

Regional Heterogeneity in Wintertime Atmospheric Nitrate Formation over China's Marginal Seas: Roles of Halogen Chemistry and Dimethyl Sulfide-Related Processes

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20 **This file includes:**

Sections S1 –S3

Table S1 – S3

Figures S1 – S12

25

30

S1. Chemical reactions contributing to nitrate formation

The CB6r3m_ae7_kmtbr chemical mechanism used in the CMAQ simulations includes multiple reactions contributing to nitrate formation. In this study, ten HNO₃-producing reactions were considered to quantify the contributions of different chemical processes to nitrate formation. These reactions include
35 gas-phase oxidation, heterogeneous hydrolysis, organic nitrate chemistry, DMS oxidation, and halogen nitrate hydrolysis:

OH+NO₂:



hetN₂O₅:



DMS:



hetNTR:



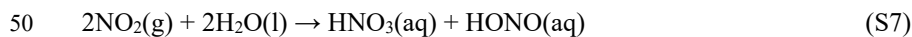
45 GasN₂O₅:



NO₃+HC:



hetNO₂:



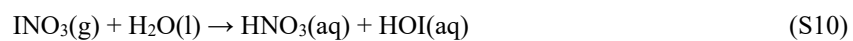
ClNO₃:



BrNO₃:



55 INO₃:



These abbreviations are used throughout the pathway analysis to represent the corresponding HNO_3 production processes. The diagnosed reaction rates were used to quantify the relative contributions of these processes to nitrate formation and to examine their responses to changes in DMS and halogen emissions.

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S2. Model Evaluation

Observations from Qinhuangdao, Tianjin, Qingdao, and Shanghai during December 2019 were used to evaluate the performance of the WRF–CMAQ modeling system. Time series of meteorological variables, including 2-m temperature, relative humidity, 10-m wind speed, and wind direction, are shown in Figure S1. Pollutant concentrations, including MDA8 O₃, NO₂, PM_{2.5}, and particulate NO₃[−], are presented in Figure S2. Summary statistics are provided in Tables S1 and S2.

The model reproduced 2-m temperature well, with mean biases (MB) ranging from −1.09 °C in Tianjin to +1.32 °C in Qingdao and correlation coefficients (R) exceeding 0.80 at all sites. Relative humidity (RH) was slightly underestimated, with the largest bias in Tianjin (MB = −8.1%, RMSE = 18.7%). In the other cities, MB values remained within −5.5%, and correlation coefficients were consistently above 0.70. Wind speed was best reproduced in Qingdao (MB = +0.46 m s^{−1}, R = 0.78), whereas Qinhuangdao showed an overestimation of 1.3 m s^{−1}. Wind direction was less accurately represented, with RMSE values reaching 129° in Qingdao and generally lower correlations; however, MB values remained within ±10° in Tianjin and Qinhuangdao.

For air quality variables, the model captured the temporal variations in MDA8 O₃ reasonably well. Mean biases ranged from +11.6 µg m^{−3} in Qinhuangdao to −5.2 µg m^{−3} in Tianjin, with correlation coefficients of approximately 0.60. NO₂ concentrations were best reproduced in Qingdao and Shanghai, with MB values of approximately +1.2 µg m^{−3} and R values exceeding 0.70. PM_{2.5} was well reproduced in Qingdao (MB = −1.4 µg m^{−3}, R = 0.81), but was overestimated in Tianjin by 21 µg m^{−3}. Particulate nitrate was well simulated in Qingdao (R = 0.95), with normalized mean biases of −8% in Qinhuangdao and −6% in Tianjin and a correlation coefficient of 0.82 in Shanghai.

The overall agreement between simulated and observed PM_{2.5} and particulate nitrate concentrations supports the use of WRF–CMAQ to diagnose nitrate formation mechanisms in China’s coastal regions. Nevertheless, biases in RH and wind fields, particularly wind direction, remain important sources of uncertainty when interpreting the subsequent sensitivity simulations and mechanism analyses.

