We would like to thank the reviewer for the constructive comments really helping to improve the paper. Below, we address each comment in full detail. Following the Reviewers' comments in black, please find our point-to-point responses in blue. Hereafter, all new added or modified sentences are marked in blue and italic in this response. The line numbers in the responses to comments are in accordance with the revised manuscript.

Reviewer #1

Xie et al. applied the WRF and CAMx models over Northeast China to investigate how chlorine chemistry in the atmosphere and on the snow-covered ground influenced atmospheric concentrations of N_2O_5, $ClNO_2$, $PM_{2.5}$ and O_3. They modeled February and March of 2024 when atmospheric measurements are available for N_2O_5 and $ClNO_2$ at a suburban location in Changchun City, Northeast China. They modified CAMx to compare two heterogeneous chemistry schemes (YU20 and BT09) that parameterize reactive uptake of N_2O_5 and HCl (from coal burning emissions) to aerosol surfaces. They also utilize the CAMx surface chemistry model to investigate how reactive uptake of N_2O_5 and HCl by snowpack may influence atmospheric N_2O_5 and $ClNO_2$. Xie et al. find that the YU20 scheme performed better than BT09 at describing the observed concentrations of N_2O_5 and $ClNO_2$. They find that reactive uptake of N_2O_5 by aerosol (YU20 scheme) is more influential than reactive uptake to snowpack and adding chlorine/chloride emissions (ACEIC inventory) in combination. They note that $ClNO_2$ formation from N_2O_5 uptake is influential on model results for PM2.5, ozone and other oxidants. They suggest that future modeling studies (for similar winter conditions) should include these emissions and processes. This study expands on previous 1D modeling studies by presenting a 3D picture of model sensitivity to algorithms and input data. The results can provide useful guidance for modeling similar conditions and planning future field campaigns.

Q1: section 2.5 (and elsewhere) I understood "anthropogenic chlorine emissions" to mean specifically the ACEIC inventory, especially gaseous HCl from coal combustion. Does the MEIC emission inventory include emissions of particulate chloride (PCl)? The ISORROPIA scheme in CAMx equilibrates HCl and PCl depending on aerosol pH and consequently emissions of both PCL and HCl contribute to available reactive chloride. Most likely, simulation Y1 includes some anthropogenic chloride emissions (i.e., PCl from MEIC) and the other simulations have more chloride/chlorine emissions (i.e., from ACEIC). The manuscript should clarify whether MEIC includes chloride emissions. Add a table summarizing mass of chloride/chlorine emissions from MEIC and ACEIC. Provide a citation for ACEIC when first mentioned.

Response:

Thank you for the insightful comments. In response to your questions, we provide the following clarifications:

1. Does the MEIC inventory include emissions of particulate chloride (PCl)?

The MEIC anthropogenic emission inventory does include PCl as a chlorine-containing species. However, in our emission preprocessing, we multiplied the emission factor of PCl from MEIC by zero, effectively setting its emissions to zero. This was done to avoid double-counting with PCl emissions from the ACEIC inventory. Consequently, in all simulations (including Y1), MEIC contributes no anthropogenic chlorine emissions (neither PCl nor HCl, etc.). All anthropogenic chlorine emissions used in the simulations are solely from the ACEIC inventory.

2. Summary table of chlorine emissions from MEIC and ACEIC

The table below (Table S1) summarizes the total emissions of chlorine-containing species from the ACEIC and MEIC inventories. As shown, all chlorine species from MEIC are either zero or not present, while ACEIC includes emissions of HCl, PCl, Cl_2, and HOCl.

Table S1 Chlorine emissions from the ACEIC and MEIC anthropogenic inventories used in this study (unit: Gg)

Inventory	HCl	PCl	Cl2	HOCl
ACEIC	361.34	173.72	17.55	79.45
MEIC	—	0.00	—	—

(Note: MEIC only contains PCl among chlorine species, but its emissions are set to zero; other species are not included, denoted by "—".)

3. Citation for the ACEIC inventory

A reference for the anthropogenic chlorine emissions inventory (ACEIC) has been added at the first mention in the manuscript (line 155).

Q2: The CAMx surface model can store pollutant mass within the snowpack, and this mass can be lost to the ground, e.g., via meltwater. Was loss of chloride from the snowpack in meltwater modeled, and was it influential?

Response:

Thank you for raising this question regarding the loss of chloride from snowpack via meltwater and its potential influence. Our response is as follows:

In the CAMx surface model, the original framework includes three surface types: soil, vegetation, and snow. After dry and wet deposition, atmospheric species deposited to the surface can undergo the following fates: (1) adsorption onto various media (e.g., vegetation, snowpack, and soil); (2) heterogeneous chemical reactions and photolysis, with some products subsequently re-emitted back to the atmosphere; and (3) loss through other processes, such as snowmelt (denoted as SnoMlt) (Figure1). The surface module allows users to specify the species and reaction pathways of interest (see schematic in Figure 2). In this study, we included N_2O_5, HCl, Cl, HNO_3, $ClNO_2$ and NO_2 in this module to represent the relevant surface reactions (see R1-R2).

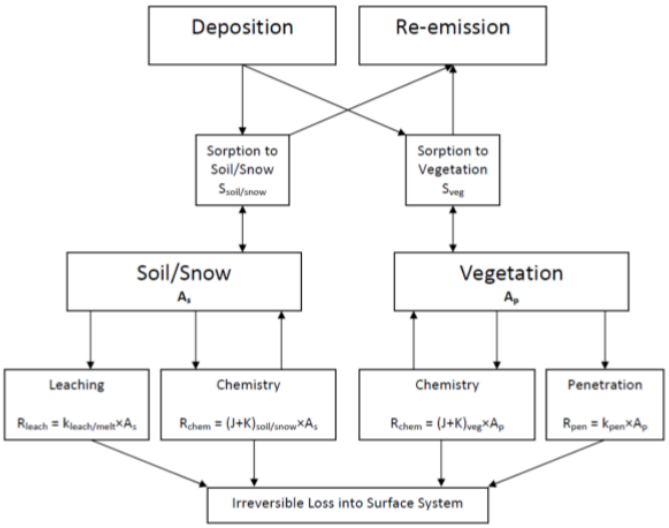


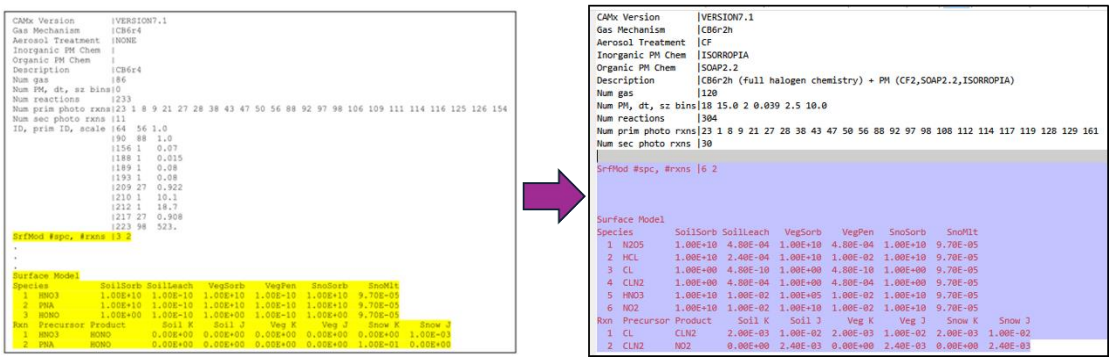
Figure 1. Schematic of the CAMx surface model (Ramboll., 2020).

$$HCl + N_2O_5 \xrightarrow{Ground} ClNO_2 + HNO_3 \quad \text{(R1)}$$

$$ClNO_2 + h\nu \xrightarrow{Ground} Cl + NO_2 \quad \text{(R2)}$$

Example of the surface chemistry module in the user's guide (yellow background))

