Supplementary materials for

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

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A1. Updated Chlorine Chemistry in GEOS-Chem

We updated the source of $ClNO_2$ from the nighttime heterogeneous reaction of N_2O_5 with Cl^- in the aerosol aqueous phase:

$$N_2O_5 + \varphi Cl^- + (1-\varphi)H_2O \rightarrow \varphi ClNO_2 + (2-\varphi)NO_3^- + 2(1-\varphi)H^+ \qquad \text{(R1)}$$

The rate of this reaction is determined by a reactive uptake coefficient $\gamma_{N_2O_5}$ representing the probability that a gas-phase N_2O_5 molecule impacting the aerosol surface will go on to react in the aqueous phase. GEOS-Chem assumes that Cl^- is present only in sulfate–nitrate–ammonium (SNA) and sea salt aerosols when doing this calculation, assuming an external mixture of aerosol types between inorganic and organic aerosols. In Wang et al.,[1] $\gamma_{N_2O_5}$ and the production yield of $ClNO_2$ (φ) were calculated from the mechanism of Bertram and Thornton[2] as a function of aerosol water content ($[H_2O]$), $[Cl^-]$ and $[NO_3^-]$. Recent atmospheric observations show evidence that $\gamma_{N_2O_5}$ is lower[3, 4] and that this may be due to organic coating of particles. Here we assume that reaction (R1) happens on internally mixed SNA, sea salt, and organic aerosols, and account for the effect of the organic coating as given by:

$$\frac{1}{\gamma_{N_2O_5}} = \frac{1}{\gamma_{\mathrm{core}}} + \frac{1}{\gamma_{coat}} \qquad (1)$$

Where γ_{core} represents the reactive uptake of Bertram and Thornton[2] mechanism, and γ_{coat} represents the retardation from the organic coating. Calculation of γ_{coat} is based on Riemer et al.[4] with the relative humidity (RH) dependence of coating properties from Gaston et al.[5] This parameterization has been described detail by McDuffie et al:[6]

$$\gamma_{\mathrm{core}} = \frac{4V}{cSA} K_H k'_{2f} \left(1 - \frac{1}{\left(\frac{k_3[H_2O]}{k_{2b}[NO_3^-]}\right) + 1 + \left(\frac{k_4[Cl^-]}{k_{2b}[NO_3^-]}\right)}\right) \qquad (2)$$

$$k'_{2f} = \beta\left(1 - e^{-\delta[H_2O]}\right) \qquad (3)$$

$$\gamma_{\text{coat}} = \frac{4RTH_{org}D_{org}R_c}{clR_p} \tag{4}$$

Where R is the ideal gas constant, c is the average gas-phase thermal velocity of N_2O_5, K_H is the unitless Henry's law coefficient for N_2O_5, V and SA are particle volume and surface area density, H_{aq} is the aqueous Henry's law constant for N_2O_5. Following Bertram and Thornton 2009, $K_H = 51$, $\beta = 1.15 \times 10^6 s^{-1}$, $\delta = 0.13\text{M}^{-1}$, $k_3/k_{2b} = 0.06$, $k_4/k_{2b} = 29$. Following McDuffie et al., 2018, $H_{org}\,D_{org} = \varepsilon *H_{aq}\,D_{aq}$ where D_{aq} is the N_2O_5 aqueous-phase diffusion coefficient. ε is a scaling coefficient, which increases linearly with the increase of RH and O:C ratio ($\varepsilon = 0.15$ O:C + 0.0016RH). R_c and R_p are the radii of the inorganic core and the whole particle with organic coating. l is the thickness of organic coating, which is calculated by the volume ratio of organic and inorganic aerosols:

$$l = R_p(1 - \alpha^{\frac{1}{3}}) \tag{5}$$

$$\alpha = \frac{1}{1+\frac{V_{organic}}{V_{inorganic}}} \tag{6}$$

The production yield of $ClNO_2$, φ, was calculated from the mechanism of Bertram and Thornton[2]:

$$\varphi = (\frac{k_2[\text{H}_2\text{O}]}{k_3[\text{Cl}^-]} + 1)^{-1} \tag{7}$$

Where $k_3/k_2 = 450$ from Roberts et al.[7]