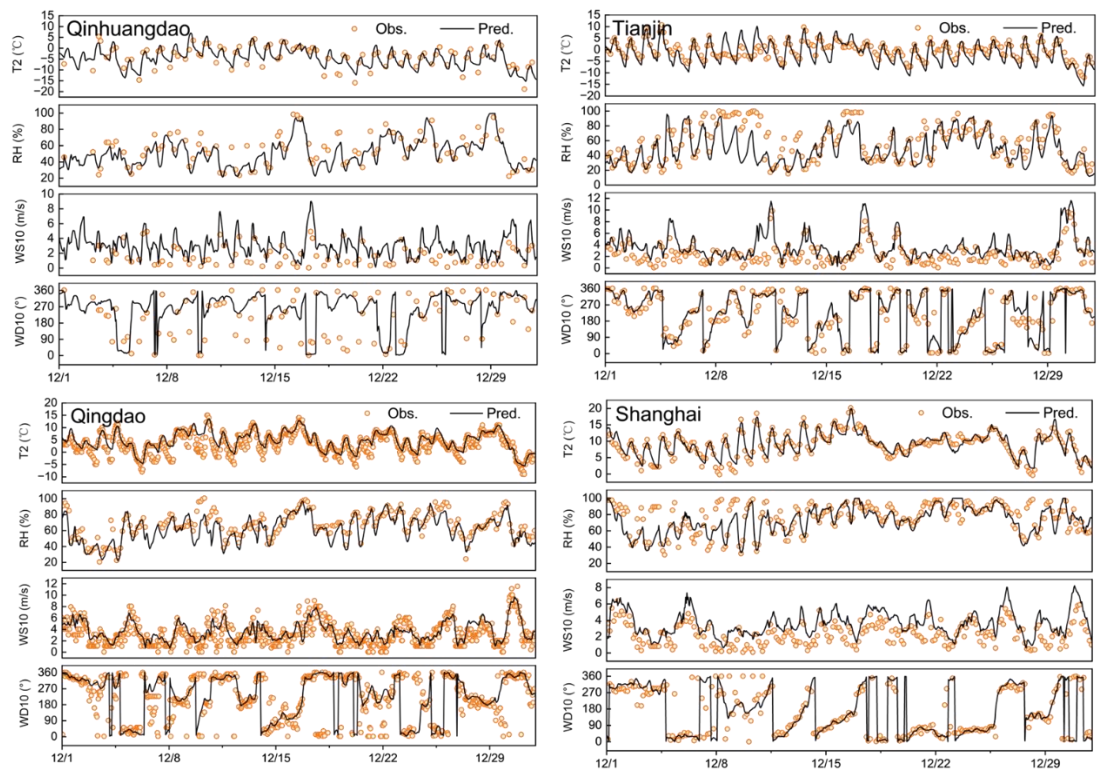


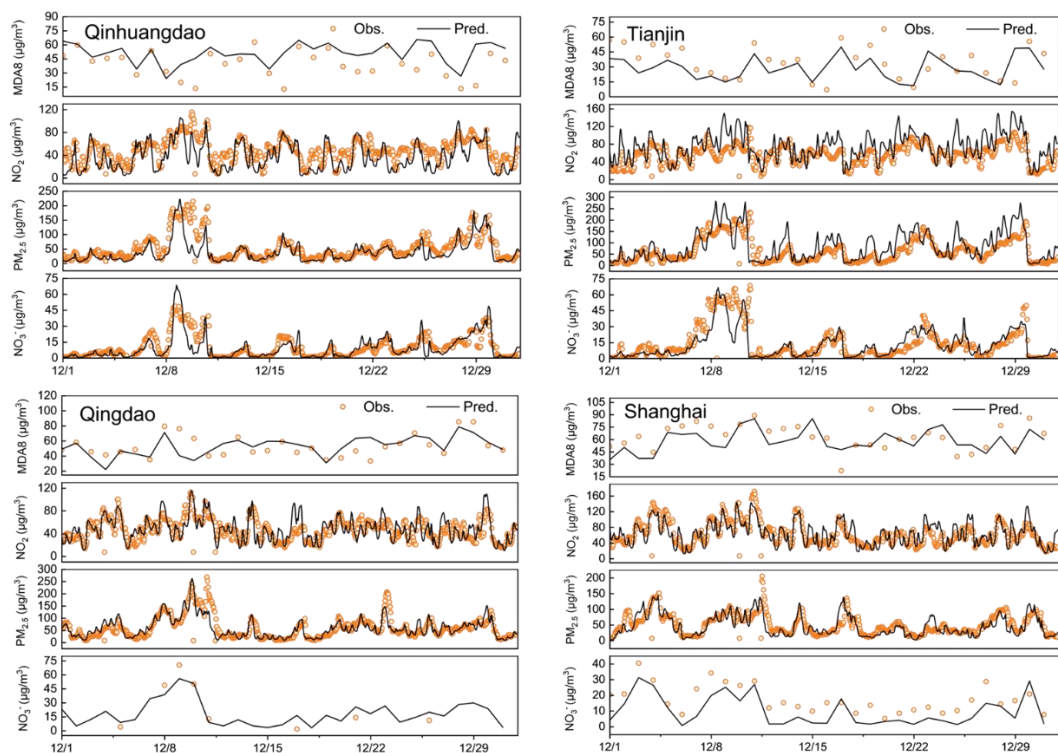
Figure S1. Time series comparison of simulated and observed parameters (T2, RH, WS10, WD10) for the four coastal cities of Qinhuangdao, Tianjin, Qingdao, and Shanghai in December 2019.

Table S1. Evaluation of WRF model performance for meteorological parameters (temperature, relative humidity, wind speed, wind direction) in four major coastal cities of China during December 2019.