Updated surface chemistry module (purple background)



```
CAMx Version      |VERSION7.1
Gas Mechanism     |CB6r4
Aerosol Treatment |NONE
Inorganic PM Chem |
Organic PM Chem   |
Description       |CB6r4
Num gas           |86
Num PM, dt, sz bins|0
Num reactions     |233
Num prim photo rxns|23 1 8 9 21 27 28 38 43 47 50 56 88 92 97 98 106 109 111 114 116 125 126 154
Num sec photo rxns |11
ID, prim ID, scale |64  56 1.0
                   |90  88  1.0
                   |156 1   0.07
                   |188 1   0.015
                   |189 1   0.08
                   |193 1   0.08
                   |209 27  0.922
                   |210 1   10.1
                   |212 1   18.7
                   |217 27  0.908
                   |223 98  523.
SrfMod #spc, #rxns 13 2
.
.
.
Surface Model
Species        SoilSorb SoilLeach   VegSorb    VegPen    SnoSorb    SnoMlt
  1  HNO3      1.00E+10  1.00E-10  1.00E+10  1.00E-10  1.00E+10  9.70E-05
  2  PNA       1.00E+10  1.00E-10  1.00E+10  1.00E-10  1.00E+10  9.70E-05
  3  HONO      1.00E+00  1.00E-10  1.00E+00  1.00E-10  1.00E+00  9.70E-05
Rxn  Precursor Product      Soil K    Soil J     Veg K     Veg J     Snow K    Snow J
  1  HNO3      HONO       0.00E+00  0.00E+00  0.00E+00  0.00E+00  0.00E+00  1.00E-03
  2  PNA       HONO       0.00E+00  0.00E+00  0.00E+00  0.00E+00  1.00E-01  0.00E+00
```

```
CAMx Version      |VERSION7.1
Gas Mechanism     |CB6r2h
Aerosol Treatment |CF
Inorganic PM Chem |ISORROPIA
Organic PM Chem   |SOAP2.2
Description       |CB6r2h (full halogen chemistry) + PM (CF2,SOAP2.2,ISORROPIA)
Num gas           |120
Num PM, dt, sz bins|18 15.0 2 0.039 2.5 10.0
Num reactions     |304
Num prim photo rxns|23 1 8 9 21 27 28 38 43 47 50 56 88 92 97 98 108 112 114 117 119 128 129 161
Num sec photo rxns |30
SrfMod #spc, #rxns |6 2
Surface Model
Species        SoilSorb SoilLeach   VegSorb    VegPen    SnoSorb    SnoMlt
  1  N2O5      1.00E+10  4.80E-04  1.00E+10  4.80E-04  1.00E+10  9.70E-05
  2  HCL       1.00E+10  2.40E-04  1.00E+10  1.00E-02  1.00E+10  9.70E-05
  3  CL        1.00E+00  4.80E-10  1.00E+00  4.80E-10  1.00E+00  9.70E-05
  4  CLN2      1.00E+00  4.80E-04  1.00E+00  4.80E-04  1.00E+00  9.70E-05
  5  HNO3      1.00E+10  1.00E-02  1.00E+05  1.00E-02  1.00E+10  9.70E-05
  6  NO2       1.00E+10  1.00E-02  1.00E+10  1.00E-02  1.00E+10  9.70E-05
Rxn  Precursor Product      Soil K    Soil J     Veg K     Veg J     Snow K    Snow J
  1  CL        CLN2       2.00E-03  1.00E-02  2.00E-03  1.00E-02  2.00E-03  1.00E-02
  2  CLN2      NO2        0.00E+00  2.40E-03  0.00E+00  2.40E-03  0.00E+00  2.40E-03
```

Figure 2. Configuration of the CAMx surface model.

Regarding the snowmelt process, the model incorporates two snowpack parameters (snow age and snow depth) to capture the dynamic evolution of snow accumulation and ablation (Figure 3). It is important to note that WRF-CAMx is a three-dimensional atmospheric chemical transport model that focuses primarily on the dynamic changes of pollutants in the atmosphere. The surface module is designed such that deposited species, after chemical transformation, are re-emitted to the atmosphere; the model only calculates the fluxes of these re-emitted species into the atmospheric column. Consequently, while the model does simulate the chemical transformation and re-release of chloride species during snowmelt, it does not account for the mass lost downward via meltwater to the soil or groundwater—such loss falls outside the gas-phase mass balance framework of the model and therefore does not directly influence the atmospheric chemical analysis in this study.

We have added the above explanation and the relevant schematic figures to help readers clearly understand the model's treatment of snowpack processes and its inherent

limitations. We appreciate your careful review.

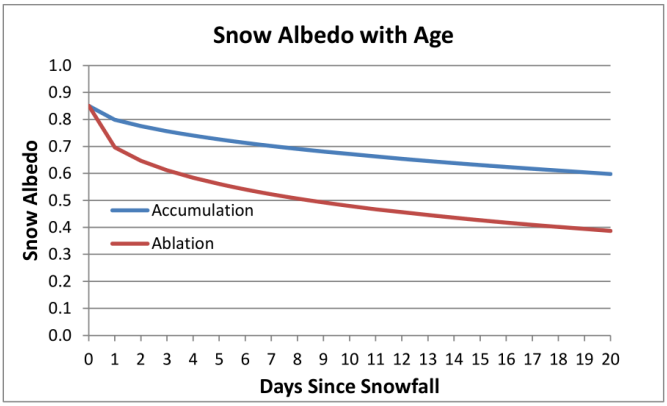


Figure 3. Relationship between snow albedo and snow age during accumulation and ablation periods (Ramboll., 2020).

Q3: The OH concentration differences mentioned at line 460 seem large (OH concentration difference ranged from -(1.73 × 10^6) cm^{-3} to 52.22 ×10^6 cm^{-3}) and I suggest double checking.

Response:

We sincerely appreciate the reviewer's in-depth discussion regarding the simulated concentration level of oxidative radical. We fully agree that the typical atmospheric OH concentration is on the order of 10^5–10^7 cm^{-3} (Holland et al., 2003; Yu et al., 2024). To address this discrepancy, we initially suspected potential sources of error such as incorrect parameterizations of OH-related chemical reactions or issues related to mass conservation in the chemical mechanism. However, these possibilities were ruled out after thorough rechecking. Subsequent investigation identified the root cause as a coding issue in the CAMx model: the simulated OH concentrations were mislabeled in the output NetCDF files. Specifically, while the model output indicated a unit of μg/m³, our analysis confirmed that the actual unit used in the model's source code was ppm (volume mixing ratio). This mislabeling led to an erroneous conversion when translating OH concentrations from μg/m^3 to cm^{-3}.

More details as follows:

1) Verification of Unit Conversion in CAMx Postprocessing

This study employed CAMx V7.10 for chemical transport modeling, with OH concentration output units in μg/m^3 (Figure 4). After unit conversion (μg/m^3 to cm^{-3}), the OH concentration range was 10^3–10^4 cm^{-3}. We confirmed that there were no errors in the conversion from μg/m^3 to cm^{-3}, as detailed below:

To convert the atmospheric OH concentration from **μg/m³** to **molecules/cm³**, follow these steps:

Step 1: Convert μg to grams

1μg=10^{-6}g g

So, **OH concentration in g/m³** = Concentration in μg/m^3 × 10^{-6}

Step 2: Convert grams to moles (using molar mass of OH)

- Molar mass of OH (Oxygen + Hydrogen) = 16 (O) + 1 (H) =**17 g/mol**
- Moles of OH per m^3 = (Concentration in g/m^3) / (17 g/mol)

Step 3: Convert moles to molecules

- Avogadro's number = 6.022×10^{23} molecules/mol
- Molecules of OH per m^3 = (Moles of OH/m^3) × (6.022×10^{23} molecules/mol)

Step 4: Convert m^3 to cm^3

1 $m^3 = 10^6$ cm^3

- Molecules of OH per cm^3 = (Molecules of OH/m^3) / 10^6

Final formula:

$$OH(molecules\ cm^{-3}) = \left(\frac{OH(\mu g\ m^{-3})}{17}\right) \times 6.022 \times 10^{23} \times 10^{-6}$$

$$OH(molecules\ cm^{-3}) = OH(\mu g\ m^{-3}) \times 3.54 \times 10^{10}$$

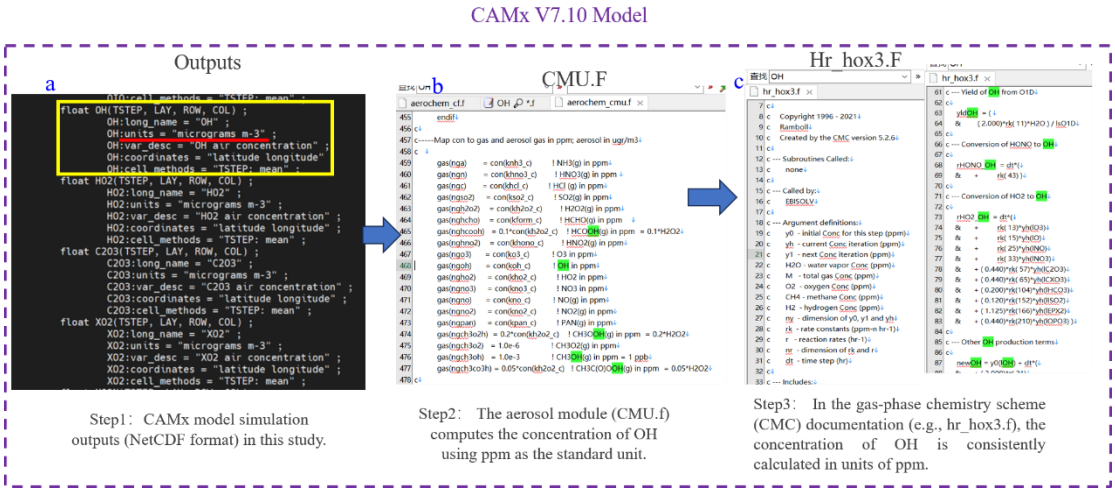


Figure 4. Unit analysis of OH concentration in CAMx codes.

2) Rechecking OH-related chemistry mechanism and the output module in CAMx

The CAMx is an open-source model, and the newly added N_2O_5 heterogeneous chemistry mechanism in this study was developed by our team and checked by Prof. Greg Yarwood (acknowledged in the paper) whom the major model developer of CAMx. Upon inspecting the source code, we found:

- OH is internally calculated in ppm in both aerosol (CMU.F) and gas-phase chemistry schemes (Figure 1b)
- The output module (IO_NCF) does not include a unit conversion step from ppm to µg/m^3 for certain gaseous species, such OH, RO_2, and HO_2. Thus, the "µg/m^3" unit labeled in the CAMx output files is incorrect, and the actual unit should be ppm.