Although a similar version of this parameterization has shown agreement with aircraft measurements in the nocturnal residual layer in the winter over the eastern US, it is still very uncertain.[3, 6] The dependence of $\gamma_{N_2O_5}$ and φ on aerosol water, NO_3^-, Cl^-, organics, and other aerosol components have been found to be quite different among different field measurements and laboratory studies.[3, 8]

A source of chlorine radicals is the formation of Cl_2 at night, which goes on to photolyze to Cl atoms in the daytime. In Wang et al.[8], a major source of Cl_2 was the heterogeneous reaction of HOCl with Cl^-:

$$\mathrm{HOCl(aq) + Cl^- + H^+ \rightarrow Cl_2 + H_2O} \qquad \text{(R2)}$$

Here we add a competing reaction between HOCl and dissolved SO_2 ($S(IV) \equiv HSO_3^- + SO_3^{2-}$):

$$\mathrm{HOCl(aq) + HSO_3^- \rightarrow HCl + HSO_4^-} \qquad \text{(R3)}$$

$$\mathrm{HOCl(aq) + SO_3^{2-} \rightarrow HCl + SO_4^{2-}} \qquad \text{(R4)}$$

with reaction rate coefficients $k_3 = 2.8\times10^5\ M^{-1}s^{-1}$ and $k_4 = 7.6\times10^8\ M^{-1}s^{-1}$ from Liu and Abbatt[9] and Fogelman et al.[10], respectively.

We also include in the model the reactive uptake of HCl on natural dust, limited by dust alkalinity. This uptake produces Cl^- on dust and is represented by a first-order uptake (γ) parameterization as described in Fairlie et al.[11] The initial reactive uptake coefficient γ_{HCl} on alkaline dust is 0.13 given by Santschi and Rossi.[12] We include a RH dependence and reduces γ_{HCl} by 100 times to account for the alkalinity availability limited by particle dissolution and diffusion following Fairlie et al.[11]

Table S1. Bimolecular reactions between Cl atom and VOCs included in model scheme.[a,b]

Reaction	*A* (cm^3 colecules^{-1} s^{-1})	*-Ea/R* (K)	Citation
Reactions have been included in previous GEOS-Chem studies [13, 14]			
$\mathrm{Cl + CH_4 \rightarrow HCl + MO2}$	7.10×10^{-12}	-1270	Burkholder et al. (2015)[15]
$\mathrm{Cl + HCOOH \rightarrow HCl + CO_2 + H_2O}$	2.00×10^{-13}	-	Sander et al.(2011)[16]
$\mathrm{Cl + CH_3O_2 \rightarrow ClO + CH_2O + HO_2}$	1.60×10^{-10}	-	Sander et al.(2011)
$\mathrm{Cl + CH_3OOH \rightarrow HCl + CH_3O_2}$	5.70×10^{-11}	-	Sander et al.(2011)
$\mathrm{Cl + C_2H_6 \rightarrow HCl + C_2H_5O_2}$	7.20×10^{-11}	-70	Sander et al.(2011)
$\mathrm{Cl + C_2H_5O_2 \rightarrow ClO + HO_2 + ALD2}$	7.40×10^{-11}	-	Sander et al.(2011)
$\mathrm{Cl + EOH \rightarrow HCl + ALD2}$	9.60×10^{-11}	-	Sander et al.(2011)
$\mathrm{Cl + ACTA \rightarrow HCl + CH_3O_2 + CO_2}$	2.80×10^{-14}	-	Sander et al.(2011)
$\mathrm{Cl + C_3H_8 \rightarrow HCl + A3O2}$	7.85×10^{-11}	-80	Sander et al.(2011)
$\mathrm{Cl + C_3H_8 \rightarrow HCl + B3O2}$	6.54×10^{-11}	-	Sander et al.(2011)
$\mathrm{Cl + ACET \rightarrow HCl + ATO2}$	7.70×10^{-11}	-1000	Sander et al.(2011)
$\mathrm{Cl + ISOP \rightarrow HCl + RIO2}$	7.70×10^{-11}	500	Sander et al.(2011)
$\mathrm{Cl + MOH \rightarrow HCl + CH_2O + HO_2}$	7.70×10^{-11}	500	Sander et al.(2011)
$\mathrm{Cl + ALK4 \rightarrow HCl + R4O2}$	2.05×10^{-10}	-	Atkinson et al. (2006)[17]
$\mathrm{Cl + PRPE \rightarrow HCl + PO2}$	3.60×10^{-12}	-	Atkinson et al. (2006)
New added in this work			
$\mathrm{Cl + TOLU \rightarrow HCl + TRO2}$	6.20×10^{-12}	-	Wang et al. (2005)[18]
$\mathrm{Cl + MTPA \rightarrow HCl + PIO2}$	5.30×10^{-10}	-	Timerghazin and Ariya (2001)[19]
$\mathrm{Cl + LIMO \rightarrow HCl + LIMO2}$	6.40×10^{-10}	-	Finlayson-Pitts et al. (1999)[20]
$\mathrm{Cl + MEK \rightarrow HCl + KO2}$	3.05×10^{-11}	80	Atkinson et al. (2006)