Parameters	City	MB	RMSE	IOA	R
T2 (°C)	Qinhuangdao	-0.44	2.85	0.89	0.81
	Tianjin	-1.09	2.83	0.88	0.84
	Qingdao	1.32	2.39	0.91	0.88
	Shanghai	0.23	1.45	0.96	0.94
		$\leq \pm 0.5$	/	$\geq \pm 0.8$	/
RH (%)	Qinhuangdao	-5.85	11.43	0.89	0.86
	Tianjin	-8.12	18.73	0.82	0.75
	Qingdao	-5.41	11.04	0.88	0.83
	Shanghai	-3.49	12.68	0.84	0.73
		/	/	/	/
WS10 (m/s)	Qinhuangdao	1.28	1.91	0.52	0.56
	Tianjin	1.17	1.80	0.78	0.78
	Qingdao	0.46	1.36	0.86	0.78
	Shanghai	1.33	1.62	0.66	0.79
		$\leq \pm 0.5$	$\leq \pm 2.0$	≥ 0.6	/
WD10 (°)	Qinhuangdao	32.76	107.61	0.73	0.57
	Tianjin	2.74	62.14	0.93	0.86
	Qingdao	8.23	128.81	0.70	0.42
	Shanghai	5.59	112.61	0.78	0.58
		$\leq \pm 10$	/	/	/

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140 **Figure S2.** Time series comparison of simulated and observed pollutants (MDA8 O₃, NO₂, PM_{2.5}, NO₃⁻) for the four
 145 coastal cities of Qinhuangdao, Tianjin, Qingdao, and Shanghai in December 2019.

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Table S2. Evaluation of CMAQ model performance for pollutant simulations in the four coastal cities of Qinhuangdao, Tianjin, Qingdao, and Shanghai in December 2019.

City	Pollutants ($\mu\text{g}/\text{m}^3$)	NMB	NME	MB	R
Qinhuangdao	MDA8 O ₃	29%	33%	11.56	0.58
	NO ₂	-25%	35%	-11.96	0.73
	PM _{2.5}	-27%	39%	-14.01	0.74
	NO ₃ ⁻	-8%	45%	-0.81	0.77
Tianjin	MDA8 O ₃	-15%	32%	-5.18	0.61
	NO ₂	33%	39%	18.25	0.72
	PM _{2.5}	34%	58%	21.48	0.71
	NO ₃ ⁻	-6%	44%	-0.74	0.76
Qingdao	MDA8 O ₃	-4%	17%	-1.97	0.54
	NO ₂	3%	24%	1.26	0.74
	PM _{2.5}	-2%	29%	-1.43	0.81
	NO ₃ ⁻	5%	33%	1.44	0.95
Shanghai	MDA8 O ₃	-7%	18%	-4.29	0.59
	NO ₂	2%	25%	1.22	0.77
	PM _{2.5}	-8%	32%	-4.18	0.76
	NO ₃ ⁻	-43%	47%	-7.44	0.82
Benchmark	MDA8 O ₃	$\leq \pm 15\%$	$< 25\%$	/	> 0.50
	NO ₂	$\leq \pm 30\%$	$\leq 75\%$	/	/
	PM _{2.5}	$\leq \pm 30\%$	$< 50\%$	/	> 0.40
	NO ₃ ⁻	$\leq \pm 60\%$	$< 75\%$	/	> 0.60

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Table S3. Global halocarbon fluxes from literature and emission factors used in this study.

Species	Ord3n3ez et al.	WMO low	WMO high	Low Emission	High Emission
	(2012)	(Gg/yr)	(Gg/yr)	Factor	Factor
	(Gg/yr)				
CHBr ₃	533	126	865	0.24	1.62
CH ₂ Br ₂	67.3	62	109	0.92	1.62
CH ₃ I	303	176	615	0.58	2.03
CH ₂ BrCl	10.0	6.48	9.72	0.65	1
CHBr ₂ Cl	19.7	19.6	56.1	1	2.85
CHBrCl ₂	22.6	16.4	22.6	0.73	1
CH ₂ ICl	234	--	--	0.58	2.03
CH ₂ IBr	87.3	--	--	0.58	2.03
CH ₂ I ₂	116	--	--	0.58	2.03
[Tg/yr]		.Macdonald et	Chance et al.		
		al. (2014)	(2014)		
HOI		1.99	4.16	1	2.09
I ₂		0.08	0.34	1	4.25

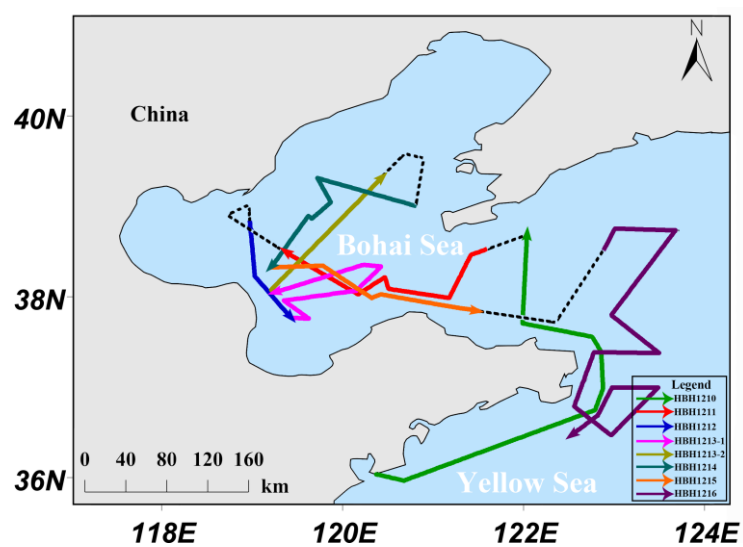


Figure S3. Trajectory for samples collected in the Yellow Sea and Bohai Sea cruise in December 2019.

