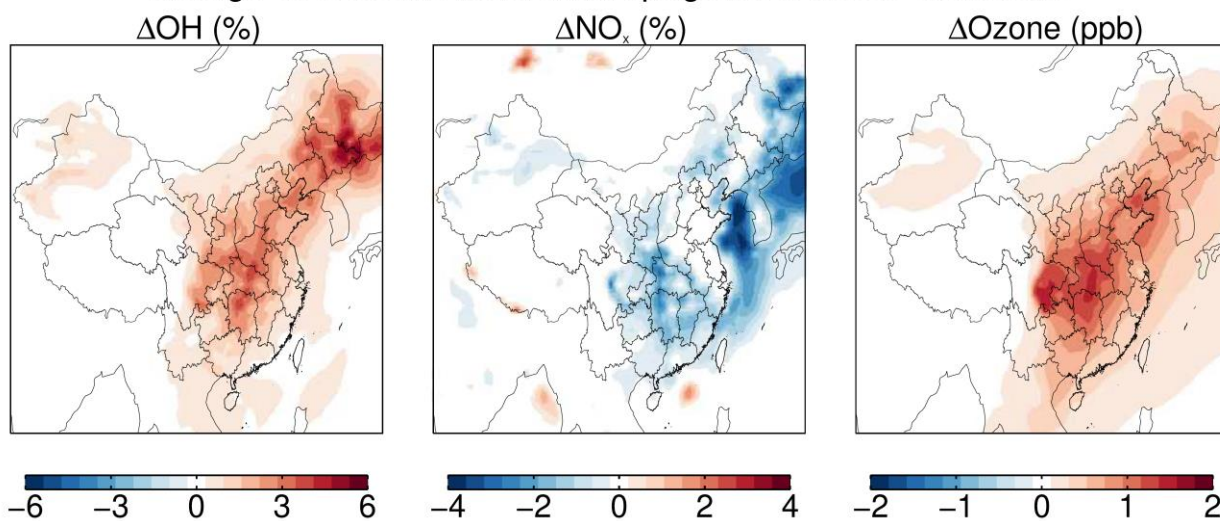


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521 **Figure 5.** Effect of anthropogenic chlorine emissions on annual mean concentrations of $PM_{2.5}$ and
522 selected components in surface air in China. Values are obtained by difference between our
523 standard GEOS-Chem simulation and a sensitivity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

525

Change in oxidants from anthropogenic chlorine emissions



526

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