3) Further cross-validation with outputted results from the CMAQ model

To further validate this issue, we analyzed OH concentrations simulated by the CMAQ model (which previously conducted by our research) over the same region. CMAQ

outputs OH in ppbv (Figure 5). After conversion, **the concentration of OH can reach a range of** 10^5 to 10^7 cm^{-3}, supporting the conclusion that our CAMx-simulated OH concentrations fall within the expected range, and the discrepancy stemmed solely from unit mislabeling. These results are also in good agreement with previously observed OH concentration ranges (Holland et al., 2003; Yu et al., 2024).

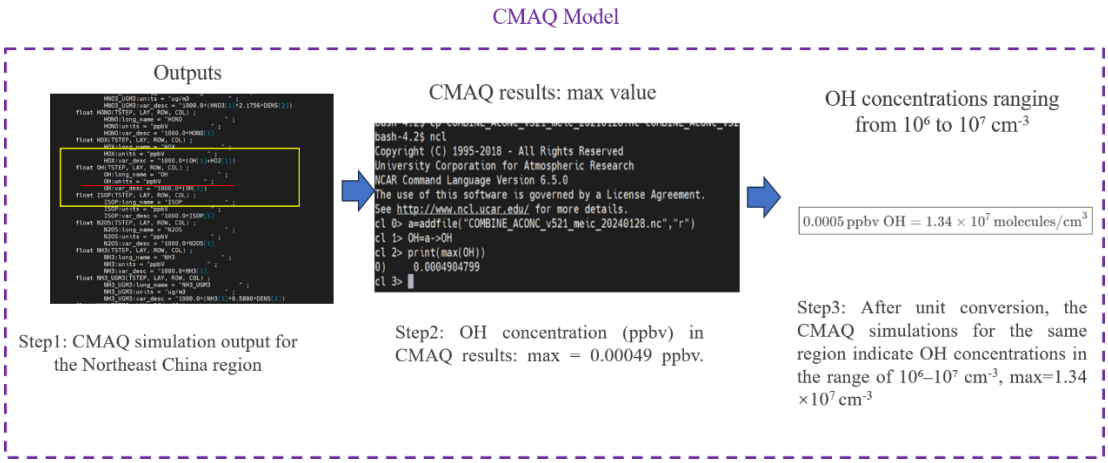


Figure 5. The concentration of OH simulated by CMAQ in the same region.

All in all, a coding error was identified in the official release of the CAMx model regarding the unit labeling of certain gaseous species in the output files: the OH, RO_2, and HO_2 concentration in the NetCDF output were incorrectly labeled as $\mu g/m^3$ (mass concentration), whereas the actual unit was ppm (volume mixing ratio). Accordingly, we have replotted Figures 7 and S4. Following thesuggestion of Reviewer 2, Figure 7 has been moved to theAppendix.

Reference：

Holland F, Hofzumahaus A, Schäfer J, et al. Measurements of OH and HO2 radical concentrations and photolysis frequencies during BERLIOZ[J]. Journal of Geophysical Research: Atmospheres, 2003, 108(D4): PHO 2-1-PHO 2-23.

Yu W, Zheng X, Tan M, et al. Field quantification of hydroxyl radicals by flow-injection chemiluminescence analysis with a portable device[J]. Environmental Science & Technology, 2024, 58(6): 2808-2816.

Q4: A suitable reference for the CAMx surface model is Karamchandani et al. (2015). A suitable reference for the CAMx model is Emery et al., (2024). The CAMx v7.1 User's Guide could be cited (Ramboll, 2021).

Response: Thank you for these helpful literature suggestions. In the revised manuscript, we have added the following references at the relevant positions in the text:

- Karamchandani et al. (2015) has been cited as a reference for the CAMx surface model (Line 183).
- Emery et al. (2024) has been cited as a reference for the CAMx model (Line 114).
- Ramboll (2021), the CAMx v7.1 User's Guide, has also been cited (Line 114).

These references have been incorporated into the manuscript at the locations indicated above. We appreciate your careful guidance.

Q5: Is Bo Sea the same as the Bohai Sea? I think Bohai Sea is more commonly seen in English.

Response: Thank you for pointing this out. Yes, “Bo Sea” and “Bohai Sea” refer to the same body of water, i.e., the Bohai Sea in northern China. We agree with your comment that “Bohai Sea” is the more commonly used and standard term in English literature. Therefore, we have revised the manuscript to replace all instances of “Bo Sea” with “Bohai Sea”. We appreciate your careful observation.

Q6: In several places numeric values are given with more precision than needed, for example line 47 “contributing approximately 28.36% to nighttime accumulation" could be “approximately 28%". Consider whether less precision would make numbers more readable.

Response: Thank you for the suggestion. We agree that excessive numerical precision can reduce readability and is often unnecessary. Accordingly, we will review all numeric values presented in the manuscript and adjust figures such as “28.36%” to a more appropriate level of precision (e.g., “approximately 28%”), thereby improving clarity while maintaining scientific accuracy. We appreciate your careful observation.

Q7: I found Figure S1 difficult to read, can the resolution be improved?

Response: Thank you for your comment. We agree that the resolution of Figure S1 is indeed too low, which affects its readability. In the revised manuscript, we will provide a higher-resolution and clearer version of Figure S1 to ensure all details are easily discernible. We appreciate you bringing this to our attention.

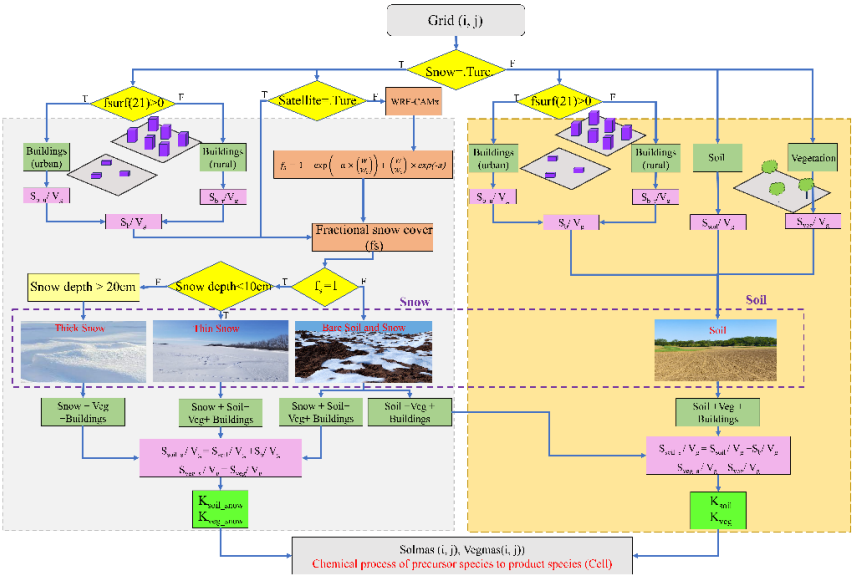


Figure S1. Characterization of S/V_g under different LU-LC.

References

Bond, A. M. H., et al., 2023. Snowpack nitrate photolysis drives the summertime atmospheric nitrous acid (HONO) budget in coastal Antarctica. Atmos. Chem. Phys. 23**,** 5533-5550.

Chen, Q., et al., 2019. HONO, particulate nitrite, and snow nitrite at a midlatitude urban site during wintertime. ACS Earth and Space Chemistry. 3**,** 811-822.

Emery, C., et al., 2024. Comprehensive air quality model with extensions: formulation and evaluation for ozone and particulate matter over the US. Atmosphere, 15(10), p.1158.

Holland F, Hofzumahaus A, Schäfer J, et al. Measurements of OH and HO2 radical concentrations and photolysis frequencies during BERLIOZ[J]. Journal of Geophysical Research: Atmospheres, 2003, 108(D4): PHO 2-1-PHO 2-23.

Karamchandani, P., et al., 2015. Implementation and refinement of a surface model for heterogeneous HONO formation in a 3-D chemical transport model. Atmospheric Environment, 112, pp.356-368.

Fu, X., et al., 2019. The significant contribution of HONO to secondary pollutants during a severe winter pollution event in southern China. Atmospheric Chemistry and Physics. 19, 1-14.

Xie, S., et al., 2025. NH3-driven HONO production as a potential unknown source during snow cover and melt. Environmental Research. 282, 121975.

Yu W, Zheng X, Tan M, et al. Field quantification of hydroxyl radicals by flow-injection chemiluminescence analysis with a portable device[J]. Environmental Science & Technology, 2024, 58(6): 2808-2816.

Zhang, S., et al., 2021. Improving the representation of HONO chemistry in CMAQ and examining its impact on haze over China. Atmospheric chemistry and physics. 21**,** 15809-15826.

Ramboll, 2020. User's guide, comprehensive air quality model with extensions, version 7.10. Available at: https://www.camx.com/Files/CAMxUsersGuide_v7.10.pdf.

We would like to thank the reviewer for the constructive comments really helping to improve the paper. Below, we address each comment in full detail. Following the Reviewers' comments in black, please find our point-to-point responses in blue. Hereafter, all new added or modified sentences are marked in blue and italic in this response. The line numbers in the responses to comments are in accordance with the revised manuscript.