[a] Reactions are given in the Arrhenius form with the rate equal to $A \cdot exp(\frac{-Ea}{RT})$. Unknown values are represented by a dash and set to 0 in the model.

[b] MO2: Methylperoxy radical; ALD2: Acetaldehyde; EOH: Ethanol; A3O2: Primary RO_2 from C_3H_8; B3O2: Secondary RO_2 from C_3H_8; ACET: Acetone; ACTA: Acetic acid; ISOP: Isoprene; RIO2: RO_2 from isoprene; MOH: Methanol; ALK4: ≥C4 alkanes; R4O2: RO_2 from ≥C4 alkanes; PRPE: Propene; PO2: RO_2 from propene; TOLU: Toluene; TRO2: Peroxy radical from toluene oxidation; MTPA: Monoterpenes; PIO2: RO_2 from Monoterpenes; LIMO: Limonene; LIMO2: RO_2 from limonene; MEK: Methyl ethyl ketone; KO2: RO_2 from > C3 ketones.

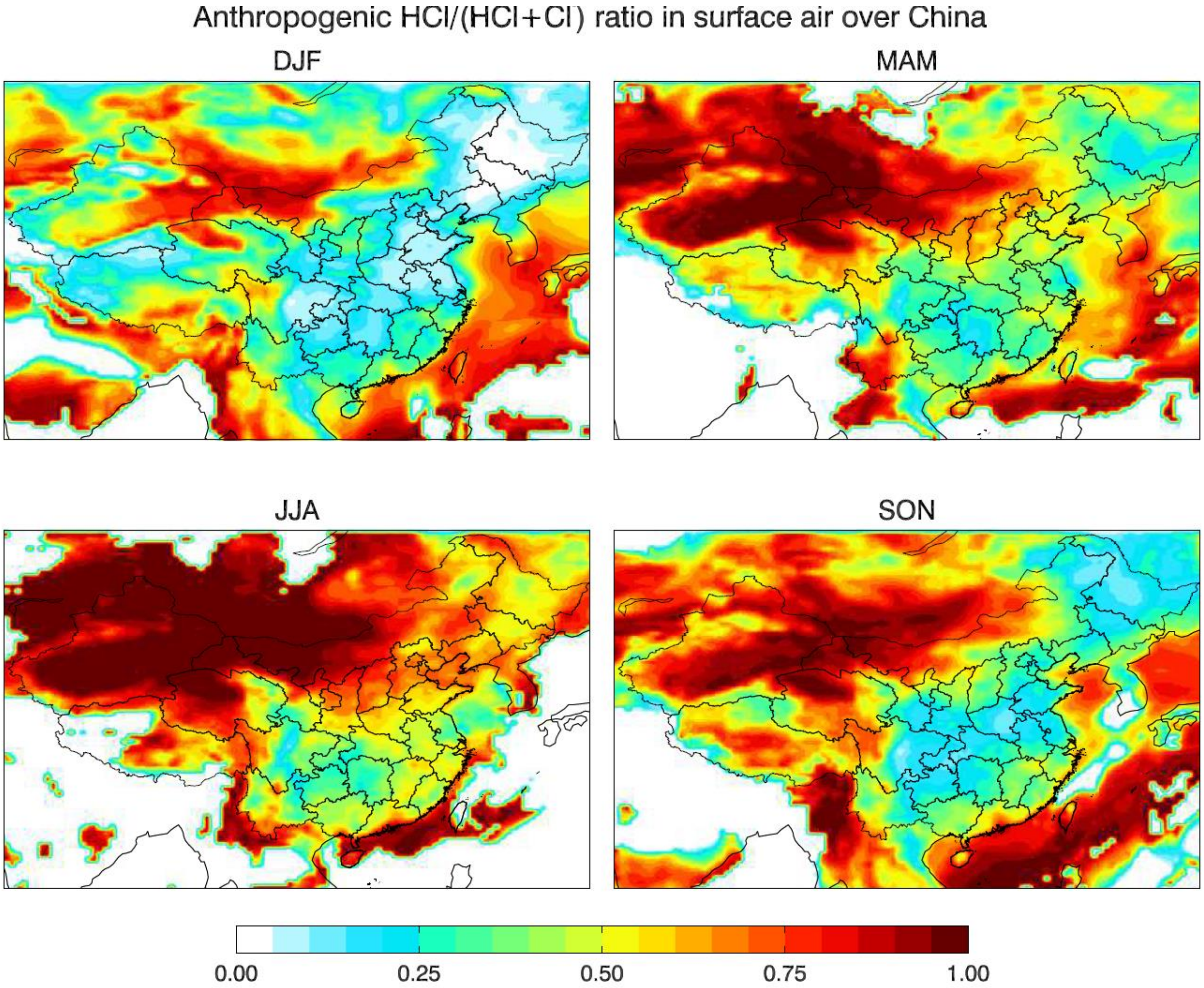

Figure S1. Seasonal mean HCl/(HCl + $PM_{2.5}$ Cl^-) ratio in surface air over China in GEOS-Chem due to anthropogenic emissions of HCl. DJF: December, January, and February (winter), MAM: March, April, and May (Spring), JJA: June, July, and August (Summer), SON: September, October, and November (fall).