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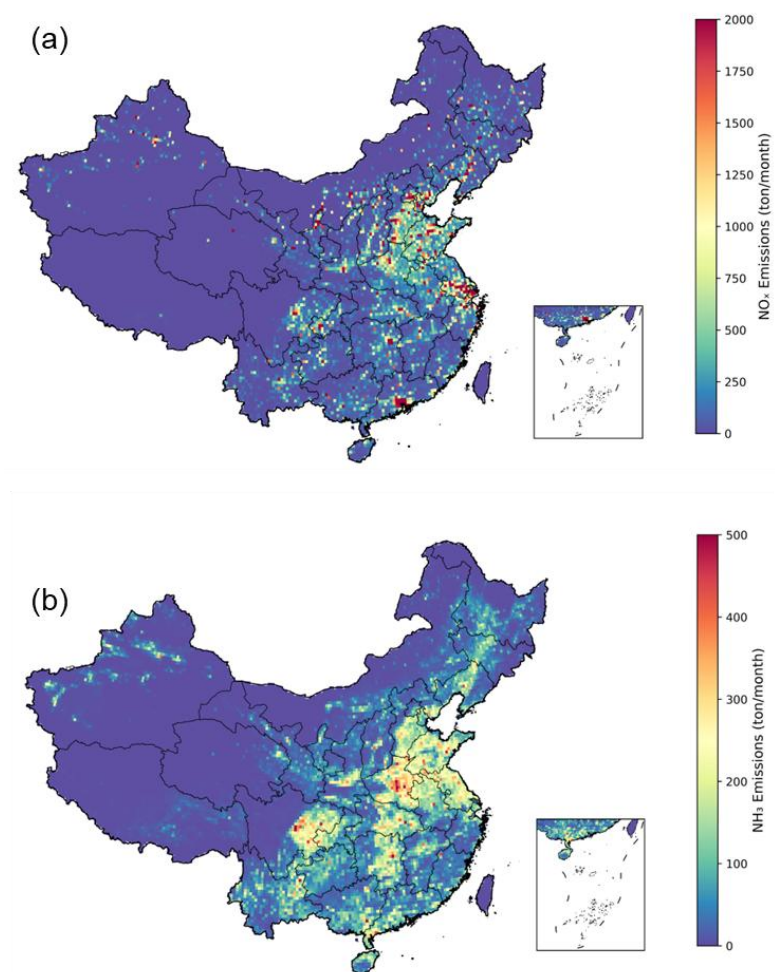


Figure S4. Spatial distribution of MEIC emissions in December 2019, showing (a) NO_x emissions and (b) NH₃ emissions.

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S3. Evaluation of Simulated Nitrate Formation Pathways Using Isotope Constraints

To further evaluate the reliability of the simulated nitrate formation pathways, the modeled pathway contributions were compared with cruise-based nitrate-isotope constraints over the Bohai and Yellow Seas. As shown in Figure S5, the model generally reproduced the dominant role of heterogeneous N_2O_5 hydrolysis in the northern marginal seas, although systematic discrepancies remained. The model tended to underestimate the contribution of $\text{OH} + \text{NO}_2$ oxidation and overestimate that of heterogeneous N_2O_5 hydrolysis. For example, in sample HBH1210, the $\text{OH} + \text{NO}_2$ pathway was underestimated by 19.1%, whereas heterogeneous N_2O_5 hydrolysis was overestimated by 36.2%. A larger discrepancy was found for HBH1212, where $\text{OH} + \text{NO}_2$ oxidation was underestimated by 47.1% and heterogeneous N_2O_5 hydrolysis was overestimated by 45.0%.

The model also underestimated the NO_3 -initiated hydrocarbon oxidation pathway, with an average difference of 9.3% between the isotope-constrained estimates and the simulations. These discrepancies may be associated with uncertainties in nocturnal chemistry, meteorological inputs, aerosol liquid water content, and the simplified representation of VOC reactivity toward NO_3 radicals. Overall, this comparison indicates that the model reproduced the broad dominance of nighttime heterogeneous nitrate formation but may overrepresent N_2O_5 hydrolysis and underrepresent VOC-related nighttime oxidation processes.