Reviewer #2

Xie et al. develop and evaluate an enhanced WRF-CAMx model that incorporates additional heterogeneous chlorine chemistry to investigate winter atmospheric chemistry over snow-covered regions of Northeast China, with a particular focus on N2O5 uptake and ClNO2 production on both aerosol and snow surfaces. The authors incorporate updated parameterizations for heterogeneous N2O5 reactions, anthropogenic chlorine emissions, and a newly developed ground-surface chemistry module that accounts for snowpack processes and ClNO2 photolysis. They report that the YU20 aerosol parameterization reproduces field observations at the DLS site in China better compared to the traditional BT09 scheme. Additionally, they show that inclusion of ground-surface chlorine chemistry improves the simulation of ClNO2 concentrations. Scenario analyses indicate that snowpack chemistry is an important nocturnal source of ClNO2, contributing approximately 28% of nighttime accumulation, while chlorine chemistry enhances atmospheric oxidizing capacity and increases PM2.5 (up to 3.65 μg m-3) and MDA8 O3 (up to 3.41 ppbv). Overall, the study highlights the importance of explicitly representing snowpack-mediated chlorine chemistry in regional air quality models to better characterize winter atmospheric oxidation and secondary pollutant formation under snow-covered conditions.

General comments

Q1：Cite and discuss Sun et al. (2026). This paper investigates winter ClNO2 sources and its impact on atmospheric oxidizing capacity at a coastal North China site (Qingdao) using field observations plus a 0-D photochemical box model (F0AM/MCM), and seems like a relevant discussion reference.

Response: We thank the reviewer for recommending the relevant and timely work by Sun et al. (2026), which examines wintertime $ClNO_2$ sources and their impact on atmospheric oxidizing capacity at a coastal site in North China. We have carefully read this paper and have incorporated it into our manuscript in the following two aspects:

Point 1: In the Introduction section, specifically in the first sentence (lines 57–59), we have added a citation to Sun et al. (2026) to better contextualize the role of reactive chlorine species in influencing the atmospheric oxidizing capacity (AOC). The revised sentence now reads:

"Reactive nitrogen and chlorine atoms are prominent active gases in the atmosphere, influencing the budget of the atmospheric oxidizing capacity (AOC) (Yang et al., 2022; Sun et al., 2026)."

Point 2: We have also included the $ClNO_2$ yield reported by Sun et al. (2026) in Table 4, alongside other literature values, to enable a direct comparison of $ClNO_2$ production efficiencies under different environmental conditions. In the corresponding discussion, we have expanded our analysis to compare our findings with those of Sun et al. (2026).

Sun W, Chen X, Jiang Y, et al. High levels of $ClNO_2$ enhance wintertime atmospheric oxidation capacity at a coastal site in North China[J]. Journal of Environmental Sciences, 2026.

Q2: Readability. Many sentences are too long (for example, lines 84-87, lines 68-71), and word choice is frequently more elevated than needed (for example, "protracted"). I recommend splitting sentences and simplifying vocabulary throughout for readability.

Response: We sincerely thank the reviewer for this valuable and constructive suggestion. We fully agree that the readability of our manuscript needs improvement, particularly regarding sentence length and word choice. Following the reviewer's advice, we have carefully revised the entire manuscript to split overlong sentences and simplify vocabulary throughout. Below we provide a point-by-point response to the specific issues raised.

Point 1:

Original (lines 112–113): *"Northeast China experiences a protracted period of winter snow cover, with the heating season extending up to half a year."*

Revised: *"Northeast China has a long winter snow cover, and the heating season lasts up to half a year."*

Point 2:

Original (lines 68–71): *"Accurately quantifying $\gamma(N_2O_5)$ values under varying environmental conditions remains challenging, as this parameter demonstrably fluctuates in response to changes in nitrate concentration, liquid moisture content, chloride abundance, and organic matter content (Bertram and Thornton, 2009; Gaston et al., 2014; McDuffie et al., 2018; Mentel et al., 1999; Mielke et al., 2013; Tham et al., 2018; Thornton and Abbott, 2005; Yu et al., 2020)."*

Revised: (lines 70-73)*"Accurately quantifying $\gamma(N_2O_5)$ values under varying environmental conditions remains challenging. This parameter demonstrably fluctuates in response to changes in nitrate concentration, liquid moisture content, chloride abundance, and organic matter content (Bertram and Thornton, 2009; Gaston et al., 2014; McDuffie et al., 2018; Mentel et al., 1999; Mielke et al., 2013; Tham et al., 2018; Thornton and Abbott, 2005; Yu et al., 2020)."*

Point 3:

Original (lines 84–87): *"Subsequent field investigations have corroborated that suppression of $\gamma(N_2O_5)$ in North China is attributable to factors including reduced aerosol liquid water content (ALWC), elevated particulate nitrate (pNO_3), and particle morphological characteristics (Wang et al., 2020), providing mechanistic insight into the observed discrepancies between simulated and measured values."*

Revised (lines 85–90): *"Subsequent field investigations in North China confirmed that the suppression of $\gamma(N_2O_5)$ is mainly driven by reduced aerosol liquid water (ALWC), high particulate nitrate (pNO_3), and particle morphology (Wang et al., 2020). This finding offers a mechanistic explanation for the discrepancies between model simulations and ambient observations."*

Point 4:

Beyond the specific sentences mentioned above, we have systematically reviewed the entire manuscript.

Q3: Scenario naming is inconsistent and hard to follow. Table 2 cleanly defines the scenario set (B1, Y0-Y4), but the text then also refers to scenarios by case name (YU20_A_chl, YU20_A_G_chl) and later switches to process-based labels (Chl_het_N2O5_a+g, Het_N2O5_a, Het_N2O5_g) for the same underlying comparisons (Y3−Y0, Y2−Y1, Y3−Y2). Help the reader by picking one naming convention and using it consistently.

Response: We thank the reviewer for pointing out this inconsistency in scenario naming, which indeed could cause confusion for readers. We recognize that the mixed use of case names and process-based

labels in the original manuscript made the scenario descriptions difficult to follow.

To address this issue, we have carefully revised Section 3.4 (lines:467-605), where the inconsistency primarily occurred, and have systematically unified all scenario references to follow a single naming convention.

Q4: Comparison to measurements. All quantitative validation (N2O5, ClNO2) comes from one station (DLS) over nine days, yet conclusions are drawn for the whole Northeast China domain. The spatial maps (Figs. 4, 5, 6, 8, 9) do not include a mark for the DLS location, please add it for reference on each spatial panel. In addition, PM2.5 and O3 are never validated against any observation or published estimates. There should be some published observations or prior studies that measured PM2.5, O3, or the other components (PNH4, PSO4, PNO3), no?

Response:

We thank the reviewer for these constructive comments. We address the concerns regarding the single-station validation and the spatial maps as follows:

- **Justification for single-station validation:**

  Our study is based on a 9-day field campaign conducted during the snow-covered period, with outdoor temperatures ranging from -10 to -20 °C. The primary objective of this single-station observation was to determine the mechanistic parameters of snowpack heterogeneous chemistry, rather than to conduct a comprehensive regional validation. Previous studies have successfully employed similar single-station field observations to derive chemical mechanisms and applied them in regional 3D numerical models. For example, Zhang et al. (2016, 2021) derived HONO mechanistic parameters from single-station observations and applied them in WRF-Chem and WRF-CMAQ models for regional simulations in North China and the Pearl River Delta. Similarly, McNamara et al. (2021) and Jeong et al. (2023) utilized single-station observations to determine chemical parameters under snow-covered conditions for regional modeling. Therefore, the use of single-station data to derive mechanistic parameters for 3D modeling is scientifically reasonable. We plan to conduct further field observations across different snow-covered periods and locations to further validate the reliability of these parameters in future work.

- **Addition of the DLS station mark to spatial maps:**

  We agree that marking the DLS station location is helpful for reference. However, Figures 4, 5, 6, 8, and 9 present the spatial patterns of the simulated fields averaged over the study period, which are used to analyze the spatial distribution differences under different scenarios. Since the time-series observations of N_2O_5 and $ClNO_2$ are already presented in Figure 3, superimposing the single-station average onto the spatially averaged maps would not be intuitive.

- **Clarification on $PM_{2.5}$, O_3, and other components:**

  The primary focus of this study is to quantify the proportional contributions of different chlorine chemistry pathways to the increments of secondary pollutants, such as $PM_{2.5}$, O_3, PNH_4, PSO_4, and PNO_3. We have verified the concentrations of N_2O_5 and $ClNO_2$ to ensure improved model prediction accuracy. Furthermore, we have included discussions and comparisons with existing literature in Sections 3.4.2 and 3.4.3 to contextualize our simulated $PM_{2.5}$ and O_3 results.

References:

Zhang, L., et al. Potential sources of nitrous acid (HONO) and their impacts on ozone: A WRF-Chem study in a polluted subtropical region. *Journal of Geophysical Research: Atmospheres*, 2016, 121(7): 3645-3662.

Zhang, S., et al. Improving the representation of HONO chemistry in CMAQ and examining its impact on haze over China. *Atmospheric Chemistry and Physics*, 2021, 21(20): 15809-15826.
McNamara, S.M., et al. Observation of N2O5 deposition and ClNO2 production on the saline snowpack. *ACS Earth and Space Chemistry*, 2021, 5(5): 1020-1031.
Jeong, D., et al. Quantifying the contributions of aerosol-and snow-produced ClNO2 through observations and 1D modeling. *ACS Earth and Space Chemistry*, 2023, 7(12): 2548-2561.

