



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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15 **Abstract.** Continental outflow interacts with marine sulfur and halogen emissions over China's marginal seas, yet their effects on nitrate formation remain poorly understood. Here, WRF–CMAQ sensitivity simulations, evaluated against shipborne observations and nitrate isotope evidence, were used to investigate wintertime nitrate formation and the roles of dimethyl sulfide (DMS) and halogen chemistry. Nitrate formation exhibited pronounced regional differences. Heterogeneous N₂O₅ hydrolysis dominated
20 over the Bohai and Yellow Seas (59.8% and 59.3%, respectively), but contributed only 38.1% over the East China Sea, where OH + NO₂ oxidation accounted for 32.1%. The DMS + NO₃ oxidation pathway contributed up to 4.8% of nitrate production, while DMS emission changes produced modest particulate nitrate enhancements (0.01–0.02 μg m⁻³). In contrast, halogen perturbations induced stronger, spatially heterogeneous and nonmonotonic responses, with local HNO₃ increases of 0.4–0.8 μg m⁻³. The combined
25 effects of DMS and halogen chemistry were largely additive, with substantial negative interactions occurring only when both emissions were enhanced. These findings highlight the regional diversity of nitrate formation pathways and the importance of marine sulfur and halogen chemistry in regulating coastal nitrate pollution.



30 1 Introduction

Since the preindustrial era, global industrialization and urbanization have increased atmospheric nitrogen emissions and deposition by nearly an order of magnitude (Galloway et al., 2004), fundamentally altering ocean productivity patterns and trophic structure (Kim et al., 2014). In the marine atmosphere, deposited nitrogen is dominated by inorganic species, with nitrate accounting for approximately half of total
35 nitrogen deposition in both polluted (Cornell et al., 2003; Russell et al., 1998) and remote marine regions (Duce et al., 2008; Galloway et al., 1989). As a major reservoir of reactive nitrogen, particulate nitrate contributes to aerosol formation and evolution (Alexander et al., 2020; Altieri et al., 2013) and serves as an important source of bioavailable nitrogen to the ocean through dry and wet deposition (Duce et al., 2008; Galloway et al., 1989; Cornell et al., 2003; Russell et al., 1998), with consequences for nutrient
40 stoichiometry (Luo et al., 2016), primary productivity (Itahashi et al., 2016; Alexander et al., 2009), and the marine carbon–nitrogen cycle (Duce et al., 2008; Kim et al., 2014). These effects are particularly important in continental–marine transition zones, where anthropogenic outflow mixes with marine emissions and introduces chemical interactions that differ fundamentally from those over either land or open oceans. China’s marginal seas represent such a transition zone, receiving substantial land-derived
45 nitrogen inputs while also being influenced by marine halogen and sulfur emissions. Yet the processes governing nitrate formation in these chemically complex environments remain incompletely understood, limiting our ability to accurately simulate coastal air quality and atmospheric nitrogen deposition.

Under typical atmospheric conditions, atmospheric nitrate is generally produced through daytime oxidation of NO_2 by OH and nighttime heterogeneous hydrolysis of N_2O_5 (Alexander et al., 2009).
50 However, in marine and coastal environments, these conventional pathways can be substantially altered by sea-derived chemical processes. Marine halogen chemistry, involving reactive chlorine, bromine, and iodine species from sea salt, perturbs atmospheric oxidants including O_3 , OH, NO_3 radicals, and N_2O_5 , thereby influencing both gas-phase HNO_3 production and heterogeneous nitrate formation (Alexander et al., 2009; Saiz-Lopez et al., 2012). Active halogens can deplete as much as ~20% of tropospheric O_3
55 over remote oceans (Saiz-Lopez et al., 2012; Sherwen et al., 2016), while heterogeneous reactions on sea-salt particles in polluted coastal regions can release reactive halogen species and modify near-surface O_3 and particulate matter (Saiz-Lopez et al., 2012; Sarwar et al., 2012; Sarwar et al., 2014; Finley and Saltzman, 2008). Modeling and field studies have further shown that chlorine activation and the



production of molecular halogens, including Cl_2 , Br_2 , and I_2 , can substantially affect atmospheric oxidizing capacity and coastal air quality (Sarwar et al., 2012; Sarwar et al., 2014; Finley and Saltzman, 2008). Collectively, these findings indicate that halogen chemistry may reshape nitrate formation in coastal transition zones. This influence is expected to be particularly important over China's marginal seas, where anthropogenic NO_x emissions coincide with abundant sea-salt-derived halogens. However, its quantitative effects on nitrate formation pathways in this region remain poorly constrained.

Besides reactive halogens, marine-emitted dimethyl sulfide (DMS) represents another important marine precursor capable of modifying coastal nitrate chemistry. Although DMS is widely recognized as a precursor of non-sea-salt sulfate aerosol (Chen et al., 2024; Stefels et al., 2007), it can also react with oxidants, including OH, NO_3 , and BrO, to form sulfate and participate in nitrate-related chemistry through NO_3 -initiated oxidation pathways (Boucher et al., 2003; Breider et al., 2010; Carter et al., 2021; Stark et al., 2007). These reactions can modify aerosol acidity and hygroscopicity, thereby affecting the gas–particle partitioning of HNO_3 (Karydis et al., 2021; Nenes et al., 2021). Reactive halogens can additionally scavenge NO_3 radicals, particularly at night, potentially suppressing or delaying DMS-related nitrate formation (Parker and Mitch, 2016). Conversely, sulfate aerosol formed from DMS oxidation can provide acidic surfaces that facilitate halogen nitrate hydrolysis, establishing a mechanistic link between marine sulfur oxidation and halogen chemistry (Tie et al., 2003). A modeling study over coastal Los Angeles suggested that jointly considering marine halogen chemistry and DMS emissions reduced HNO_3 and HO_x , highlighting coupled effects on nitrate formation and atmospheric oxidizing capacity (Muñiz-Unamunzaga et al., 2018). Nevertheless, most previous studies have focused on either the sulfate-forming role of DMS or the independent effects of halogen chemistry (Stark et al., 2007; Fung et al., 2022; Zhao et al., 2022). The nonlinear coupling between DMS-related processes and marine halogen chemistry, as well as its impact on nitrate formation in East Asian continental–marine transition regions, remains poorly constrained.