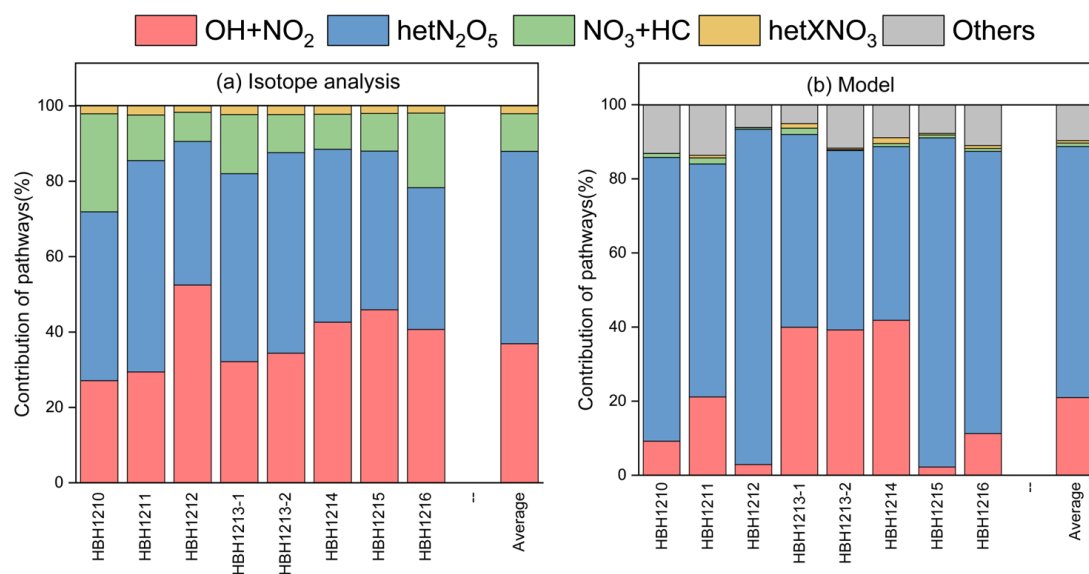


Figure S5. Comparison of nitrate formation pathway contributions from cruise-based isotopic observations (a) and model simulations (b).

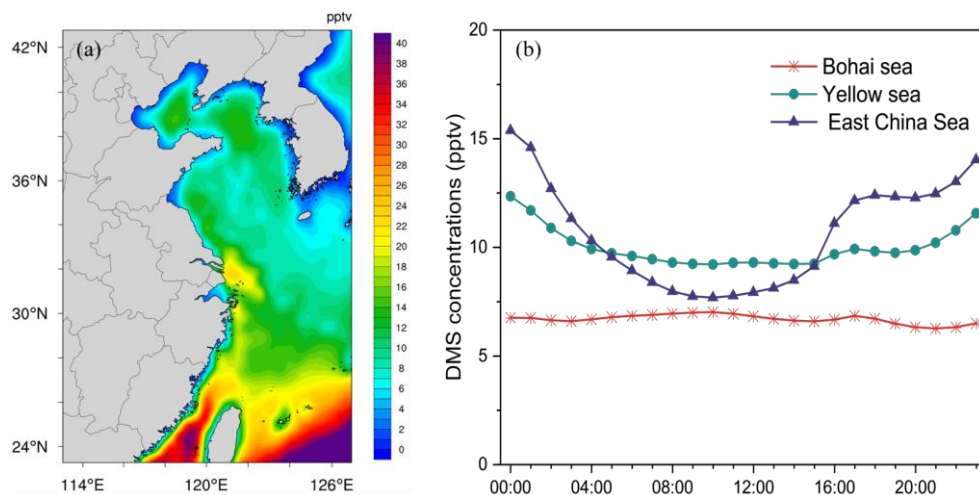


Figure S6. Spatial distribution of atmospheric DMS concentration over China's coastal seas (a) and diurnal variation of DMS concentration in different sea regions (b)