Q5: BT09 results are referenced but never shown. The BT09 vs. YU20 comparison (section 3.2.1) is supported only by summary statistics (MB/NMB/RMSE/IOA) attributed to Table S3, no time series or spatial output for the BT09 (B1) scenario appears anywhere in the manuscript. Since this is discussed thoroughly, please show the actual BT09 output (at least in the SI) so the reader can understand your claim that the YU20 is better.

Respond: We thank the reviewer for this important observation. We agree that a direct visual comparison of the BT09 and YU20 simulation results is necessary to substantiate our claim that the YU20 parameterization better reproduces the observed N_2O_5 and $ClNO_2$ concentrations under snow-covered regions.

To address this issue, we have made the following revisions:

Point 1: We have added a new figure (Figure S3, now included in the Supplementary Information) that presents the time series of simulated N_2O_5 and $ClNO_2$ concentrations using both the BT09 (B1) and YU20 parameterizations, alongside the corresponding field observations. This figure enables readers to directly compare the performance of the two schemes throughout the entire measurement period.

Point 2: We have also clarified that the summary statistics (MB/NMB/RMSE/IOA) previously presented in Table S3 remain in the Supplementary Information, and we now explicitly cross-reference the new time series figure (Figure S3) in the same section to provide a complete picture of the model–observation comparison.

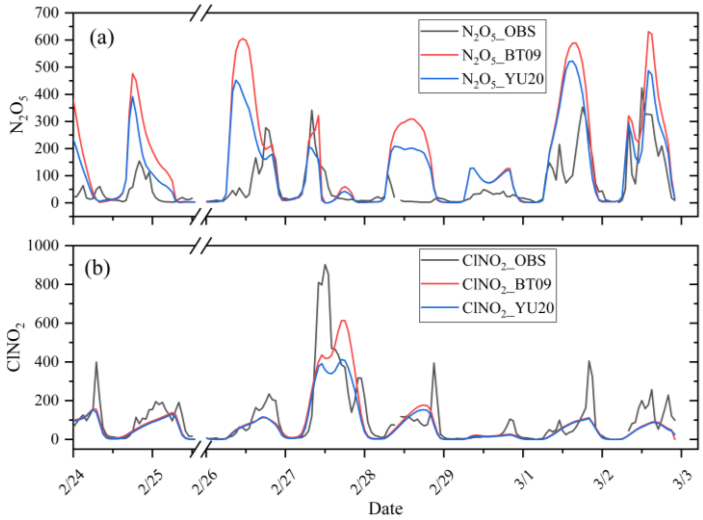


Figure S3 Comparison between simulated and observed concentrations of N_2O_5 and $ClNO_2$ under the BT09 and YU20 schemes.

Q6: YU20 and snowpack chemistry across the entire modeling domain. The manuscript argues that YU20 reproduces the observations better than BT09 under snow-covered, high-latitude conditions at the

study site, while citing previous work (Xie et al., 2025; Dai et al., 2020) showing that BT09 performs better under snow-free or marine conditions. However, YU20 together with the ground snow-chemistry module is applied uniformly across the entire modeling domain, including regions discussed in the results that are not predominantly snow-covered (e.g., the Bohai Sea and the Beijing-Tianjin-Hebei coastal region; lines 452-454). The ground-surface reactions (Table 1) appear to be parameterized based on surface-temperature categories rather than an explicit snow-cover mask, even though the underlying N2O5 uptake coefficients and ClNO2 yields were derived from snowpack-specific studies (Wang et al., 2020; Jeong et al., 2023). Additionally, although the Supplement presents ERA5 snow-cover, snow-depth, snow-density, and albedo datasets, it is unclear whether these products are actually used to determine where snowpack chemistry is active, or are only used to verify the representativeness of the assumed snow properties. Please clarify whether snowpack reactions are restricted (or weighted) according to snow-cover fraction, or whether temperature alone serves as the proxy for snow presence. If the latter, please justify this assumption, particularly for regions with little or no snow cover where the manuscript still discusses the impacts of snowpack chlorine chemistry.

Response:

We sincerely thank the reviewer for this very insightful and critical comment. We realize that our original manuscript did not clearly articulate the implementation of snowpack chemistry in the model, which led to the reviewer's reasonable concerns. Below we provide a detailed clarification of our modeling setup.

Point 1: Dynamic selection between YU20 and BT09 schemes based on snow cover

In the CAMx chemical mechanism code, we did not apply the YU20 scheme uniformly across the entire modeling domain. Instead, we implemented an explicit conditional switching scheme within the surface chemistry module based on real-time snow cover information. Specifically, for each model grid cell (at 27 km × 27 km resolution), we added a judgment statement that dynamically selects between the two parameterization schemes according to the following criterion:

- **If** snow water equivalent (SWE) > 0.01 m **or** snow depth > 0.01 m → the grid cell is considered snow-covered → **YU20 scheme** is applied;
- **Else** → the grid cell is considered snow-free → **BT09 scheme** is applied.

This dynamic switching is executed at each model time step, meaning that the choice between YU20 and BT09 is not a static domain-wide assignment but a time-varying and spatially explicit process that responds to the evolving snow conditions throughout the simulation period. Therefore, for regions with little or no snow cover (e.g., the Bohai Sea and the Beijing-Tianjin-Hebei coastal region), the model automatically defaults to the BT09 scheme, which is appropriate for snow-free or marine conditions. The YU20 scheme is only activated in grid cells where substantial snowpack is present (e.g., Northeast China during winter). This addresses the reviewer's concern about the applicability of YU20 in non-snow-covered regions.

Line:279-281: *"Given the above enhancements, the YU20 and BT09 schemes were selected for snow-covered and snow-free regions, respectively, in the subsequent scenario simulations."*

Point 2: Clarification of temperature-based parameterization in Table 1

We also recognize that the temperature-based categorization of $\gamma(N_2O_5)$ and $\phi(ClNO_2)$ in Table 1 may have caused confusion regarding whether temperature serves as a proxy for snow presence. We would like to clarify that temperature is not used as a proxy for snow cover; rather, it is a simplified practical approach for model computation. In reality, the uptake coefficient of N_2O_5 ($\gamma(N_2O_5)$) and the $ClNO_2$ yield ($\phi(ClNO_2)$) on snow surfaces are fundamentally determined by the ionic concentrations within

the snowpack and the liquid brine layer fraction (fbrine), as described in detail in the Supplemental Information (Text S1). To facilitate the implementation in the numerical model, we derived a simplified relationship between these parameters and surface temperature (illustrated in Figure S2), which serves as a convenient proxy for the underlying physicochemical conditions (e.g., brine layer formation is strongly temperature-dependent). This temperature-based lookup table is merely a computational simplification and should not be interpreted as temperature being the sole or primary criterion for snow presence.

Point 3: Snow depth and reaction interface

In addition to the scheme selection described above, snow depth also directly influences the model's treatment of heterogeneous reactions through its effect on the reactive surface area. As snow accumulates, the porosity and total surface area of the snowpack increase, providing a larger reaction interface for the uptake of atmospheric pollutants deposited onto the surface. Furthermore, the penetration depth of deposited species into the snowpack, as well as the actinic flux (and thus photolysis rates) within the snow, are both modulated by snow depth and snow albedo (France et al., 2011). These dependencies are accounted for in our model through the coupled snowpack chemistry module.

Point 4: Revisions made to the manuscript

To prevent any future misunderstanding, we have made the following revisions to the manuscript:

1. In **Section 2.3**, we have added a clear description of the dynamic snow-cover-based switching mechanism between the YU20 and BT09 schemes, explicitly stating the SWE/snow depth threshold (0.01 m) and the time-varying nature of the selection;
2. In the caption of **Table 1** and the corresponding text, we have clarified that the temperature-based $\gamma(N_2O_5)$ and $\phi(ClNO_2)$ values are a practical computational simplification, and that the underlying dependencies (on ion concentrations and fbrine) are fully described in Text S1 and Figure S2;

France J L, King M D, Lee-Taylor J, et al. Calculations of in-snow NO2 and OH radical photochemical production and photolysis rates: A field and radiative-transfer study of the optical properties of Arctic (Ny-Ålesund, Svalbard) snow[J]. Journal of Geophysical Research: Earth Surface, 2011, 116(F4).

Q7: Readability of multi-panel figures. Figures 4, 5, 6, 7, and 8 pack many panels with only caption text to distinguish rows/columns. Since N2O5 changes very little across scenarios in several of these, consider moving those panels to the SI, and add explicit column/row headers directly above the panels (e.g., "Y0," "Y3," "Diff," "%Diff").

Response: We thank the reviewer for the constructive suggestion regarding the readability of the multi-panel figures. We have carefully revised Figures 4, 5, 6, 7, and 8 in accordance with your advice.

Specific comments

Q8: Section 2.2 (model configuration, ~line 146): 29 vertical layers are specified, please state the model top height.

Response:

We thank the reviewer for pointing out this omission in our model configuration description. We agree that specifying the model top height is essential for readers to fully understand the model setup and to evaluate the vertical extent of the simulation domain.