Here, we employed the WRF-CMAQ regional chemical transport model, constrained by nitrate-isotope evidence, to investigate wintertime nitrate formation over China's marginal seas. Through a suite of sensitivity simulations, we quantified region-specific nitrate formation pathways, evaluated the separate roles of marine halogen chemistry and DMS-related processes, and tested whether their combined effects can be represented by linear superposition. By explicitly diagnosing nonadditive DMS–halogen interactions, this study reveals how marine sulfur–halogen coupling regulates coastal nitrate



chemistry. These findings advance the understanding of nitrate formation in continental–marine
 90 transition zones and provide a stronger basis for simulating coastal PM_{2.5} pollution and atmospheric
 nitrogen deposition.

2 Materials and methods

2.1 Model configuration

Within the CMAQ modeling framework, the Integrated Reaction Rate (IRR) module in the Process
 95 Analysis (PA) tool was used to diagnose the formation reactions of total nitrate ($\text{TNO}_3 = \text{HNO}_3 + \text{NO}_3^-$)
 for December 2019. The HNO_3 -producing reactions included in the CB6r3m_ac7_kmtbr mechanism and
 used for nitrate formation pathway analysis are summarized in Section S1. Meteorological fields were
 generated using WRF v3.8, configured with the same physical parameterizations as in our previous
 studies (Wang et al., 2019; Sarwar et al., 2015), and driven by 6-hourly $1^\circ \times 1^\circ$ NCEP-FNL reanalysis
 100 data. Two one-way nested domains were used (Fig. 1): D01, with a horizontal resolution of $36 \text{ km} \times 36$
 km, covered China and neighboring regions of South and East Asia, while D02, with a horizontal
 resolution of $12 \text{ km} \times 12 \text{ km}$, focused on China's coastal seas. The model was vertically resolved into 14
 layers extending from the surface to the upper troposphere, with the first model layer centered at
 approximately 31 m above ground level. WRF outputs were processed using MCIP v4.3 to provide
 105 meteorological inputs for CMAQ.

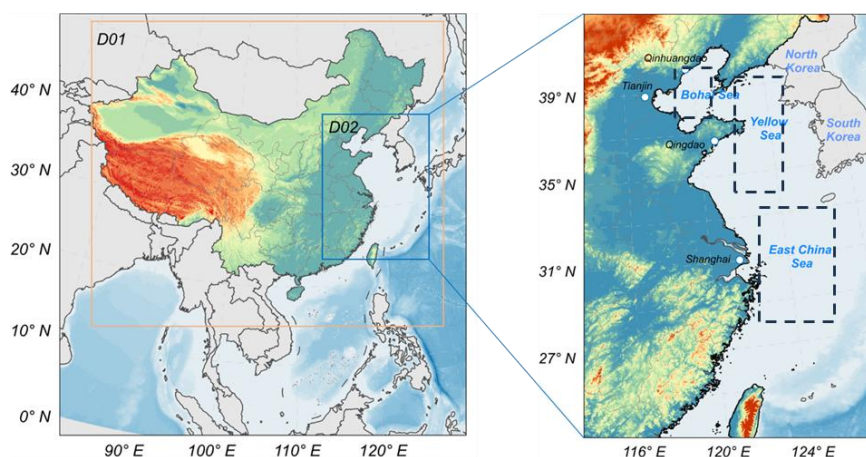


Figure 1. Schematic diagram of the model simulation domains. The outer CMAQ domain (D01) covers China and parts of South and East Asia, whereas the nested domain (D02) focuses on China's coastal seas and adjacent coastal regions. White dots indicate four coastal cities selected as representative sites for China's coastal areas.



110 Air quality simulations were conducted using CMAQ v5.3.3 with the cb06r3m_ae7_kmtbr gas-
phase chemical mechanism and the AERO7 aerosol module. The cb06r3m_ae7_kmtbr mechanism
combines the CB6R3 mechanism with online halogen chemistry. Compared with the standard CB06
mechanism, cb06r3m_ae7_kmtbr explicitly represents chlorine-, bromine-, and iodine-related reactions
and their effects on O₃, HO_x, NO_x, N₂O₅, and halogen nitrate formation. This capability is particularly
115 important for coastal and marine environments, where sea-salt-derived halogens and inorganic iodine
emissions can substantially perturb oxidant levels and nitrate formation pathways. Anthropogenic
emissions over mainland China were obtained from the MEIC inventory (<http://meicmodel.org/>),
whereas emissions for the rest of Asia were obtained from the MIX regional inventory
(<https://www.meicmodel.org/dataset-mix>). Ship emissions were taken from the SEIM dataset
120 (<https://seims.zju.edu.cn/>). Biogenic emissions were calculated using MEGAN v2.0.4
(<http://lar.wsu.edu/megan/>). Because halogen species and DMS are not included in the MEIC inventory,
inorganic halogen emissions were generated online in CMAQ, and the ocean input file was supplemented
with sea-surface DMS from the 0.5° × 0.5° Asian climatology (Zhao et al., 2022) and chlorophyll-a from
the 4 km MODIS-Aqua Level-3 dataset (<https://oceandata.sci.gsfc.nasa.gov/l3/>). Initial and lateral
125 boundary conditions for D01 were derived from a global GEOS-Chem simulation, and boundary
conditions for D02 were provided by the D01 simulation. To minimize the influence of initial conditions,
a 7-day spin-up period was applied before the 1–31 December analysis period.

This unified modeling configuration allowed us to quantify the individual and combined effects of
marine halogen chemistry and DMS-related processes on nitrate aerosol chemistry over China's coastal
130 seas and adjacent coastal regions.

2.2 Marine Halogen and DMS Emissions

Marine halogen emissions were grouped into three categories: sea-salt aerosol (SSA; primarily
containing Cl and Br), inorganic iodine species such as I₂ and HOI, and halocarbon compounds, including
CHBr₃, CH₂Br₂, CH₂BrCl, CHBr₂Cl, CHBrCl₂, CH₃I, CH₂ICl, CH₂I₂, and CH₂I₂ (Sarwar et al., 2019;
135 Carpenter et al., 2013; Ordóñez et al., 2012; Wang et al., 2019). Halocarbons are produced primarily by
marine phytoplankton and macroalgae, with elevated concentrations typically observed in biologically
active ocean regions (Sarwar et al., 2015). These emissions can be simulated online in CMAQ v5.3.3.

The SSA emission scheme in CMAQ uses the improved parameterization proposed by Gantt et al.



(2015), which refines the original source function developed by Gong (2003). The main improvements include incorporation of a sea-surface temperature (SST) correction factor to account for SST-dependent SSA fluxes and adjustment of the source-function shape factor to better represent submicron SSA emissions. Emissions of inorganic iodine and halocarbons were incorporated into CMAQ by Sarwar et al. (2019). Specifically, the inorganic iodine parameterization for I₂ and HOI follows Carpenter et al. (2013) and relates their fluxes to ozone, aqueous iodine, and surface wind speed, whereas halocarbon emissions are estimated using the chlorophyll-a-based approach of Ordóñez et al. (2012). In this study, multiple simulation scenarios were designed to evaluate the effects of DMS and halogen emissions on atmospheric chemical processes. The detailed configuration of each scenario is summarized in Table 1.