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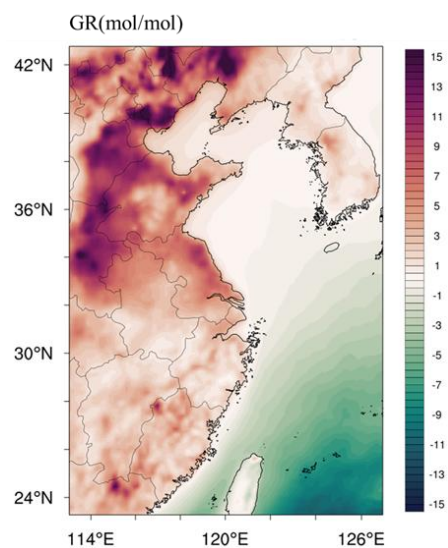
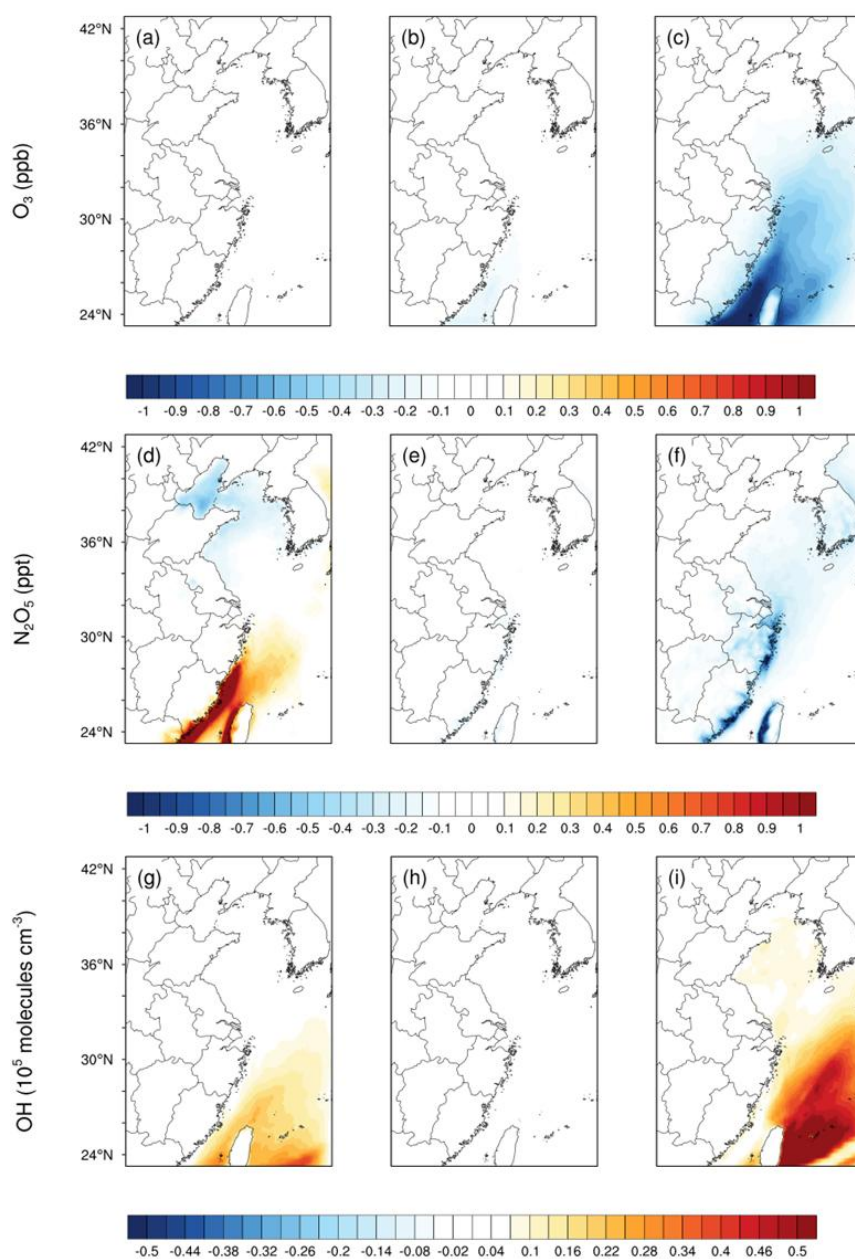


Figure S7. Spatial distribution of the gas ratio (GR) over China's coastal regions in December 2019. GR was used as an indicator of NH_3 availability, with $\text{GR} > 1$, $0 < \text{GR} < 1$, and $\text{GR} < 0$ representing NH_3 -rich, NH_3 -neutral, and NH_3 -poor conditions, respectively.

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280 **Figure S8.** Changes in the concentrations of (a–c) O_3 , (d–f) N_2O_5 , and (g–i) OH radicals in China's coastal regions under different halogen emission coefficients. From left to right, columns represent the low-, medium-, and high-emission scenarios, respectively.

