Supplement of

The impact of chlorine chemistry combined with heterogeneous \( \text{N}_2\text{O}_5 \) reactions on air quality in China

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Table S1. Anthropogenic chlorine emissions from different sectors in China in the model.

| Species | Sectors                          | Emissions Gg Cl a⁻¹ |
|---------|----------------------------------|---------------------|
| HCl     | Power plant                      | 17                  |
|         | Heat plant                        | 2.2                 |
|         | Industry                          | 148                 |
|         | Residential                       | 20                  |
|         | Prescribed waste incineration emissions | 4.4              |
|         | Others                            | 26                  |
|         | Total                             | 218                 |

| Cl₂     | Power plant                      | 0.71                |
|         | Heat plant                        | 0.13                |
|         | Industry                          | 6.2                 |
|         | Residential                       | 0.82                |
|         | Others                            | 1.1                 |
|         | Total                             | 8.9                 |

| Cl⁻     | Residential                       | 169                 |
|         | Industry                          | 102                 |
|         | Power plant                       | 108                 |
|         | Total                             | 379                 |

Table S2. Field measurements of CINO₂ and N₂O₅ from literatures

| Site     | Longitude  | Latitude    | Period                 | Species                     | Reference                  |
|----------|------------|-------------|------------------------|-----------------------------|----------------------------|
| Taizhou  | 120.00° E  | 32.55° N    | May 23 – June 15, 2018 | N₂O₅                        | Li et al. (2020)           |
| Changping| 116.23° E  | 40.22° N    | May 13 – June 23, 2016 | CINO₂                       | Le Breton et al. (2018)    |
| Beijing  | 116.36° E  | 39.97° N    | June 11 – 16, 2017     | CINO₂                       | Zhou et al. (2018)         |
| Wangdu   | 115.20° E  | 38.66° N    | June 20 – July 9, 2014 | CINO₂ and N₂O₅              | Tham et al. (2016)         |
| Mount Tai| 117.10° E  | 36.25° N    | July 24 – August 27, 2014 | CINO₂ and N₂O₅          | Wang et al. (2017)         |
| Mount TaiMoShan | 114.13° E | 22.41° N | November 15 – December 6, 2013 | CINO₂ | Wang et al. (2016) |
Table S3. Normalized mean bias (NMB) and correlation coefficients (r) between observed and simulated aerosol components at different observation sites

| Site       | Case   | SO$_4^{2-}$ | NO$_3^-$ | NH$_4^+$ | Cl$^-$ | OM      |
|------------|--------|-------------|----------|----------|--------|---------|
|            | NMB    | r           | NMB      | r        | NMB    | r       | NMB    | r       |
| Dongying   | Base   | -33%        | 0.89     | -41%     | 0.87   | -40%    | 0.83   | -36%    | 0.68   | 49%    | 0.77   |
|            | McDuffie | -40%       | 0.84     | -40%     | 0.88   | -42%    | 0.88   | -35%    | 0.68   | 49%    | 0.77   |
|            | NoEm   | -40%        | 0.84     | -40%     | 0.86   | -46%    | 0.85   | -89%    | -0.05  | 49%    | 0.77   |
| Guangzhou  | Base   | -8.2%       | 0.19     | 129%     | 0.18   | 65%     | 0.25   | 39%     | 0.71   | 20%    | 0.28   |
|            | McDuffie | -8.4%      | 0.18     | 143%     | 0.16   | 71%     | 0.26   | 56%     | 0.71   | 21%    | 0.27   |
|            | NoEm   | -7.0%       | 0.16     | 141%     | 0.16   | 64%     | 0.23   | -79%    | 0.61   | 22%    | 0.26   |
| Gucheng    | Base   | -43%        | 0.34     | -11%     | 0.72   | -27%    | 0.67   | -4.7%   | 0.40   | -11%   | 0.60   |
|            | McDuffie | -44%      | 0.33     | -12%     | 0.73   | -27%    | 0.67   | -4.0%   | 0.39   | -12%   | 0.60   |
|            | NoEm   | -43%        | 0.33     | -13%     | 0.73   | -41%    | 0.66   | -96%    | 0.10   | -12%   | 0.60   |