Table 1. Simulation scenarios for DMS and halogen emissions

Scenario ID	Scenario	DMS Emission	Halogen Emission
S0	DMS_0_Hal_0 (Blank)	×	×
S1	DMS_medium_Hal_medium (Base)	medium	Medium
S2	DMS_0_Hal_high	×	high
S3	DMS_0_Hal_low	×	low
S4	DMS_high_Hal_0	high	×
S5	DMS_medium_Hal_0	medium	×
S6	DMS_low_Hal_0	low	×
S7	DMS_low_Hal_high	low	high
S8	DMS_low_Hal_low	low	low
S9	DMS_medium_Hal_high	medium	high
S10	DMS_medium_Hal_low	medium	low
S11	DMS_high_Hal_high	high	high
S12	DMS_high_Hal_low	high	low

* DMS emissions were prescribed at four levels: 0 (excluded), 0.5 (low), 1 (medium, derived from *in situ* sea surface water DMS concentrations using CMAQ's online oceanic flux module with SST and chlorophyll-*a*), and 2 (high). Halogen emissions were set at three levels (low, medium, high), as described in Section 2.2 and Tables S2-S3.

In the base scenario (DMS_medium_Hal_medium), DMS emissions were prescribed at the reference level (scaling level = 1) and derived from *in situ* sea-surface DMS concentrations using CMAQ's online oceanic flux module constrained by SST and chlorophyll-*a*. Halogen emissions were



155 also set to the medium level. Specifically, SSA emissions were calculated using the source function developed by Gantt et al. (2015). Inorganic iodine species, including I_2 and HOI, were assigned an emission scaling factor of 1 following Sarwar et al. (2019) and halocarbon compounds were assigned a scaling factor of 1 based on the method proposed by Ordóñez et al. (2012).

In the high-halogen scenario (Hal_high), SSA emissions were still calculated using the scheme of
160 Gantt et al. (2015), whereas the emission scaling factors for both inorganic iodine species and halocarbons were increased. Conversely, in the low-halogen scenario (Hal_low), SSA emissions were calculated using the original source function of Gong (2003) and lower scaling factors were applied to both inorganic iodine species and halocarbons. The scaling factors for inorganic iodine species, including I_2 and HOI, were determined based on the estimates reported by Macdonald et al. (2014) and Chance et
165 al. (2014). Under the Hal_high scenario, the scaling factors for HOI and I_2 were 2.09 and 4.25, respectively, whereas both factors were set to 1 under the Hal_low scenario. The scaling factors for halocarbons and inorganic iodine species were calculated from the ratios of global annual fluxes and are summarized in Table S3.

The high-emission scenarios were designed as upper-bound sensitivity experiments rather than as
170 representations of spatially uniform ambient conditions. The high-DMS case doubled the climatology-constrained base emission, whereas the high-halogen case applied literature-based upper scaling factors to marine iodine and halocarbon emissions. These scenarios were used to explore whether nitrate responses remain additive when both marine sulfur and halogen influences are simultaneously enhanced and to characterize the potential upper-bound chemical response to uncertainties in marine emission
175 estimates.

3 Results and discussion

3.1 Spatial Heterogeneity in Nitrate Concentrations and Formation Pathways across Marine Regions

3.1.1 Spatial Distribution of Nitrate Concentrations across Marine Regions

180 Model performance for meteorological variables and major pollutants is summarized in Section S2, Figures S1–S2, and Tables S1–S2. Model evaluation against shipborne observations further demonstrated that the simulation captured the spatial variability of marine nitrate concentrations ($R = 0.97$; Figure 2a). The mean bias (MB), normalized mean bias (NMB), and normalized mean error (NME) were $0.64 \mu\text{g}$



185 m^{-3} , 7%, and 41%, respectively, indicating that the model generally captured the spatial variability of
 marine nitrate concentrations, despite appreciable errors at individual sampling locations. The simulated
 monthly mean nitrate concentrations showed a clear regional gradient over China's coastal seas (Figure
 2b). Mean nitrate concentrations in the Bohai Sea ($15.80 \pm 17.41 \mu\text{g m}^{-3}$) were approximately twice those
 in the Yellow Sea ($7.71 \pm 11.14 \mu\text{g m}^{-3}$) and over twenty times those in the East China Sea (0.64 ± 2.09
 190 $\mu\text{g m}^{-3}$). This spatial pattern is consistent with previous observations showing a similar decline in nitrate
 concentrations from the Bohai Sea to the southern Yellow Sea, largely attributed to the decreasing
 influence of continental pollution (Zhao et al., 2024).

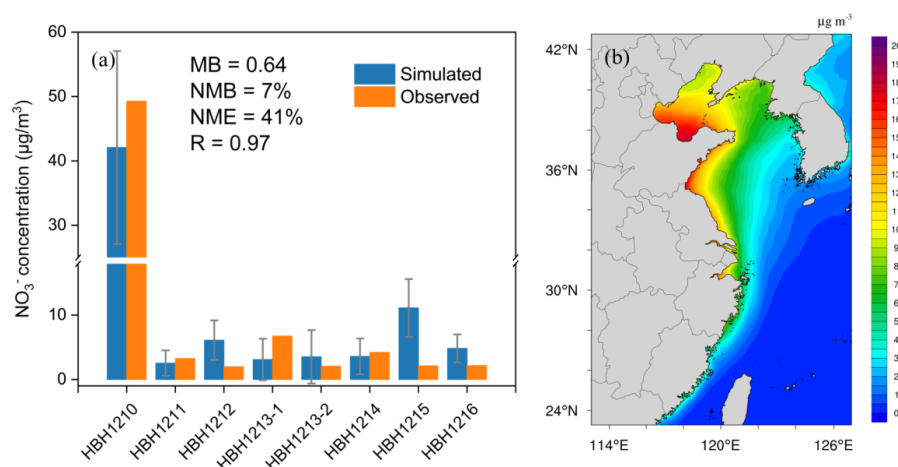


Figure 2. (a) Comparison of observed and simulated nitrate concentrations along the cruise track. (b) Spatial distribution of simulated monthly mean atmospheric nitrate concentrations over China's coastal seas.