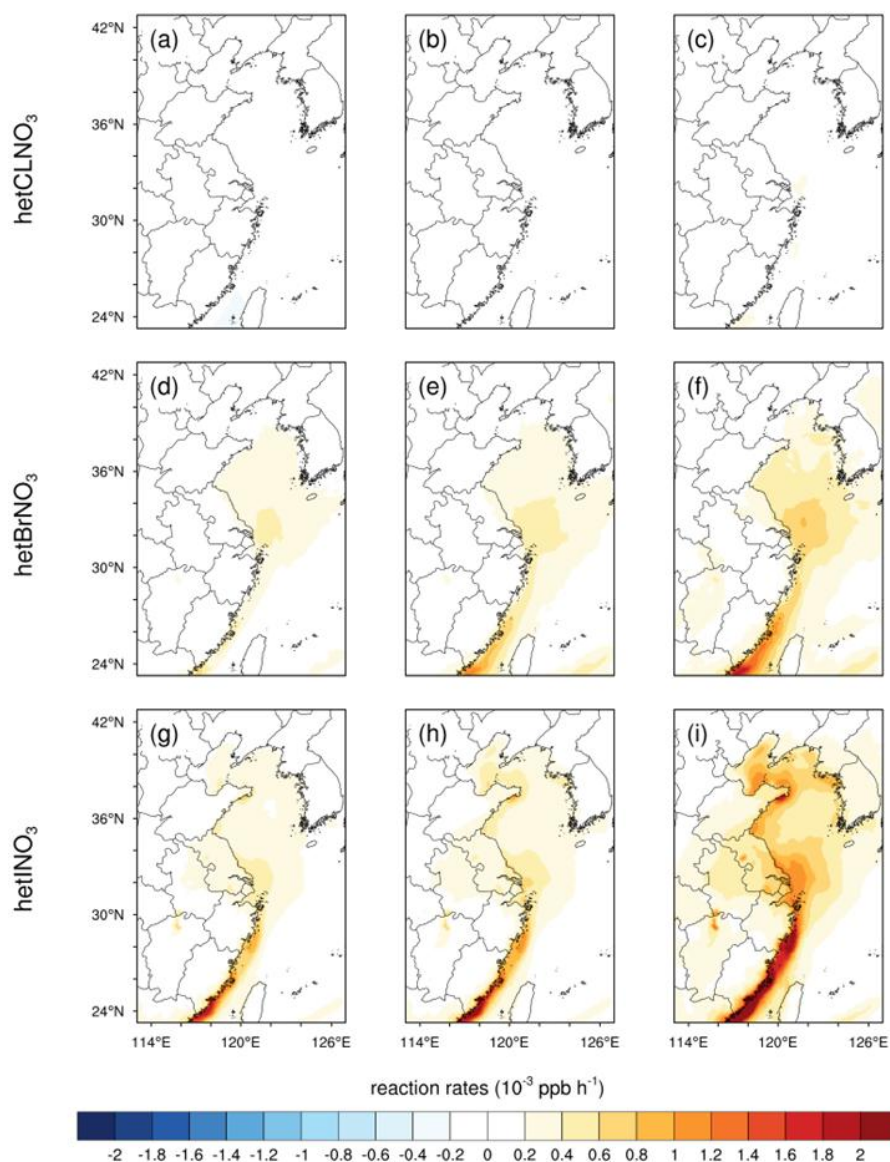


Figure S9. Variations in (a–c) hetCLNO_3 , (d–f) hetBrNO_3 , and (g–i) hetINO_3 reaction rates in China's coastal regions under different halogen emission factors in December 2019. From left to right, columns represent the low-, medium-, and high-emission scenarios, respectively.

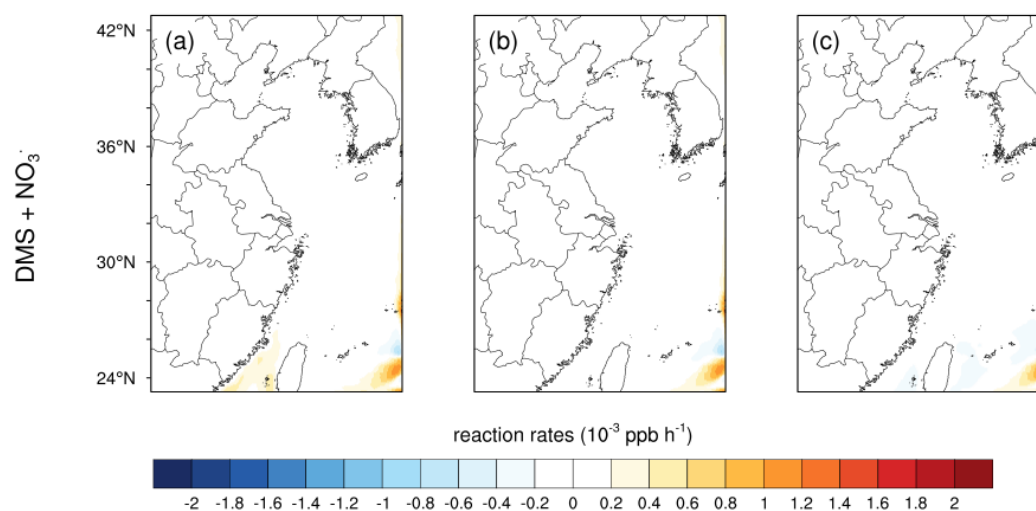


Figure S10. Variations in HNO_3 formation rates through the DMS pathway in China's coastal regions under different halogen emission scenarios in December 2019. From left to right, panels (a–c) represent the low-, medium-, and high-emission scenarios, respectively.

