

*Thank you for your careful review and constructive suggestions. These suggestions are quite valuable to us, and help improve our manuscript a lot.*

Point-to-point responses

*We appreciate the reviewers for their valuable and constructive comments, which are very helpful for the improvement of the manuscript. We have revised the manuscript carefully according to the reviewers' comments. We have addressed the reviewers' comments on a point-to-point basis as below for consideration, where the reviewers' comments are cited in **black**, and the responses are in **blue**.*

Zhang et al present a measurement report of reactive halogen species in the arctic using MAX-DOAS to measure BrO and IO. The authors present a clear report of measurements and methods along with satellite validation. I recommend publication after correction of one broader issue with the paper and some minor corrections.

Broad issues: The article has “Measurement Report” in the title, but the paper reads more like a research article. The challenge here is that it doesn't present any new findings, just more data verifying findings and publications of 20 years ago with new data. As a measurement report, this is good. As the conclusions read, it feels like the authors are overstating the novelty of the work. All of the trends and correlations and explanations are the same as previous studies. I recommend that the authors modify language in the abstract and conclusions to more consistently match the “Measurement Report” nature of the article consistent with the title. The authors allude to chemistry model optimization but don't provide any justification as to which models or how these data would be applied.

Re: Thank you for this comment.

We sincerely appreciate the reviewer's professional and constructive feedback. The abstract and conclusions have undergone substantial revisions to better align with the manuscript's designation as a "Measurement Report." Specifically, we have refined the terminology in these sections to emphasize the dataset's role as a high-precision benchmark rather than a new mechanism discovery. Furthermore, we have explicitly identified the specific models (e.g., GEOS-Chem) that our data support and provided a detailed justification for how these observations can be applied to optimize parameterization schemes.

*The following content has been added:*

**Abstract:**

Arctic reactive halogen species (RHS) are pivotal in mediating polar air-sea interactions and global biogeochemical cycling. Based on ship-borne MAX-DOAS observations from the 12th Chinese National Arctic Research Expedition (July to September 2021), this study provides a systematic performance assessment of TROPOMI, GEMS, and GOME-2 satellite products in the Arctic ( $R > 0.6$ ). Our findings indicate that tropospheric BrO variability is predominantly governed by sea-ice contact (SIC) duration, accounting for 48.63% of the variance in a Generalized Additive Model (GAM). Potential BrO source regions are identified in western Greenland, the high-latitude Canadian Arctic, and the Marginal Ice Zone (MIZ). Implementing a dynamic boundary layer height (BLH) constraint enhanced the correlation from 0.73 to 0.77. Meteorological conditions exert significant modulation on activation efficiency. For instance, correlations reached 0.84 under

southwesterly flow, whereas snowfall reduced the correlation from 0.84 during snow-free periods to 0.61 during snowfall events. Conversely, IO spatial variability is primarily driven by marine biogenic emissions, exhibiting a positive correlation with chlorophyll-a concentrations ( $R = 0.64$ ) and clustering in phytoplankton-rich regions such as the Bering Strait. In the marginal ice zone (MIZ), the moderate correlation between BrO and IO ( $R = 0.5$ ) suggests their co-evolution at the shared ice-ocean-atmosphere interface. These high-resolution datasets provide critical a priori constraints for atmospheric chemistry models. Specifically, they facilitate the optimization of polar emission parameterizations and reactive halogen budgets, thereby enhancing the predictive accuracy of GEOS-Chem and WRF-Chem for polar atmospheric processes and improving the robustness of global climate assessments.

## **Conclusion**

This study presents the spatial distributions of trace gases (NO<sub>2</sub>, HCHO, BrO, and IO) captured during the 12th Chinese Arctic Scientific Expedition (July - September 2021) along a transect from Shanghai to the Arctic. Utilizing ship-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS), we establish a robust ground-truth baseline to assess the performance of TROPOMI, GEMS, and GOME-2 satellite products in polar regions. Statistical analyses yield correlation coefficients between 0.61 and 0.79, validating the efficacy of satellite remote sensing for monitoring atmospheric composition over the Arctic and adjacent oceans. Our findings demonstrate that tropospheric BrO is primarily controlled by Sea Ice Contact (SIC) duration, which accounts for 48.63% of the variance in a Generalized Additive Model (GAM). Potential BrO source regions are identified in western Greenland, the high-latitude Canadian Arctic, and the Marginal Ice Zone (MIZ). The R value between BrO and SIC improved from 0.73 to 0.77 after incorporating dynamic boundary layer height (BLH) constraints. Furthermore, meteorological conditions significantly modulate bromine activation: southwesterly winds enhanced the correlation to 0.84, whereas snowfall weakened it from 0.87 to 0.61. In contrast to the complex physico-chemical regulation of BrO, IO variability is predominantly driven by biogenic emissions, correlating strongly with chlorophyll-a ( $R=0.64$ ), particularly in phytoplankton-rich regions like the Bering Strait. Notably, we observe a distinct spatial divergence between the source regions of sea-ice-driven BrO and biogenic IO. However, a moderate correlation ( $R=0.5$ ) persists within the MIZ, suggesting that the ice-ocean-atmosphere interface facilitates shared precursors or formation pathways for these reactive halogens. In conclusion, this study provides high-precision validation for Arctic satellite retrievals and systematically characterizes the drivers of polar halogen species. These data offer critical constraints for optimizing emission parameterizations and halogen budget accounting in chemical transport models, such as GEOS-Chem and WRF-Chem.