195 The spatial heterogeneity in nitrate concentrations likely reflects differences in precursor emissions,
 regional transport, and meteorological conditions. High nitrate concentrations over the Bohai Sea were
 consistent with the spatial distribution of NO_x emissions (Figure S4), particularly the intense emissions
 from the Beijing–Tianjin–Hebei region. The relatively enclosed setting of the Bohai Sea may further
 enhance the influence of nearby continental emissions (Zhao et al., 2024). The Yellow Sea exhibited
 200 intermediate nitrate concentrations, reflecting the combined influence of continental outflow from
 northern China and marine air masses (Cha et al., 2020; Zhao et al., 2024). In contrast, the greater
 influence of relatively clean marine air over the East China Sea reduced the impact of continental
 pollution and suppressed nitrate accumulation (Zhang et al., 2011). Seasonal variations in meteorological
 conditions and air mass origins further influenced the regional distribution of nitrate (Zhang et al., 2011;



205 Zhang et al., 2015). Taken together, this pronounced regional gradient indicates a transition from anthropogenic precursor control over nitrate abundance in the Bohai Sea to progressively stronger modulation by marine air masses and ocean-derived sulfur and halogen chemistry over the Yellow and East China Seas. This transition establishes distinct chemical regimes of nitrate formation, which are examined in the following sections.

210 3.1.2 Spatial Variability in Reaction Rates and Relative Contributions of Nitrate Formation Pathways

Nitrate formation exhibited a pronounced north-to-south transition across China's coastal seas (Figure 3). In the Bohai and Yellow Seas, heterogeneous N_2O_5 hydrolysis accounted for approximately 60% of nitrate production and, together with $\text{OH} + \text{NO}_2$ oxidation, contributed nearly 90% of the total.

215 Other pathways were individually minor, with the combined contributions of $\text{DMS} + \text{NO}_3$ oxidation and halogen nitrate chemistry remaining below 4% over the Yellow Sea. The dominance of N_2O_5 hydrolysis may be favored by nighttime conditions over northern coastal China, including abundant aerosol liquid water, high relative humidity, and elevated NO_x and O_3 levels. Consistent with this finding, nitrate dual-isotope analysis in coastal Tianjin attributed approximately 68.6% of wintertime nitrate formation to

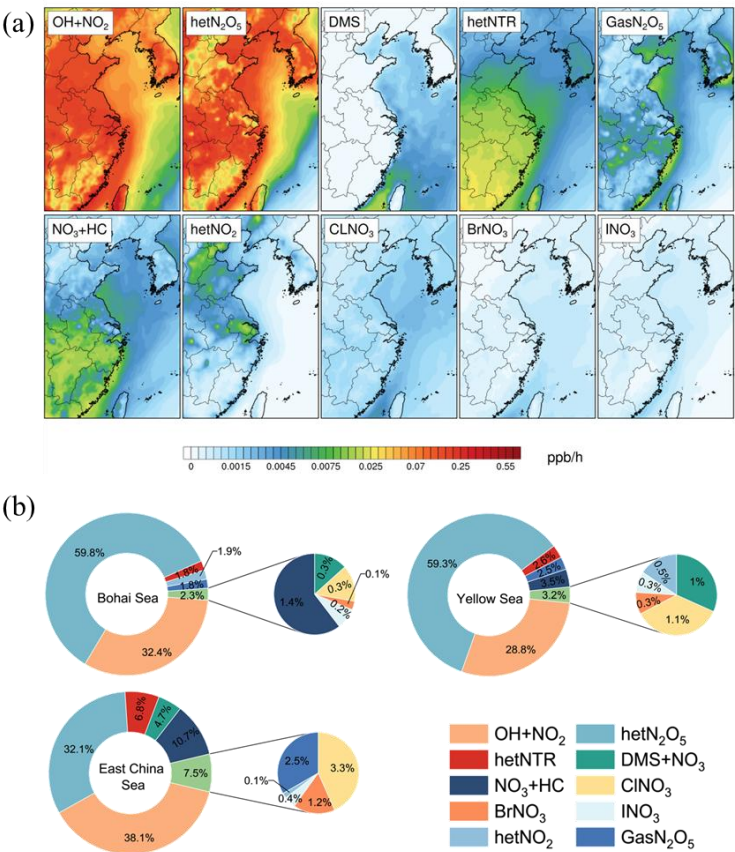
220 heterogeneous N_2O_5 hydrolysis (Zhang et al., 2022). Earlier observations over the Yellow and East China Seas also revealed strong continental influences on atmospheric nitrogen species, particularly during the winter monsoon (Zhang et al., 2011). The dependence of N_2O_5 uptake on aerosol liquid water, nitrate loading, and chloride content may partly explain regional differences in the importance of heterogeneous N_2O_5 hydrolysis (Bertram and Thornton, 2009).

225 In contrast, nitrate formation over the East China Sea involved a more diverse range of chemical pathways. Heterogeneous N_2O_5 hydrolysis remained the largest contributor (38.1%), followed by $\text{OH} + \text{NO}_2$ oxidation (32.1%). Other pathways, including NO_3 oxidation of hydrocarbons, organic nitrate hydrolysis, $\text{DMS} + \text{NO}_3$ oxidation, and reactions involving halogen species, also contributed to nitrate production. Compared with northern coastal regions, the relative contribution of N_2O_5 hydrolysis

230 decreased, while daytime oxidation and alternative formation pathways became more important. This spatial variation may reflect differences in NO_x concentrations, atmospheric oxidants, and air mass characteristics across coastal and marine environments. Similar variations in atmospheric nitrogen chemistry have been reported in previous field studies. Zhai et al. (2023) found that $\text{OH} + \text{NO}_2$ oxidation



dominated nitrate formation under clean conditions in the Yangtze River Delta, whereas heterogeneous
235 N_2O_5 hydrolysis became more important during polluted periods. Wang et al. (2024) further showed that
nighttime NO_3 chemistry over the South China Sea varied with air mass origin, highlighting the influence
of regional transport and chemical conditions on nighttime oxidation processes. Together, these findings
suggest that the relative importance of nitrate formation pathways depends strongly on regional
atmospheric conditions.



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Figure 3. Monthly mean nitrate formation pathways in December 2019: (a) spatially distribution of reaction rates and (b) relative contributions of individual pathways across marine regions.