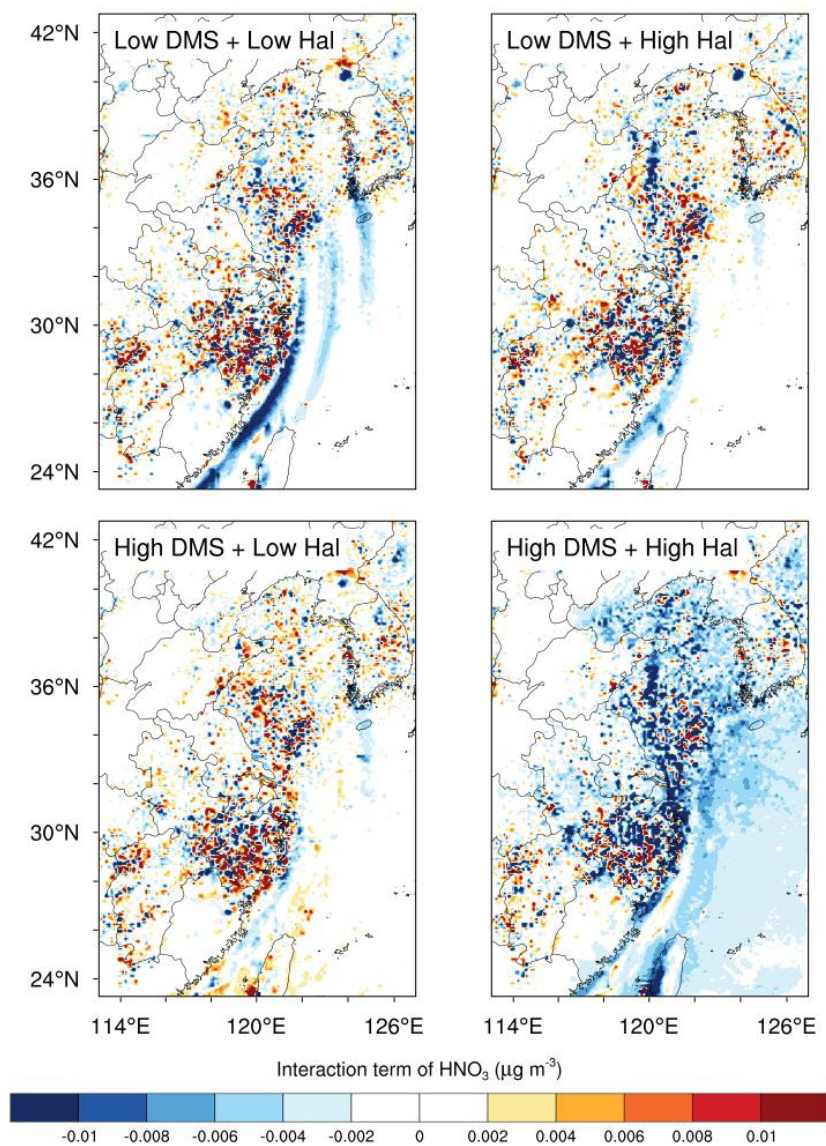


Figure S11. Spatial distribution of the interaction term for HNO_3 under combined DMS and halogen emission scenarios over eastern China. Panels show the low-DMS/low-halogen, low-DMS/high-halogen, high-DMS/low-halogen, and high-DMS/high-halogen cases, respectively.

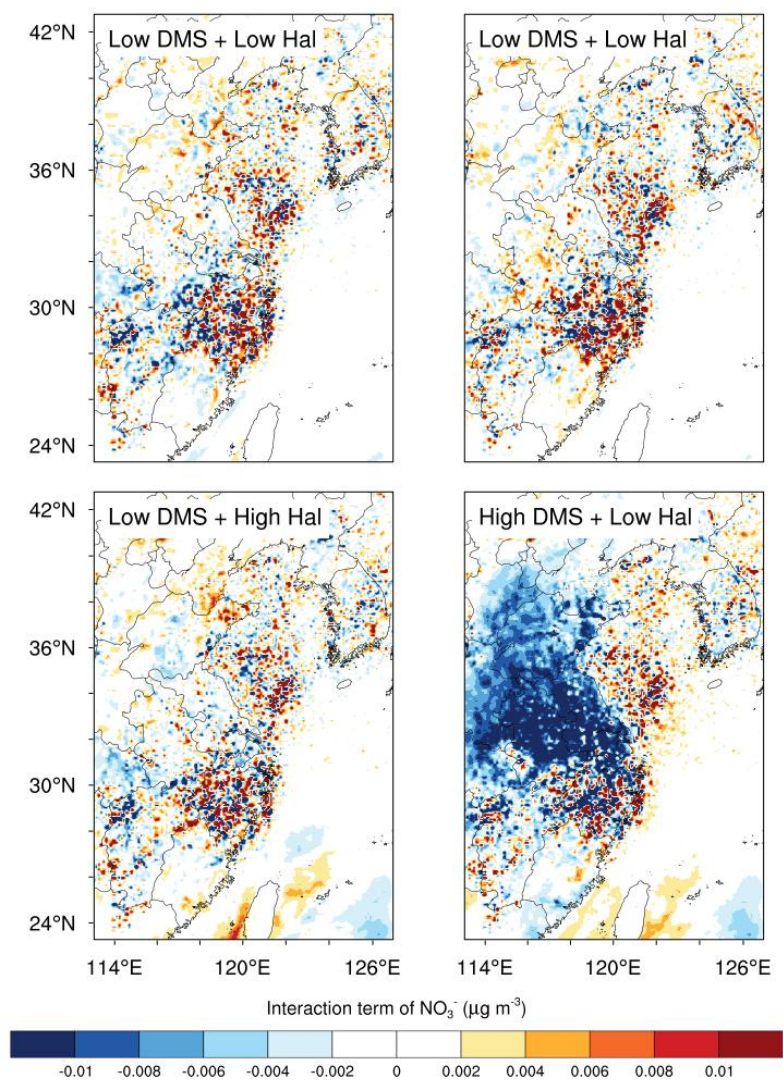


Figure S12. Spatial distribution of the interaction term for particulate nitrate (NO_3^-) under combined DMS and halogen emission scenarios over eastern China. Panels show the low-DMS/low-halogen, low-DMS/high-halogen, high-DMS/low-halogen, and high-DMS/high-halogen cases, respectively.

Reference

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