### **Minor Corrections:**

Pagination is inconsistent and starts over at the various sections.

Re: Thank you for this comment.

We apologize for the formatting error in the previous version of the manuscript. We have corrected the pagination settings to ensure that page numbers are now consistent and continuous throughout the entire document, from the title page to the references.

Line 37: “provides critical in-situ validation”. Here we are missing how this data is critical.

Re: Thank you for this comment.

We sincerely thank the reviewer for their professional and constructive feedback. We recognize that the term "in situ" is technically imprecise in this context, as MAX-DOAS is a remote sensing technique rather than a point-source measurement method. Accordingly, we have replaced "in situ" with "ship-based MAX-DOAS" throughout the revised manuscript.

The scientific value of this dataset is primarily reflected in the following four aspects:

1. Direct Comparability: Since both satellite sensors and ship-based MAX-DOAS measure slant SCDs, the resulting data inter-comparisons are direct, robust, and highly credible.
2. Bridging Observational Gaps: Oceans account for approximately 70% of the Arctic, yet these regions remain largely devoid of long-term ground-based observation stations. Our ship-based campaign provides a rare and critical dataset for these observational "blind spots."
3. Robust Benchmark: Extreme Arctic conditions such as high surface albedo, low temperatures, and persistent cloud cover frequently compromise satellite retrievals. These ship-based measurements offer a reliable benchmark for evaluating satellite sensor performance under such challenging scenarios.
4. Model Constraints: This dataset provides essential observational constraints for optimizing emission schemes in chemical transport models, such as GEOS-Chem and WRF-Chem, thereby enhancing the accuracy of global climate assessments.

*The following content has been added:*

- 1). By filling critical observational gaps in the Arctic marine boundary layer, this report provides essential empirical constraints for upgrading the parameterizations of halogen chemical cycles in atmospheric chemistry models (e.g., GEOS-Chem and WRF-Chem), thereby enhancing the accuracy of polar air–sea interaction simulations and global climate assessments.
- 2). Ground-based stations deliver high resolution ship-based DOAS data but are predominantly located in terrestrial or island regions of Antarctica and the Arctic.

Line 75: "marine boundary layer are severely scarce" Remove severely, scarce is sufficient unless you quantify how much the data is available compared to how much is necessary, severe sounds like an overstatement.

Re: Thank you for this comment.

We thank the reviewer for their professional and constructive suggestion. The word "severely" has been removed to avoid potential overstatement and to maintain a more objective and scientific tone. The sentence has been revised to: "...data on NO<sub>2</sub>, HCHO, and RHS in the marine boundary layer are scarce".

*The following content has been added:*

Since approximately 70% of polar areas consist of oceans, data on NO<sub>2</sub>, HCHO, and RHS in the marine boundary layer are scarce.

Lines 81-82, 88, 99: Phrases are in quotation marks. Are these direct quotes from an un-cited source? Where are these phrases coming from? In general, direct quotations are not appropriate, and if given,

the reference must follow immediately from the single source.

Re: Thank you for this comment.

We appreciate the reviewer's suggestion regarding the use of quotation marks. We would like to clarify that these terms were not direct quotations from unreferenced literature. Our initial intent in using quotation marks was to highlight specific scientific concepts and research objectives. Following the reviewer's advice, we have removed all quotation marks throughout the revised manuscript.

*The following content has been added:*

- 1). Moreover, it enables point line integrated mobile observations aboard research vessels, serving as a robust tool for studying atmospheric composition in polar oceanic regions.
- 2). In recent years, Arctic sea-ice extent has exhibited a significant declining trend, which directly impacts key processes in polar atmospheric chemistry (e.g., the extent and intensity of bromine explosions).

Lines 93-100: Here the authors refer extensively to a figure found in the Supplement. If the article spends this much space on the figure, it needs to be in the regular paper and not the supplement.