Beyond the two conventional nitrate formation pathways, marine-specific oxidation chemistry
became increasingly important toward the East China Sea. The DMS + NO_3 oxidation pathway remained
245 negligible ($<1\%$) north of 35°N but increased to 4.8% in the East China Sea, consistent with isotope-
based estimates that attributed approximately 6–6.5% of particulate nitrate to nocturnal DMS + NO_3



radical reactions (Carter et al., 2021). Although halogen pathways contributed less than 5% overall, their relative importance increased by nearly an order of magnitude from the Bohai Sea to the East China Sea, indicating that marine halogen chemistry becomes increasingly competitive under clean and better-ventilated conditions. These results indicate that, although OH + NO₂ oxidation and N₂O₅ hydrolysis remain the dominant nitrate formation pathways, DMS-related reactions and halogen nitrate formation can make regionally important contributions in specific marine environments. These quantitative estimates provide a basis for evaluating the extent to which marine sulfur and halogen chemistry modulate nitrate formation across China's coastal seas.

To assess whether the simulated pathway differences were consistent with observational constraints, we further compared the modeled pathway apportionment with nitrate isotope estimates derived from cruise observations over the Bohai and Yellow Seas (Section S3; Figure S5). The comparison generally supports the model finding that heterogeneous N₂O₅ hydrolysis dominated nitrate formation in the northern marginal seas. Despite the overall agreement, the model tended to overestimate heterogeneous N₂O₅ hydrolysis while underestimating OH + NO₂ oxidation and NO₃-initiated hydrocarbon oxidation. The overestimation of heterogeneous N₂O₅ hydrolysis likely reflects uncertainties in the representation of aerosol liquid water and heterogeneous uptake under highly polluted conditions (Zhai et al., 2023). The underestimation of hydrocarbon oxidation by NO₃ radicals may result from the simplified representation of VOC composition and reactions between NO₃ radicals and individual hydrocarbon species in the chemical mechanism (Nguyen et al., 2015). These uncertainties, together with the increasing importance of marine sulfur and halogen chemistry toward the East China Sea, highlight the need to further quantify the influence of these marine processes on regional nitrate formation.

3.2 Quantifying the Roles of Halogen Chemistry and DMS-Related Processes in Wintertime Nitrate Formation

3.2.1 Contribution of DMS-Related Processes to Wintertime Nitrate Formation

Modeled atmospheric DMS concentrations exhibited a pronounced offshore gradient under the baseline simulation (Figure S6a), consistent with the spatial distribution of marine productivity and biological activity. The East China Sea showed the highest DMS levels, likely reflecting the influence of the Kuroshio Current, whereas the semi-enclosed Bohai Sea exhibited relatively weak diurnal variability. In contrast, the Yellow Sea showed a pronounced diurnal cycle, mainly driven by daytime oxidation by



OH radicals (Figure S6b).

Sensitivity simulations showed that marine DMS emissions generally enhanced nitrate concentrations by up to approximately $0.01\text{--}0.02\ \mu\text{g m}^{-3}$ in responsive coastal regions (Figure 4). DMS emissions enhanced HNO_3 production through the $\text{DMS} + \text{NO}_3$ oxidation pathway. Whether this additional HNO_3 partitioned into particulate nitrate depended largely on NH_3 availability. As indicated by the gas ratio (GR; Figure S7), regions with higher GR values were characterized by sufficient NH_3 to neutralize newly formed HNO_3 and promote its partitioning into particulate NO_3^- . In contrast, in NH_3 -limited regions with lower GR values, the additional nitrate tended to remain mainly as gaseous HNO_3 . These results indicate that the particulate nitrate response to DMS emissions is regulated by both HNO_3 production and local gas–particle partitioning conditions.

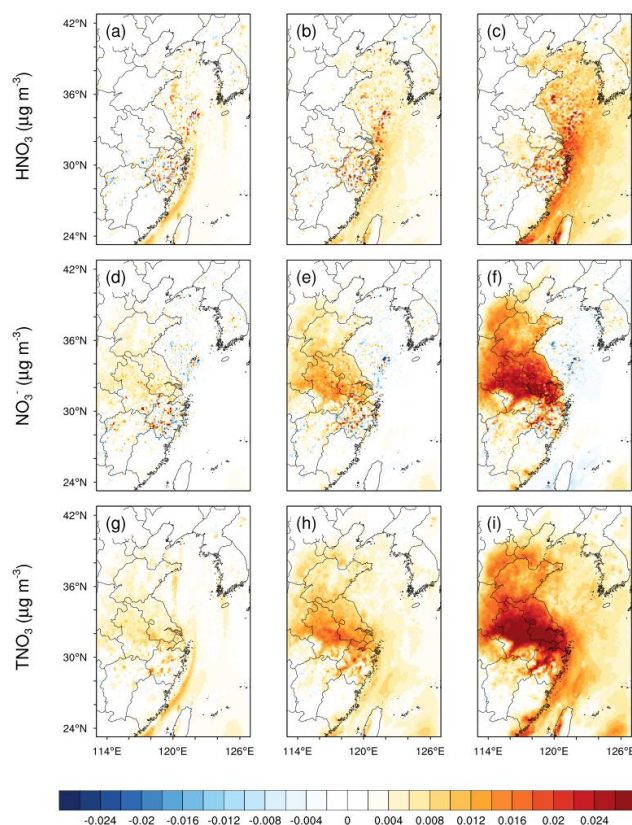


Figure 4. Spatial changes in HNO_3 (a–c), NO_3^- (d–f), and TNO_3 (g–i) under low-, medium-, and high-DMS-emission scenarios over China's coastal seas. Columns from left to right represent increasing DMS emission levels. Positive values indicate concentration increases relative to the blank simulation (S_0), in which both DMS and halogen emissions were excluded.



The influence of marine DMS on atmospheric aerosols has primarily been investigated in relation to sulfate formation and cloud condensation nuclei (Zhao et al., 2022). Its effects on nitrate are less well understood, particularly in coastal environments where multiple marine chemical processes interact. Muñiz-Unamunzaga et al. (2018) reported a 14% decrease in particulate nitrate over downtown Los Angeles when marine DMS emissions and halogen chemistry were included together, mainly associated with reduced HNO_3 concentrations. In contrast, our simulations showed a modest increase in particulate nitrate in some coastal regions. This difference should be interpreted with caution because the previous study considered the combined effects of DMS and halogen chemistry, whereas our sensitivity experiments focused on changes in DMS emissions. Our results therefore provide further evidence that marine DMS can influence wintertime nitrate formation, although its contribution remains relatively small. More importantly, they highlight the role of NH_3 availability in regulating the conversion of additional HNO_3 into particulate nitrate over China's coastal seas.

