



Supplement of

The impact of chlorine chemistry combined with heterogeneous N_2O_5 reactions on air quality in China

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а .	9	Emissions	
Species	Sectors	Gg Cl a ⁻¹	
HCI	Power plant	17	
	Heat plant	2.2	
	Industry	148	
	Residential	20	
	Prescribed waste incineration emissions	4.4	
	Others	26	
	Total	218	
Cl ₂	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 S1. Anthropogenic chlorine emissions from different sectors in China in the model.

Table S2. Field measurements of ClNO₂ and N_2O_5 from literatures

Site	Longitude	Latitude	Period	Species	Reference
Taizhou	120.00° E	32.55° N	May 23 – June 15, 2018	N_2O_5	Li et al. (2020)
Changping	116.23° E	40.22° N	May 13 – June 23, 2016	CINO ₂	Le Breton et al. (2018)
Beijing	116.36° E	39.97° N	June 11 – 16, 2017	ClNO ₂	Zhou et al. (2018)
Wangdu	115.20° E	38.66° N	June 20 – July 9, 2014	ClNO ₂ and N ₂ O ₅	Tham et al. (2016)
Mount Tai	117.10° E	36.25° N	July 24 – August 27, 2014	ClNO ₂ and N ₂ O ₅	Wang et al. (2017)
Mount TaiMoShan	114.13° E	22.41° N	November 15 – December 6, 2013	CINO ₂	Wang et al. (2016)

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Site	Case -	SO 4 ²⁻		NO ₃ -		$\mathrm{NH_{4^+}}$		Cl-		OM	
		NMB	r	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

 Table S3. Normalized mean bias (NMB) and correlation coefficients (r) between observed and simulated aerosol components at different observation sites



Figure S1. Spatial distributions of annual chlorine emissions from (a) sea salt aerosol, (b) CH₃Cl, (c) CH₂Cl₂ and (d) CHCl₃.



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 γ_{N205} for different simulation cases over China in 2018.



Figure S4. Annual mean φ_{CINO2} for different simulation cases over China in 2018. The values of φ_{CINO2} for the NoHet and NoChem cases are zero and not shown here.



Figure S5. Annual mean ratios of ClNO₂ to HNO₃ for different simulation cases over China in 2018. Ratios of ClNO₂ to HNO₃ 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 O₃ 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 N₂O₅ + Cl chemistry on annual mean surface concentrations of (a) NO₃⁻, (b) NH₄⁺ and (c) SO₄²⁻ in China, estimated as the differences between the Base and NoHet cases.



Figure S9. Effects of the heterogeneous N₂O₅ + Cl chemistry on annual mean ratio of (a) NO_x to NO_y and (b) NO₃⁻ to NO_y in China, estimated as the differences between the Base and NoHet cases. Note that here NO_x = NO + NO₂ + ClNO₂ and NO_y = NO + NO₂ + ClNO₂ + HNO₃ + 2×N₂O₅ + NO₃ + HONO + HNO₄ + NO₃⁻ + various organic nitrates.



Figure S10. Impacts of chlorine chemistry other than the heterogeneous N₂O₅ + Cl chemistry on annual surface mean surface concentrations of MDA8 O₃ 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) NH4⁺ and (b) SO4²⁻ 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
 N₂O₅ + Cl chemistry on annual mean surface concentrations of (a) Cl atoms and (b) MDA8 O₃ in China, estimated as the differences between the NoHet and NoEmHet cases



Figure S13. Effects of the heterogeneous N₂O₅ + Cl chemistry without anthropogenic and biomass burning chlorine emissions on annual mean surface concentrations of (a) nighttime max ClNO₂ and (b) MDA8 O₃ in China, estimated as the differences between the NoEm and NoEmHet cases

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