To address this issue, we have added a detailed description of the WRF vertical layers in Section 2.2 (lines 146). Specifically, we have included a new table (Table 1) that lists the full vertical stratification of the WRF model. The model top is set at 17,083 m, corresponding to a pressure level of 50 hPa. This configuration ensures that the model domain extends well above the planetary boundary layer and covers the majority of tropospheric chemical and dynamical processes relevant to our study.

The added text now reads as follows:

"The WRF model was configured with 29 vertical layers, with the model top located at 17,083 m (50 hPa).

Table 1. Detailed table of optimized vertical level settings for the WRF model

Level	Sigma	Height (m)	Pressure (mb)	Depth (m)
29	0	17083	50	2531
28	0.04	14552	88	2472
27	0.1	12080	145	2153
26	0.175	9927	216	1636
25	0.25	8291	288	1334
24	0.325	6957	359	1134
23	0.4	5823	430	674
22	0.45	5149	478	621
21	0.5	4528	525	577
20	0.55	3951	573	540
19	0.6	3411	620	408
18	0.64	3003	658	389
17	0.68	2614	696	372
16	0.72	2242	734	357
15	0.76	1885	772	344
14	0.8	1541	810	330
13	0.84	1211	848	229
12	0.87	971	877	156
11	0.89	815	896	154
10	0.91	661	915	151
9	0.93	510	934	75
8	0.95	361	953	73
7	0.96	288	962	73
6	0.97	215	972	72
5	0.98	143	981	58
4	0.988	85	989	35
3	0.993	50	993	29
2	0.997	21	997	21
1	1	0	1000	-

Q9: Section 2.3 (~line 160): Define pNO3 at first use.

Response: We thank the reviewer for this careful observation. We agree that abbreviations should be defined upon first use to ensure clarity for all readers.

Following this suggestion, we have revised Section 2.3 (line 169) in the manuscript. Specifically, we have expanded "pNO_3" to "particulate nitrate (PNO_3)" at its first occurrence in the manuscript.

Q10: Lines 228-230: "the resulting nitric acid further stabilizes the reaction system" is unclear, please rephrase, and add a reference or show the relevant reaction pathway.

Response: We thank the reviewer for pointing out the inaccuracy in our previous explanation. We have re-evaluated the mechanism and corrected the text in Lines 224–230. We removed the incorrect statement regarding the relative reaction rates of hydrolysis versus chlorination.

Instead, we have clarified that the low $ClNO_2$ concentration is primarily driven by the limitation of the precursor N_2O_5. The revised text emphasizes that abundant chloride reactants are available in the winter environment of Northeast China, making N_2O_5 the limiting factor. We also explicitly cited the observation during period T4 (where N_2O_5<120 pptv yielded no $ClNO_2$ peak) to support this conclusion.

Revised Text (for Lines 240–248):

"This phenomenon is attributed to the role of N_2O_5 as the primary precursor of $ClNO_2$. In winter, the northeastern region of China exhibits abundant chloride-containing aerosols, providing a non-limiting reservoir of reactive chloride. Consequently, the formation of $ClNO_2$ is governed predominantly by the availability of N_2O_5 rather than by chloride supply. This is evidenced by the observation that during T4, when N_2O_5 mixing ratios remained below ~120 pptv, no discernible $ClNO_2$ peaks were detected, despite the persistent presence of chloride species. The positive correlation between N_2O_5 and $ClNO_2$ further supports that the latter's production is precursor-limited under the prevailing winter conditions."

Q11: Lines 237-239: After the statement that photolysis is "accompanied by the release of chlorine atoms", please provide an appropriate reference.

Response: We thank the reviewer for this careful observation. We agree that the statement regarding chlorine atom release during photolysis should be supported by appropriate references to substantiate the scientific background.

Following this suggestion, we have added two relevant references at the corresponding position in the manuscript (lines 261–263), which respectively address the photolytic production of chlorine atoms from snowpack chemistry and from aerosol-related $ClNO_2$ sources:

$$ClNO_2 + h\nu \rightarrow Cl + NO_2$$

Jeong, D., McNamara, S. M., Chen, Q., Mirrielees, J., Edebeli, J., Kulju, K. D., Wang, S., Hayani, L., Kirpes, R. M., and Lata, N. N.: Quantifying the contributions of aerosol-and snow-produced ClNO2 through observations and 1D modeling, ACS Earth Space Chem., 7, 2548-2561, https://doi.org/10.1021/acsearthspacechem.3c00237, 2023.

Thornton J. A., Kercher J. P., Riedel T. P., Wagner N. L., and Cozic J.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, Nature, 464(7286): 271-274, https://doi.org/10.1038/nature08905, 2010.

Q12: Figure 2 caption: The gray shaded (T1, T2, T3, T5, T6) and cyan shaded (T4) regions are explained only in the body text, not in the caption, please add this. Please also note in the caption what happened around 2/26 (for example, "no measurements available"), since there is an apparent data gap.

Response: We thank the reviewer for this constructive suggestion. We agree that the figure caption should be self-explanatory and that the data gap should be clearly indicated to avoid any confusion for readers.

Following this suggestion, we have revised the Figure 2 caption to include: (1) a clear explanation of the gray and cyan shaded regions, and (2) a note specifying the period of missing data due to instrument maintenance.

The revised Figure 2 caption now reads as follows:

"Figure 2. Field observations of N_2O_5 and $ClNO_2$ at the DLS station from February 23 to March 3,2024. (a) Time series of N_2O_5 and $ClNO_2$ mixing ratios. The gray shaded periods (T1, T2, T3, T5, and T6) represent episodes with concurrent elevated N_2O_5 and $ClNO_2$ peaks, while the cyan shaded period (T4) indicates an episode where no such concurrent peak was observed. The data gap between 14:00 on February 25 and 10:00 on February 26 is due to instrument maintenance, during which no measurements were available. (b) Diurnal variations of N_2O_5 and $ClNO_2$ over the entire observation period."

Q13: Figure 2, panel (b): The ClNO2 axis unnecessarily extends to 800 pptv, please rescale to the actual data range for better visibility.

Response: Following this suggestion, we have rescaled the $ClNO_2$ axis in Figure 2b to better represent the actual data range.

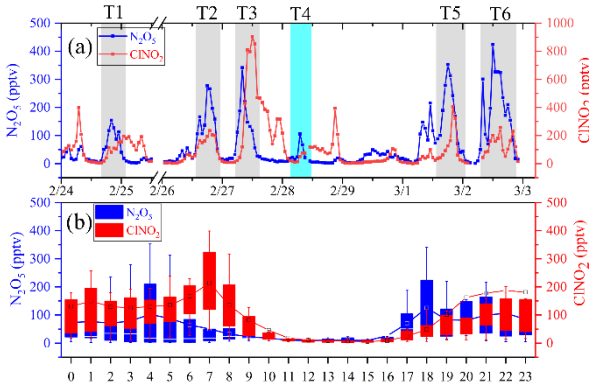


Figure 2 Field observations of N_2O_5 and $ClNO_2$ at the DLS station from February 23 to March 3, 2024. (a) Time series. The gray shaded periods (T1, T2, T3, T5, and T6) represent episodes with concurrent elevated N_2O_5 and $ClNO_2$ peaks, while the cyan shaded period (T4) indicates an episode where no such concurrent peak was observed. The data gap between 14:00 on February 25 and 10:00 on February 26 is due to instrument maintenance, during which no measurements were available. (b) Diurnal variation.

Q14: Line 268: "winter chlorine emissions" is used without definition, please specify what this refers to.

Response: We thank the reviewer for this careful observation. We agree that the term "winter chlorine emissions" was too vague and should be explicitly defined to specify the chemical species involved.

Following this suggestion, we have revised lines 295-297 in the manuscript to clearly identify the chlorine-containing species. The revised sentence now reads as follows:

"This improvement can be attributed to the significant impact of atmospheric humidity changes under snow-covered conditions, along with an increase in anthropogenic chlorine emissions (e.g., Cl_2, PCI, HCI, and HOCI) during winter in high-latitude regions."

Q15: Section 3.2.1, ~page 10 (first use of MB, NMB, RMSE, IOA): These acronyms are used starting here but only formally defined at page 12, please define at first use.

Response: We thank the reviewer for this careful observation. We agree that all acronyms should be defined at their first appearance in the text to ensure clarity for readers.

we have revised section 3.2.1 (lines:270-275) to include the full definitions of MB, NMB, RMSE, and IOA at their first use.

Q16: Section 3.2.2 / Figure 3: The model appears to overestimate N2O5 relative to observations, but this is not discussed. Please comment and, if possible, suggest an explanation.

Respond: We highly appreciate the reviewer's valuable comment regarding the overestimation of simulated N_2O_5 relative to observational data in Section 3.2.2 and Figure 3. Relevant discussion on this simulation bias has been supplemented in the revised manuscript, and detailed explanations are provided below.