3.2.2 Contribution of Halogen Chemistry to Wintertime Nitrate Formation

Marine halogen emissions generate reactive halogen species that alter atmospheric oxidants, including O_3 , OH , and NO_3 radicals, thereby influencing daytime and nighttime nitrate formation over coastal China (Sherwen et al., 2016; Sarwar et al., 2012). To quantify these effects, we examined changes in HNO_3 , particulate NO_3^- , and TNO_3 under low-, medium-, and high-halogen emission scenarios. The simulated responses were nonlinear and spatially heterogeneous (Figure 5). Under the low-halogen scenario, HNO_3 decreased over northern China but increased by $0.4\text{--}0.8\text{ }\mu\text{g m}^{-3}$ over the East China Sea and southeastern coastal regions. Particulate NO_3^- and TNO_3 showed a similar north–south contrast, with decreases in the north and increases over southeastern coastal and marine regions. The medium-halogen scenario produced substantially weaker responses, suggesting compensation among competing chemical processes. Under the high-halogen scenario, HNO_3 increased over northern and eastern China, whereas particulate NO_3^- and TNO_3 increased mainly in northern regions but decreased along the southeastern coast. These contrasting patterns indicate that nitrate responses do not increase monotonically with halogen emissions, but depend on the balance among HNO_3 production, heterogeneous reactions, and gas–particle partitioning.

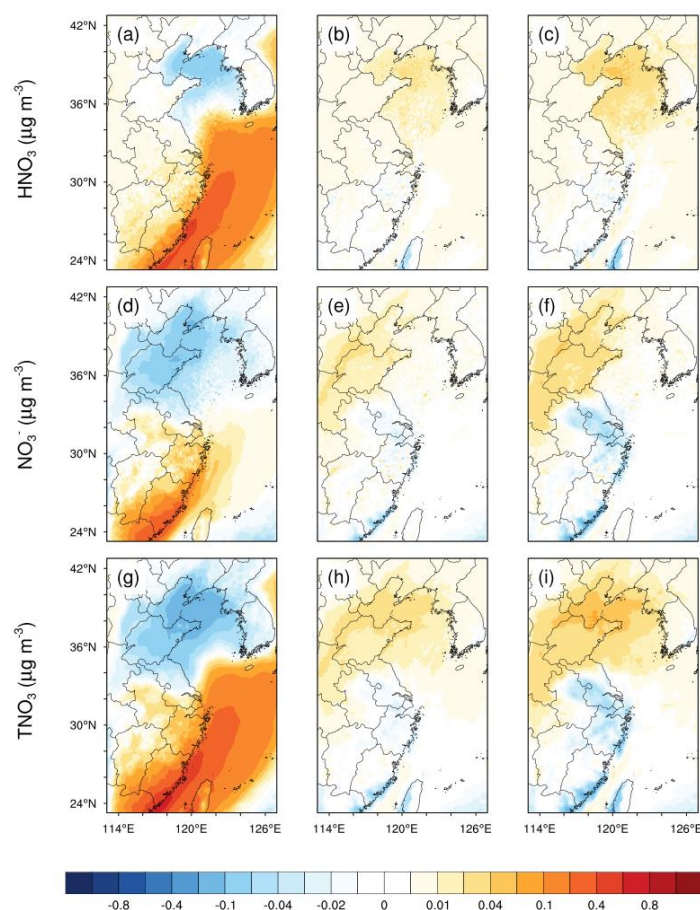


Figure 5. Simulated spatial responses of HNO_3 , NO_3^- , and TNO_3 under low, medium, and high halogen emission scenarios over eastern China. Panels (a–c), (d–f), and (g–i) show changes in HNO_3 , NO_3^- , and TNO_3 , respectively. The three columns represent low, reference, and high halogen emission conditions. Concentration changes (Δ , $\mu\text{g m}^{-3}$) are calculated relative to the corresponding simulations without halogen emissions. Warm and cool colors indicate increases and decreases, respectively. The same color scale is applied to all panels.

Changes in the $\text{OH} + \text{NO}_2$ pathway and heterogeneous uptake of N_2O_5 help explain these nonlinear responses. Halogen-induced perturbations in O_3 , OH , and N_2O_5 altered the oxidant environment controlling nitrate formation (Figure S8). The $\text{OH} + \text{NO}_2$ reaction rate increased mainly over southeastern coastal and adjacent marine regions under the low-halogen scenario, with broader positive responses under the high-halogen scenario (Figure 6a–c). The sensitivity of atmospheric oxidants to halogen chemistry has been demonstrated in earlier simulations. Sherwen et al. (2016) reported reductions of 18.6% in the global tropospheric O_3 burden and 8.2% in global mean OH following the inclusion of



halogen chemistry, while Sarwar et al. (2019) found a 25% reduction in annual mean surface O_3 over seawater in hemispheric CMAQ simulations incorporating bromine and iodine chemistry. Although these results cannot be directly compared with our regional reaction rate changes, they demonstrate the substantial influence of marine halogens on atmospheric oxidation. Our simulations further indicate that regional $OH + NO_2$ reaction rates can increase despite the overall oxidant reductions reported at larger spatial scales. Such responses may reflect the combined effects of changes in OH and NO_2 concentrations. Halogen-mediated HOX recycling, involving reactions such as $XO + HO_2 \rightarrow HOX + O_2$ followed by HOX photolysis ($X = Cl, Br, \text{ or } I$), can also modify radical cycling and OH concentrations (Simpson et al., 2007; Vogt et al., 1996; Rolletter et al., 2025; Sherwen et al., 2016; Sarwar et al., 2015).

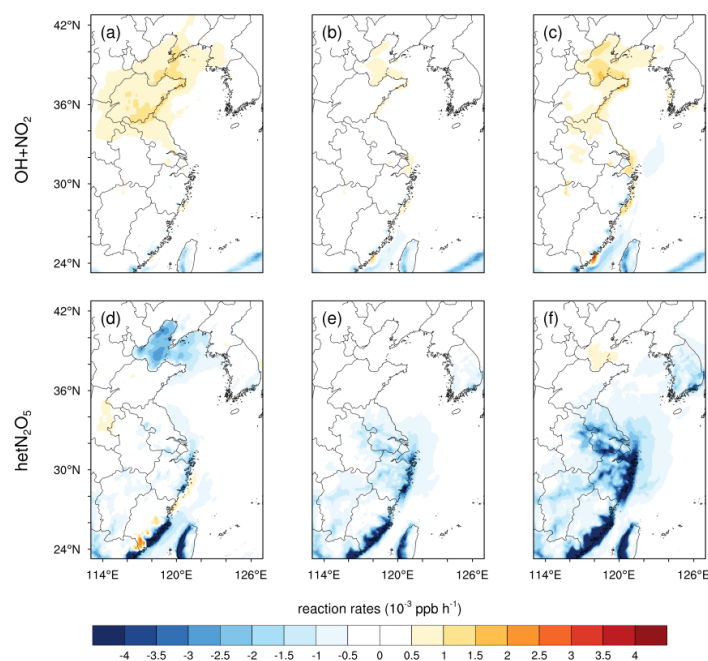


Figure 6. Changes in major nitrate formation reaction rates under different marine halogen emission conditions over eastern China in December 2019. Panels (a–c) show changes in HNO_3 production via $OH + NO_2$ oxidation, while panels (d–f) show changes in heterogeneous N_2O_5 hydrolysis rates. The three columns represent low, reference, and high halogen emission conditions, respectively. Positive and negative values indicate increases and decrease in reaction rates relative to the corresponding simulations without halogen emissions.