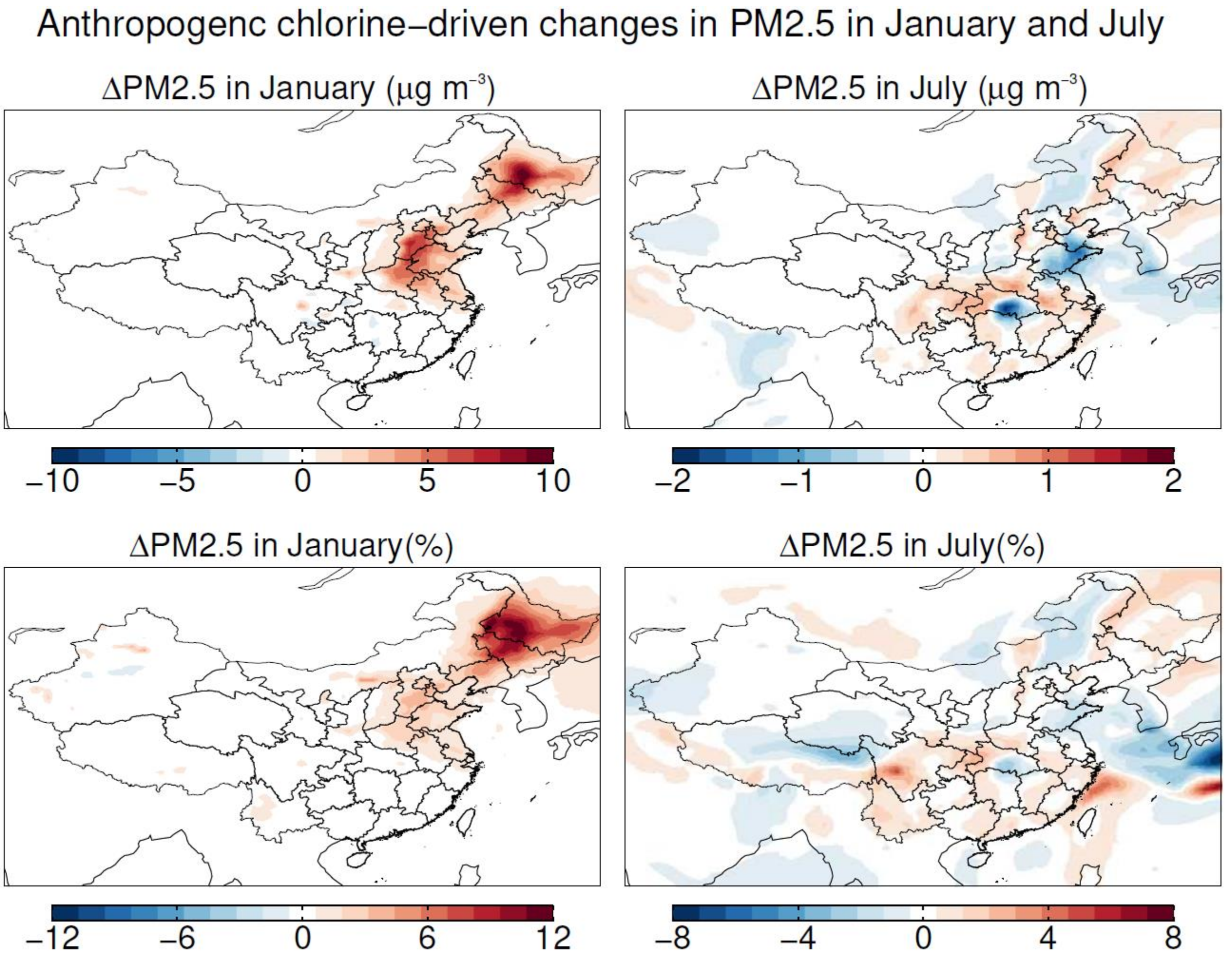

Figure S2. Effects of anthropogenic chlorine emissions on monthly mean surface PM2.5 concentrations in China in January (left) and July (right). Upper panels show absolute effects and lower panels show relative effects.