1. As a major nocturnal reservoir of NOx ($NO+NO_2$), atmospheric N_2O_5 concentration is strongly governed by its nitrogen-oxide precursor emissions. Although the Multi-resolution Emission Inventory for China (MEIC) adopted in this study is a widely-used domestic emission dataset, prominent uncertainties remain in its NOx emission estimates. Our comparison reveals that modelled NO_2 concentrations exceed in-situ observations. The northeastern research area consists of urban industrial-source zones and snow-covered rural background regions. As documented by Chen et al. (2025), the MEIC v1.4 inventory improperly disperses industrial emissions across rural grids over Northeast China. The over-allocated rural-grid NOx emissions consequently drive-up simulated pollutant concentrations.
2. Spatial-scale mismatch also accounts for part of the N_2O_5 overestimation. The model runs at a horizontal resolution of 27 km, while field observations are collected from discrete single monitoring sites. Grid-averaged outputs cannot perfectly represent the localized environmental conditions at observation stations.
3. Furthermore, considerable uncertainties exist in the parameterization describing heterogeneous hydrolysis of N_2O_5 within the chemical mechanism (Zhou et al., 2025), which introduces extra deviations to N_2O_5 simulation.

In summary, the model-predicted overestimation of N_2O_5 is jointly induced by three factors: (1) uncertainties in NOx emissions derived from the MEIC inventory; (2) spatial-scale mismatch between the 27-km model grids and point-site observations; (3) inherent uncertainties in the parameterization scheme for N_2O_5 heterogeneous hydrolysis.

References

Chen L, Cai Z, Sun K, et al. Deriving regional and point source nitrogen oxides emissions in China from TROPOMI using the directional derivative approach with nonlinear chemical lifetime fitting[J]. Earth System Science Data Discussions, 2025, 2025: 1-28.

Zhou W, Du H, Liu M, et al. Role of N_2O_5 heterogeneous hydrolysis in summer nitrate formation in Beijing: insights from direct measurements and model simulations[J]. npj Clean Air, 2025, 1(1): 40.

Q17: Line 342: pCl and HCl values are discussed but it's not stated where they are shown (in Figure 5), please cite the figure explicitly here.

Response: We appreciate the reviewer for pointing out this omission. We have revised the text on Line

372 to explicitly cite Figure 5 when discussing the values of pCl and HCl.

Q18: Section 3.3.2 (ClNO2 flux discussion, ~lines 409-421): The comparison to McNamara et al. (2021) and Jeong et al. (2023) never states the flux produced by the authors' own simulation (this study), please add it for direct comparison.

Response: We thank the reviewer for this constructive suggestion. We agree that when comparing our results with previous studies, it is essential to clearly present the $ClNO_2$ production efficiency (yield) derived from our own simulation to enable a direct and meaningful comparison.

To address this issue, we have taken the following actions:

Point 1: We have added the $ClNO_2$ yield range from our study to Table 4, alongside the literature values from McNamara et al. (2021), Jeong et al. (2023), and other relevant studies, enabling readers to directly compare our results with previous findings.

Point 2: In our study, the $ClNO_2$ yield was not prescribed as a fixed value. Instead, it was dynamically calculated at each model time step based on the simulated ion concentrations (e.g. chloride and nitrate) within the snowpack and the liquid brine layer fraction (fbrine). The detailed calculation procedure and the governing equations are provided in the Supplemental Information (Text S1 or Text R10).

Point 3: To facilitate the application of this dynamic scheme in the numerical model, we further simplified the dynamic calculations into a temperature-dependent interval parameterization, with the specific $ClNO_2$ yield values defined for different temperature ranges in Table 1. This parameterization serves as a practical computational approximation that captures the overall temperature dependence of the yield while maintaining computational efficiency.

Q19: Section 3.3.2, "unknown ClNO2 sources" framing (~lines 369-373): Suggest citing Wang, H., Peng, C., Wang, X., Lou, S., Lu, K., Gan, G., Jia, X., Chen, X., Chen, J., Wang, H., Fan, S., Wang, X., and Tang, M., "N2O5 uptake onto saline mineral dust: a potential missing source of tropospheric ClNO2 in inland China," *Atmos. Chem. Phys.*, 22, 1845-1859, 2022 (https://doi.org/10.5194/acp-22-1845-2022).

Response: We thank the reviewer for recommending this relevant and important reference. We agree that Wang et al. (2022) is highly pertinent to our discussion of unknown CINO2 sources, as their work identifies saline mineral dust as a potential missing source of tropospheric CINO2 in inland China through N_2O_5 uptake-a mechanism that may also have implications for our study region.

Following this suggestion, we have added the citation to Wang et al. (2022) in Section 3.3.2 (lines 399-401). The revised sentence now reads as follows:

"*The existing air quality models typically underestimate CINO2 concentrations compared to observed values, suggesting the presence of unknown sources (Wang et al., 2022).*"

Reference:

Wang, H., Peng, C., Wang, X., Lou, S., Lu, K., Gan, G., Jia, X., Chen, X., Chen, J., Wang, H.: N_2O_5 uptake onto saline mineral dust: a potential missing source of tropospheric ClNO2 in inland China, Atmospheric Chemistry and Physics, 22(3), 1845-1859, https://doi.org/10.5194/acp-22-1845-2022, 2022.=-20223889

Q20: Table 4: This literature summary of ClNO2 yields omits the values derived from the authors' own study (this study), please add a row for direct comparison.

Response: we have added a new row to Table 4 that presents the $ClNO_2$ yield range derived from our

own observation.

Q21: Line 401: Consider showing the N2O5 ↔ NO3 + NO2 thermal reaction (temperature-dependent, k_T) explicitly here, since the text refers to low winter temperatures favoring the equilibrium shift toward N2O5.

Response: We thank the reviewer for this constructive suggestion. We agree that explicitly showing the thermal dissociation reaction of N_2O_5 and its temperature-dependent rate constants at this location will help readers better understand the discussion of how low winter temperatures favor the equilibrium shift toward N_2O_5.

Following this suggestion, we have added the reaction equation and the corresponding rate constant expressions from userguid V7.1 in Section 3.3.2 (line 401), as follows:

$$N_2O_5 \leftrightarrow NO_2 + NO_3$$

Where the rate constant expression: $k(0) = 3.6E\text{-}30(T / 300)\ \text{^}\ \text{-}4.1$ and

$k(\text{inf}) = 1.90E\text{-}12(T / 300)\ \text{^}\ 0.2$.

We believe this addition clarifies the temperature dependence of the N_2O_5 thermal quilibrium.

Q22： Section 3.4.1 / Figure 7 (lines 441-442): The text does not clearly state that the figure's panels show OH, RO2, and HO2, please clarify in the caption or text.

Response: We thank the reviewer for this careful observation. We agree that the figure caption should clearly indicate what each panel represents to ensure that readers can immediately understand the figure without referring back to the main text.

we have revised the Figure 7 caption to explicitly state that the three columns of panels correspond to OH, RO_2 and HO_2 radicals, respectively. The revised caption now reads as follows:

Figure 7. The quantitative contribution of different pathways of chlorine chemistry on atmospheric oxidizing capacity. The three columns of panels represent the changes in concentrations of OH (left), RO_2 (middle), and HO_2 (right) radicals, respectively. (a–f) The bottom two rows in each group show the corresponding relative changes (%).

Q23: Section 3.4.1: Are there any direct gas-phase Cl + VOC reactions in the mechanism, or is Cl's entire effect on AOC indirect (via changes to OH/RO2/HO2, which then affect VOC oxidation)? Please state this explicitly.

Response: Thank you for this thoughtful comment. We explicitly clarify the chlorine-driven effects on atmospheric oxidation capacity (AOC) under the CB6r2h halogen-chemistry mechanism here and have added this statement in the revised manuscript.

The CB6r2h chemical mechanism incorporates a total of 88 halogen-related reactions (CAMx-v7.10 User Guide). Both direct gas-phase reactions between chlorine atoms (Cl) and volatile organic compounds (VOCs), as well as indirect radical-mediated influences on AOC, are included in this scheme.

For direct pathways, atomic-chlorine-initiated VOC oxidation covers multiple classes of organic species:

Alkanes: Cl + CH_4, Cl + PAR, Cl + ETHA and Cl + PRPA;

Alkene: Cl + ISOP;

Oxygen-containing VOC-related reactions, such as OH + FMCL and ClO + MEO_2, which

involve halogen-radical-VOC interactions.

Apart from direct VOC consumption, chlorine chemistry exerts an indirect control on AOC by perturbing the cycling of core atmospheric radicals (OH, HO_2 and RO_2). Representative reactions including OH + HCl → Cl and OH + HBr → Br illustrate the mutual interaction between halogen species and the hydroxyl radical. Such halogen-radical feedback alters ambient-OH abundance and further modulates the overall VOC-oxidation capacity.

In conclusion, chlorine affects atmospheric oxidation capacity via dual pathways in the CB6r2h mechanism: direct gas-phase oxidation against VOCs, and indirect regulation of radical cycles for OH, HO_2 and RO_2.

Table A-2. Listing of the CB6r2h halogen mechanism (see Table A-1 for a complete listing of CB6r2). k_{298} is the rate constant at 298 K and 1 atmosphere using units in molecules/cm^3 and 1/s. For photolysis reactions k_{298} shows the photolysis rate at a solar zenith angle of 60° and height of 600 m MSL/AGL. See Table A-3 for species names. See Section 3.1 on temperature and pressure dependencies.