Figure S1. Spatial distributions of annual chlorine emissions from (a) sea salt aerosol, (b) CH$_3$Cl, (c) CH$_2$Cl$_2$ and (d) CHCl$_3$. 
Figure S2. Spatial distribution of observation sites. Locations of the Northeast Plain (NP), North China Plain (NCP), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Sichuan Basin (SCB) are highlighted by red rectangles.
Figure S3. Annual mean $\gamma_{\text{N}_2\text{O}_5}$ for different simulation cases over China in 2018.
Figure S4. Annual mean $\phi_{\text{CINO}_2}$ for different simulation cases over China in 2018. The values of $\phi_{\text{CINO}_2}$ for the NoHet and NoChem cases are zero and not shown here.
Figure S5. Annual mean ratios of ClNO$_2$ to HNO$_3$ for different simulation cases over China in 2018. Ratios of ClNO$_2$ to HNO$_3$ for the NoHet and NoChem cases are zero and not shown here.

Figure S6. Annual mean correlation coefficients ($r$) between observed and simulated (a) MDA8 O$_3$ and (b) PM$_{2.5}$ over China in 2018.
Figure S7. Effects of chlorine chemistry on annual mean surface concentrations of (a) HO₂, (b) OH, (c) NO₃⁻, (d) NH₄⁺ and (e) SO₄²⁻ in China, estimated as the differences between the Base and NoChem cases.
Figure S8. Effects of the heterogeneous N\textsubscript{2}O\textsubscript{5} + Cl chemistry on annual mean surface concentrations of (a) NO\textsubscript{3}\textsuperscript{-}, (b) NH\textsubscript{4}\textsuperscript{+} and (c) SO\textsubscript{4}\textsuperscript{2-} in China, estimated as the differences between the Base and NoHet cases.

Figure S9. Effects of the heterogeneous N\textsubscript{2}O\textsubscript{5} + Cl chemistry on annual mean ratio of (a) NO\textsubscript{x} to NO\textsubscript{y} and (b) NO\textsubscript{3} to NO\textsubscript{x} in China, estimated as the differences between the Base and NoHet cases. Note that here NO\textsubscript{x} = NO + NO\textsubscript{2} + ClNO\textsubscript{2} and NO\textsubscript{3} = NO + NO\textsubscript{2} + CINO\textsubscript{2} + HNO\textsubscript{3} + 2 X N\textsubscript{2}O\textsubscript{5} + NO\textsubscript{3} + HONO + HNO\textsubscript{4} + NO\textsubscript{y} + various organic nitrates.
Figure S10. Impacts of chlorine chemistry other than the heterogeneous $\text{N}_2\text{O}_5 + \text{Cl}$ chemistry on annual surface mean surface concentrations of MDA8 O$_3$ in China, estimated as the differences between the NoHet and NoChem cases.

Figure S11. Effects of anthropogenic and biomass burning chlorine emissions on annual mean surface concentrations of (a) $\text{NH}_4^+$ and (b) $\text{SO}_2^-$ in China, estimated as the differences between the Base and NoEm cases.
Figure S12. Effects of anthropogenic and biomass burning chlorine emissions without the heterogeneous \( \text{N}_2\text{O}_5 + \text{Cl} \) chemistry on annual mean surface concentrations of (a) Cl atoms and (b) MDA8 \( \text{O}_3 \) in China, estimated as the differences between the NoHet and NoEmHet cases.

Figure S13. Effects of the heterogeneous \( \text{N}_2\text{O}_5 + \text{Cl} \) chemistry without anthropogenic and biomass burning chlorine emissions on annual mean surface concentrations of (a) nighttime max ClNO\(_2\) and (b) MDA8 \( \text{O}_3 \) in China, estimated as the differences between the NoEm and NoEmHet cases.
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