Unlike the daytime $OH + NO_2$ pathway, heterogeneous N_2O_5 hydrolysis exhibited a distinct nighttime response, with suppressed reaction rates over large parts of the coastal seas under the low-halogen scenario but enhanced rates in northern coastal regions under higher halogen loading (Figure



6d–f). These changes may reflect variations in N_2O_5 concentrations and heterogeneous uptake processes.

350 Bertram and Thornton (2009) demonstrated that N_2O_5 uptake is sensitive to aerosol water, nitrate, and halide content, while Lopez-Hilfiker et al. (2012) showed that reactions of N_2O_5 with halide-containing surfaces can produce photolabile halogen species, with product distributions influenced by chloride and bromide. These findings suggest that aerosol composition may further influence nighttime reactive nitrogen chemistry, although the relative contributions of changes in N_2O_5 concentrations and

355 heterogeneous uptake cannot be distinguished from the simulated reaction rate responses alone. Together with the daytime $\text{OH} + \text{NO}_2$ pathway, these nighttime processes help explain the nonlinear effects of halogen emissions on wintertime nitrate formation.

In addition to modifying the major nitrate formation pathways, enhanced halogen emissions affected reactions involving halogen nitrates, particularly bromine and iodine species (Sherwen et al., 2016; Vogt et al., 1996). ClNO_3 hydrolysis changed only slightly among the scenarios, whereas BrNO_3 and INO_3

360 pathways showed stronger responses, particularly under the high-halogen scenario (Figure S9). This indicates that bromine- and iodine-related nitrate formation pathways were more sensitive to changes in halogen emissions than the corresponding chlorine pathway. By comparison, HNO_3 production through the $\text{DMS} + \text{NO}_3$ oxidation pathway remained weak (Figure S10). These results suggest that the simulated

365 nitrate responses were more closely associated with changes in oxidant conditions, heterogeneous N_2O_5 hydrolysis, and halogen nitrate chemistry than with the direct DMS-related pathway.

The importance of marine chemistry for coastal nitrate pollution was also highlighted by Muñiz-Unamunzaga et al. (2018), who reported reductions in particulate nitrate of 14% over downtown Los Angeles and 7% over San Bernardino, accompanied by a 6–10% decrease in HNO_3 concentrations over

370 the urban area. These changes resulted from the combined inclusion of marine DMS emissions and halogen chemistry. In our simulations, varying halogen emissions produced both positive and negative nitrate responses across China's coastal regions, with local HNO_3 increases of $0.4\text{--}0.8\text{ }\mu\text{g m}^{-3}$ over the East China Sea and southeastern coast. Although the sensitivity experiments differ, both studies indicate that marine chemical processes can substantially alter coastal nitrate formation. Our results further reveal

375 that the response to halogen emissions is nonlinear and spatially heterogeneous, reflecting the combined influence of daytime $\text{OH} + \text{NO}_2$ oxidation, nighttime heterogeneous N_2O_5 hydrolysis, and halogen nitrate chemistry. These findings emphasize the importance of accounting for marine halogen chemistry in regional simulations of coastal nitrate pollution.



3.3 Nonadditive Coupling Between Halogen Chemistry and DMS-Related Processes

To evaluate whether marine halogens and DMS interact nonlinearly in regulating nitrate formation, we defined an interaction term as follows:

$$I_{(x,y)} = C_{x,y} - C_{x,0} - C_{0,y} + C_{0,0},$$

where $C_{x,y}$ is the combined DMS–halogen scenario, $C_{x,0}$ and $C_{0,y}$ are the corresponding DMS-only and halogen-only simulations, respectively, and $C_{0,0}$ is the blank case without DMS or halogen perturbations. An interaction term close to zero indicates an approximately additive response, whereas positive and negative values indicate that the combined response is greater or smaller than the linear sum of the individual effects, respectively. The interaction analysis was conducted for four combinations: low DMS + low halogen, low DMS + high halogen, high DMS + low halogen, and high DMS + high halogen.

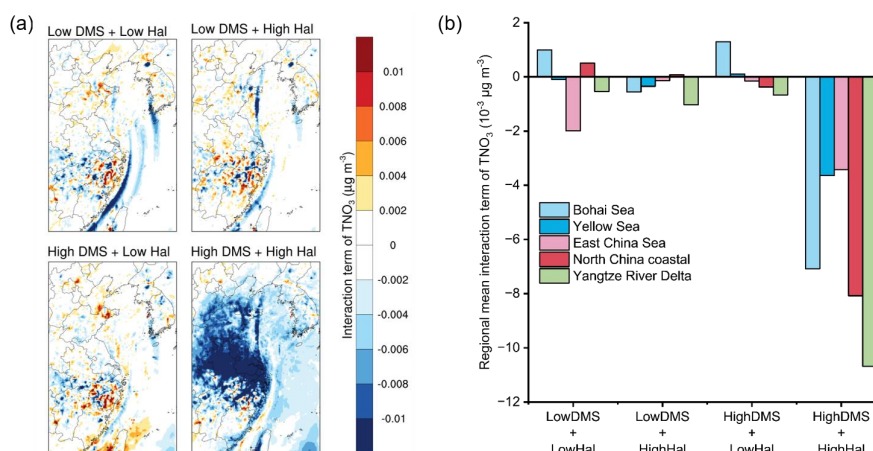


Figure 7. (a) Spatial distribution and (b) regional mean interaction terms of TNO₃ under combined DMS and halogen emission scenarios over eastern China.

The interaction between DMS-related processes and halogen chemistry showed a strong dependence on the emission scenario (Figure 7). Interaction terms remained close to zero under the low-DMS/low-halogen, low-DMS/high-halogen, and high-DMS/low-halogen scenarios, indicating that the combined effects on total TNO₃ were approximately additive under these conditions. In contrast, the high-DMS/high-halogen scenario produced widespread negative interaction terms across northern and central eastern China, indicating that the combined TNO₃ response was smaller than the sum of the individual DMS and halogen effects. Regional averages showed a similar pattern, with the largest negative



interactions occurring in the North China coastal/inland region and the Yangtze River Delta coastal region.