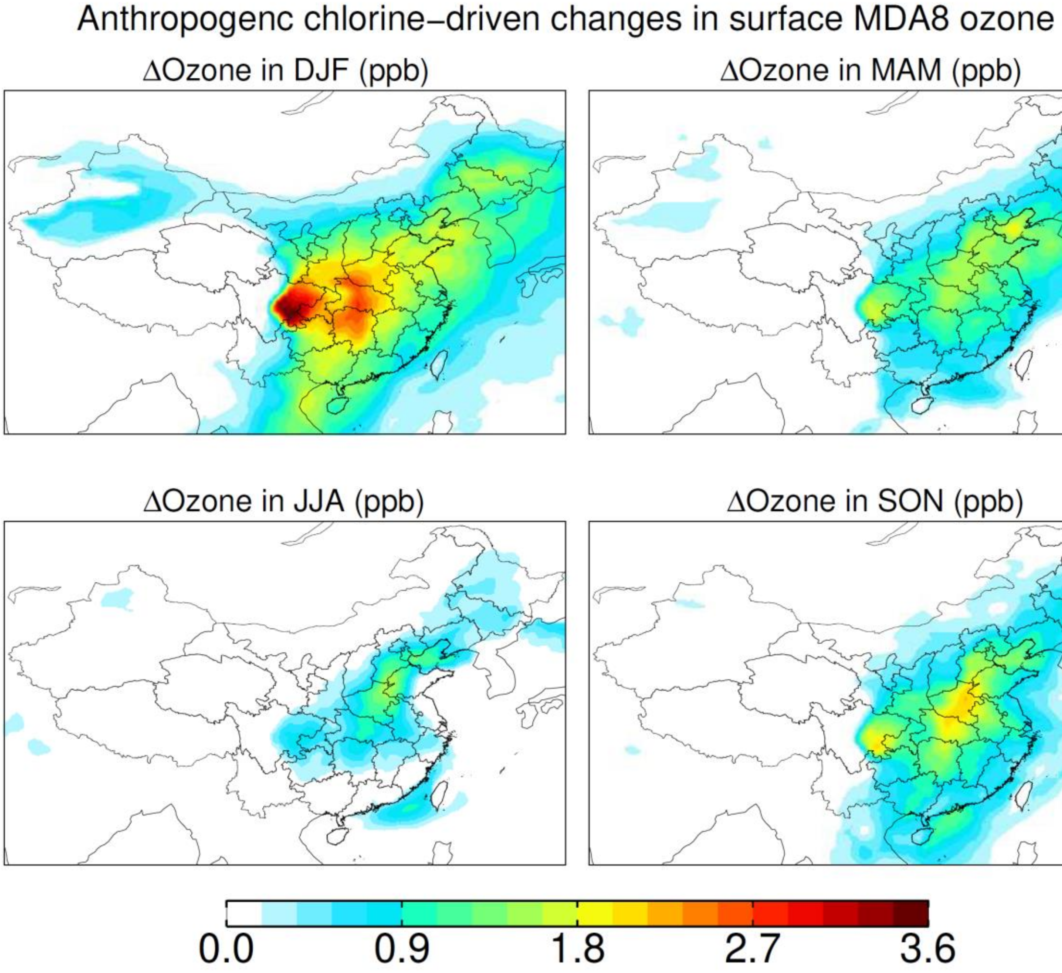

Figure S3. Enhancement of anthropogenic chlorine emissions on seasonal mean surface MDA8 ozone mixing ratios in China. DJF: December, January, and February (winter), MAM: March, April, and May (Spring), JJA: June, July, and