Number	Reactants and Products	Rate Constant Expression	k_{298}
1	CL2 = 2 CL	Photolysis	1.56E-3
2	HOCL = CL + OH	Photolysis	1.34E-4
3	CL + O3 = CLO	k = 2.30E-11 exp(-200/T)	1.18E-11
4	CLO + CLO = 0.3 CL2 + 1.4 CL	k = 1.63E-14	1.63E-14
5	CLO + NO = CL + NO2	k = 6.40E-12 exp(290/T)	1.69E-11
6	CLO + HO2 = HOCL	k = 2.70E-12 exp(220/T)	5.65E-12
7	CLO + NO2 = CLN3	Falloff: F=0.6; n=1 k(0) = 1.80E-31 (T/300)^-3.4 k(inf) = 1.50E-11 (T/300)^-1.9	2.34E-12
8	CLN3 = CLO + NO2	Falloff: F=0.6; n=1 k(0) = 4.48E-5 (T/300)^-1 exp(-12530/T) k(inf) = 3.71E+15 (T/300)^3.5 exp(-12530/T)	3.11E-4
9	CLN3 = CLO + NO2	Photolysis	4.97E-6
10	CLN3 = CL + NO3	Photolysis	4.67E-4
11	CLN3 + H2O = HOCL + HNO3	k = 2.50E-22	2.50E-22
12	OH + HCL = CL	k = 6.58E-13 (T/300)^1.2 exp(58/T)	7.93E-13
13	OH + FMCL = CL + CO	k = 3.67E-11 exp(-1419/T)	3.14E-13
14	FMCL = CL + CO + HO2	Photolysis	6.10E-8
15	CLO + MEO2 = CL + FORM + HO2	k = 4.10E-13 exp(-800/T)	2.80E-14
16	CL + CH4 = HCL + MEO2	k = 6.60E-12 exp(-1240/T)	1.03E-13
17	CL + PAR = HCL	k = 5.00E-11	5.00E-11
18	CL + ETHA = HCL + 0.991 ALD2 + 0.991 XO2H + 0.009 XO2N + RO2	k = 8.30E-11 exp(-100/T)	5.93E-11
19	CL + PRPA = HCL + ACET + 0.97 XO2H + 0.03 XO2N + RO2	k = 1.40E-10	1.40E-10
20	CL + ISOP = FMCL + ISPD + 0.96 XO2H + 0.04 XO2N + RO2	k = 4.30E-10	4.30E-10
21	HCL + N2O5 = CLN2 + HNO3	k = 6.00E-13	6.00E-13
22	CLN2 = CL + NO2	Photolysis	2.86E-4

Ramboll. The CAMx v7.1 User's Guide. Version 7.1, Ramboll, https://www.camx.com/Files/CAMxUsersGuide_v7.10.pdf, 2021.

Q24: Section 3.4.1 (OH/RO2/HO2 differences, Fig. 7): The reported concentration changes are numerically small, please put these into relative context against some known process or baseline magnitude so their significance can be judged; if still negligible, consider moving this analysis to the SI.

Response: We thank the reviewer for this constructive suggestion. We agree that the absolute concentration changes of OH/RO_2/HO_2 reported in this section are numerically small. To improve the readability and focus of the main text, we have moved the analysis of these radicals and the corresponding Figure 7 to the Supplementary Information (SI).

Q25: Line 550: It is unclear whether the referenced "observed" MDA8 O3 value is a real observation or model output, please clarify. More broadly, is there any O3 measurement available to compare to in this section?

Respond: We appreciate the reviewer's careful reminder for clarification on the MDA8 O_3 data at line 550.

The MDA8 O_3 value mentioned here corresponds to model-simulated output rather than field observation data. To eliminate textual ambiguity, we have replaced the misleading word "observed" with "simulated" throughout the revised manuscript.

For the whole-model evaluation, we have validated the simulation performance of secondary pollutants (including $PM_{2.5}$ and ozone) alongside N_2O_5 and $ClNO_2$ against in-situ observations. Nevertheless, the analysis in this section aims to quantify the ozone contribution yielded by different chemical pathways through scenario-run differences. This part focuses on the incremental ozone contribution from individual pathways instead of direct model-observation comparison. Accordingly, we compare our pathway-induced ozone increments with results from existing published literature.

Q26: Section 2.2 (model description, ~lines 149-153): Please briefly characterize the anthropogenic chlorine emission schemes. What are the major emission sources, and how do the two schemes differ?

Respond: The EDGAR and MEIC datasets described at Lines 149–153 are general multi-species anthropogenic emission inventories for common air pollutants and greenhouse gases, rather than specialized chlorine emission inventories. For anthropogenic chlorine simulation in our model, we independently adopt the dedicated anthropogenic chlorine emissions inventory (ACEI) as the chlorine input dataset. Below we briefly characterize EDGAR and MEIC, elaborate their major source sectors, and summarize their core differences as requested.

1. Brief characterization & major emission sources of the two general inventories

- EDGAR (Emissions Database for Global Atmospheric Research)

Developed by the Joint Research Centre (JRC) of the European Commission, EDGAR is a global bottom-up emission database with consistent IPCC accounting frameworks.

Spatial resolution: Global 0.1° × 0.1° gridded data, covering more than 220 countries worldwide.

Covered species: Greenhouse gases, conventional air pollutants, particulate matter, BC/OC, and speciated VOCs.

Major anthropogenic source sectors: Energy production, industrial processes, transportation, residential & commercial combustion, agriculture, and waste disposal.

Application: Widely adopted for global and regional atmospheric modeling research to provide complete cross-border emission backgrounds.

- MEIC (Multi-resolution Emission Inventory for China)

Developed by the research team led by Zhang Qiang and He Kebin at Tsinghua University, MEIC is a China-localized bottom-up gridded emission inventory.

Spatial resolution: Standard 0.25° × 0.25°, with coverage limited exclusively to mainland China.

Species: SO_2, NO_x, CO, NMVOC, NH_3, $PM_{2.5}$, PM_{10}, BC, OC, CO_2, and refined VOC speciation.

Major anthropogenic source sectors: Five core domestic categories, including power generation, industry, residential combustion, transportation, and agriculture.

Application: The most widely used localized emission dataset for Chinese regional air quality simulations, built on detailed domestic statistical activity data.

2. Key differences between EDGAR and MEIC

- **Spatial coverage range**

EDGAR provides continuous global gridded emissions across all countries and regions. MEIC only contains emission information within China's territory. If MEIC were used alone for our simulation domain (which includes land areas outside China), all non-Chinese grid cells would be assigned zero emissions, introducing severe artificial biases in lateral boundary transport and distorting the final simulation results.

- **Data accuracy and spatial granularity within China**

MEIC incorporates high-resolution domestic activity statistics and region-specific emission factors tailored to China's industrial and energy conditions, delivering far more reliable emission estimates over Chinese grids. Although EDGAR also features a 0.1° global grid, its activity data for China rely on coarse cross-border statistical records and carry larger regional uncertainties.

- **Target research scope**

EDGAR is designed for global-scale climate and atmospheric studies, while MEIC is optimized for China-specific air pollution and carbon mitigation research.

3. Hybrid emission processing strategy adopted in this study

To balance complete global boundary conditions and high-fidelity emissions over China, we construct a merged general emission field for conventional pollutants: EDGAR serves as the baseline global dataset, and all Chinese grid cells are overwritten with refined MEIC emission values. This configuration avoids artificial zero-emission boundaries and improves the accuracy of pollutant simulations within China. Notably, this merging scheme only applies to conventional air pollutants and GHGs; anthropogenic chlorine concentrations are separately imported from the dedicated ACEI inventory, independent of EDGAR and MEIC.

Q27: Supplementary Information, Table S2: The k'2f term is given as a fully numeric expression for Yu (2020) ("3.0×10^4 x [H2O]"), but for Bertram (2009) it is left as the symbolic formula with no numeric values for beta and delta provided anywhere in the manuscript or SI.

Respond: We have now supplemented the fitted-out numerical values of the two parameters derived from the observational results in Bertram et al. (2009), and added a clear footnote beneath Table S2. The calibrated constants are $\beta = 1.15\times10^6\pm3\times10^5 s^{-1}$ and $\delta = 1.3\times10^{-1}\pm5\times10^{-2}$ M^{-1} (Bertram et al., 2009). All symbolic-form parameters are now annotated in the revised supplementary table for readability.

Table S2. Heterogeneous chemical reaction parameter scheme of N_2O_5 on aerosol surface

Parameter	CAMx Bertram (2009)	Yu (2020)
Source	Laboratory simulation	Field observations (China)
k'_{2f}	$\beta - \beta e^{(-\delta[H_2O])}$	$3.0 \times 10^4 \times [H_2O]$
k_3/k_{2b}	0.06	0.033
k_4/k_{2b}	29	3.4
k_4/k_3	483	103

Note: Determined values: $\beta = 1.15\times10^6\pm3\times10^5 s^{-1}$; $\delta = 1.3\times10^{-1}\pm5\times10^{-2}$ M^{-1} (Bertram et al., 2009).

Q28: Supplementary Information, Figure S3: The panel titles shown in the figure do not match the titles given in the corresponding figure caption, please correct these.

Respond: Thank you for pointing out the inconsistency between panel titles and the figure caption in

Supplementary Figure S3. We have revised the sub-panel labels of Figure S3 to keep them consistent with the caption. The caption is kept as:

"Figure S3. Monthly average spatial distribution of snow parameters (snow depth, snow cover, snow albedo, and density)."