400 These results suggest that substantial nonadditivity emerged primarily when both marine influences were enhanced.

The simulated nonadditivity may be associated with interactions among DMS oxidation, atmospheric oxidants, and aerosol composition. DMS is oxidized by OH, NO₃, and reactive halogen species, providing a chemical link between marine sulfur and halogen chemistry (Stark et al., 2007; Breider et al., 2010). Breider et al. (2010) estimated that BrO accounted for approximately 16% of the global DMS oxidation sink and suggested a possible feedback mechanism involving DMS oxidation, aerosol acidity, and bromine release from sea salt. In hemispheric CMAQ simulations, Zhao et al. (2021) found that including DMS chemistry increased annual mean sulfate concentrations by 0.33 μg m⁻³ while decreasing particulate nitrate by 0.07 μg m⁻³ over seawater. They attributed the nitrate decrease primarily to reduced ammonia availability associated with additional sulfate formation. These findings indicate that DMS can influence nitrate concentrations indirectly through changes in aerosol composition, in addition to its interactions with atmospheric oxidants. In our simulations, the DMS + NO₃ oxidation pathway made only a minor contribution to HNO₃ production (Figure S10), whereas halogen emissions altered daytime OH + NO₂ oxidation and nighttime heterogeneous N₂O₅ hydrolysis (Figure 6). The negative interaction under high-DMS/high-halogen conditions may therefore reflect coupled changes in oxidant concentrations and aerosol chemistry. However, the relative contributions of these processes cannot be resolved from the interaction terms alone. Negative interaction signals were also evident in HNO₃ and particulate NO₃⁻ (Figures S11–S12), indicating that the nonadditive response extended to both gas-phase and particulate nitrate.

420 The importance of jointly representing marine DMS and halogen chemistry was also demonstrated by Muñiz-Unamunzaga et al. (2018), who reported reductions in particulate nitrate of 14% over downtown Los Angeles and 7% over San Bernardino, accompanied by a 6–10% decrease in urban HNO₃ concentrations. Although Zhao et al. (2021) and Muñiz-Unamunzaga et al. (2018) demonstrated that marine chemical processes can modify nitrate concentrations, neither study explicitly quantified the nonadditive interaction between DMS-related processes and halogen chemistry using a factorial comparison. Our results extend these findings by distinguishing the combined response from the sum of the individual effects. The near-zero interaction terms under most scenarios indicate limited nonadditivity, whereas the pronounced negative interaction under high-DMS/high-halogen conditions reveals stronger



coupling between the two marine chemical influences.

430 The simultaneous enhancement of DMS and halogen emissions represents an idealized sensitivity
 experiment rather than typical ambient conditions, and the magnitude of the negative interaction should
 therefore not be directly extrapolated to current coastal atmospheric conditions. Nevertheless, the results
 demonstrate that the combined effects of marine DMS-related processes and halogen chemistry on nitrate
 are not necessarily additive and can vary with emission conditions. This finding highlights the importance
 435 of considering interactions between marine sulfur and halogen chemistry when evaluating nitrate
 formation over coastal regions.

4 Conclusion

Wintertime nitrate formation over China's marginal seas exhibits pronounced regional differences
 in chemical pathways. In the Bohai and Yellow Seas, heterogeneous N_2O_5 hydrolysis dominated nitrate
 440 production, contributing 59.8% and 59.3%, respectively, highlighting the importance of nighttime
 chemistry in regions strongly influenced by continental pollution. Over the East China Sea, its
 contribution decreased to 38.1%, while $\text{OH} + \text{NO}_2$ oxidation accounted for 32.1%, alongside greater
 contributions from alternative pathways involving DMS and halogen chemistry. These differences reveal
 a more diverse distribution of nitrate formation pathways over the East China Sea, reflecting the influence
 445 of both continental and marine chemical processes.

Sensitivity simulations revealed distinct effects of marine DMS and halogen emissions on nitrate
 formation. The $\text{DMS} + \text{NO}_3$ oxidation pathway contributed up to 4.8% of nitrate production over the East
 China Sea, although changes in DMS emissions produced only modest particulate nitrate enhancements
 of approximately $0.01\text{--}0.02 \mu\text{g m}^{-3}$ in responsive coastal regions. In contrast, halogen chemistry induced
 450 stronger, spatially heterogeneous, and nonmonotonic nitrate responses. Under the low-halogen scenario,
 HNO_3 increased locally by $0.4\text{--}0.8 \mu\text{g m}^{-3}$ over the East China Sea and southeastern coastal regions.
 These responses were associated with changes in daytime $\text{OH} + \text{NO}_2$ oxidation, nighttime heterogeneous
 N_2O_5 hydrolysis, and halogen nitrate chemistry. The interaction analysis further showed that the
 combined effects of DMS and halogen chemistry were approximately additive under most tested
 455 scenarios, whereas pronounced negative interactions emerged when both emissions were enhanced.
 Because this represents an upper-bound sensitivity experiment, the magnitude of the interaction should



not be directly extrapolated to typical ambient conditions.

These findings highlight the importance of accounting for regional chemical differences and marine influences when evaluating coastal nitrate formation. The dominance of heterogeneous N_2O_5 hydrolysis in the northern coastal seas emphasizes the importance of anthropogenic nitrogen emissions and nighttime chemistry, whereas the greater diversity of pathways over the East China Sea points to an increased role for marine chemical processes. Incorporating DMS-related processes, halogen chemistry, and their potential interactions into chemical transport models may improve predictions of coastal nitrate concentrations and their responses to changing emissions. Overall, this study demonstrates that nitrate formation over China's marginal seas varies substantially across chemical environments, highlighting the importance of marine sulfur and halogen chemistry in understanding coastal atmospheric nitrogen cycling.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

490 **Zhenze Liu**: Conceptualization, Methodology, Software, Formal analysis, Visualization, Writing–original draft. **Jianhua Qi**: Conceptualization, Supervision, Funding acquisition, Writing–review & editing. **Yuanzhe Ni**: Investigation, Data curation, Validation. **Xiaohuan Liu**: Investigation, Data curation, Validation. **Gang Yuan**: Investigation, Data curation, Validation. **Mingxu Liu**: Formal analysis, Methodology, Writing–review & editing.

495 **Data availability**

The publicly available datasets used in this study are accessible from their respective sources as described in Sect. 2. The data underlying all figures in the main text are available on Zenodo at <https://doi.org/10.5281/zenodo.23360635>. Additional model outputs and observational data used for model evaluation are available from the corresponding author upon reasonable request.

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