August (Summer), SON: September, October, and November (fall).

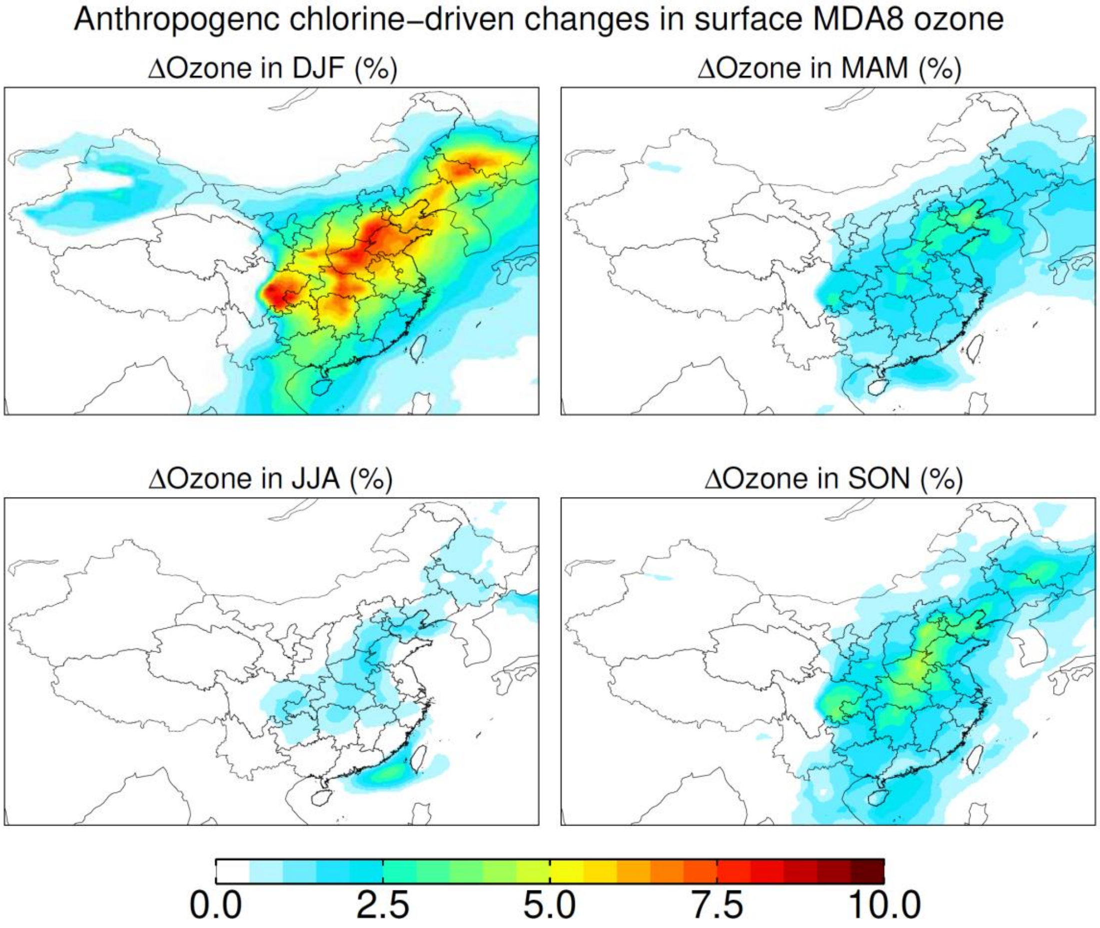

Figure S4. Same as Figure S3 but shows the relative enhancement instead of absolute enhancement.

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