Re: Thank you for this comment.

We sincerely thank the reviewer for these professional and constructive suggestions. To ensure the main text remains focused on the study's core findings, the previously over-detailed description of Fig. S2 has been significantly condensed in the revised manuscript. The discussion now prioritizes the scientific significance of sea ice variations for halogen chemistry. Accordingly, Fig. S2 is retained in the supplementary materials.

*The following content has been added:*

Significant reductions in Arctic sea-ice extent and concentration were observed in August 2021, particularly in the Beaufort Sea and Bering Strait (Fig. S2). These changes alter the saline water-sea surface-atmosphere exchange interface and influence marine phytoplankton distribution, which may further modulate the release and formation of reactive halogen species.

Line 174, Fig 2: The various fit windows only show the fit of the species of interest for the specific fit window. NO<sub>2</sub> for instance, is fitted in all of those windows but only shown in one. Other fitted species help to understand fit interference and structured residuals. Are there major differences in the NO<sub>2</sub> retrieved values, even within overlapping windows in the UV? Please provide some commentary (or reference to previous work) as to why these fitting windows were chosen? The cited references span a variety of groups and instruments, it would be good to know why these were chosen (for instance, why does the BrO fit not use the Ring parameter?).

Re: Thank you for this comment.

We sincerely thank the reviewer for their professional and constructive feedback. To address the consistency of NO<sub>2</sub> retrievals across different spectral ranges, we compared the DSCDs obtained from the UV (335-370 nm) and visible (460-490 nm) windows (Fig. R1). For a representative fit, the UV retrieved DSCD was  $1.90 \times 10^{16}$  molecule.cm<sup>-2</sup>, (Fig. R1a) showing excellent agreement with the  $1.92 \times 10^{16}$  molecule.cm<sup>-2</sup> obtained from the visible window (Fig. R1b). Correlation analysis (Fig. R2) further demonstrates strong consistency between the two windows, with a correlation coefficient of  $R = 0.83$ .

Regarding the reviewer's inquiry on the selection of the UV fitting window: The choice is primarily motivated by the high surface albedo of sea ice and snow in the UV range within the Arctic (Meinander et al., 2008; Perovich et al., 1998; Warren, 2019). Research has demonstrated that high surface albedo significantly enhances multiple scattering within the marine boundary layer, thereby increasing the sensitivity of MAX-DOAS to trace gases in the lower atmosphere (Wagner et al., 2007; Bösch et al., 2018). Consequently, the UV window has been widely adopted for NO<sub>2</sub> retrieval in various polar and shipborne studies (De Laat et al., 2024; Luo et al., 2018; Wagner et al., 2007, 2010; Xing et al., 2023).

Finally, we apologize for the clerical oversight regarding the BrO fit settings. In our actual retrieval process, the Ring parameter was indeed included to account for Rotational Raman Scattering (the Ring effect). This error has been corrected in the revised manuscript, and the updated settings are detailed in Table R1.

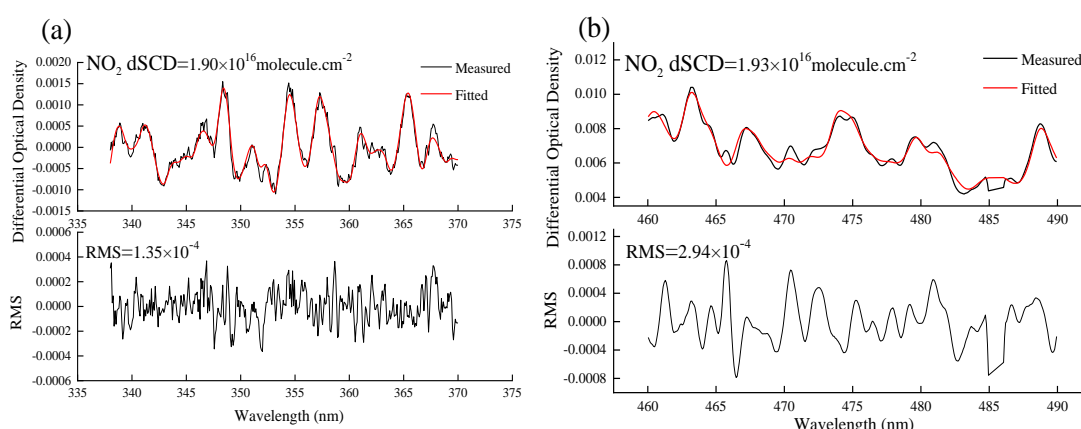


Figure R1. Example of NO<sub>2</sub> fitting in the UV (335-370 nm) and visible (460-490 nm) windows.

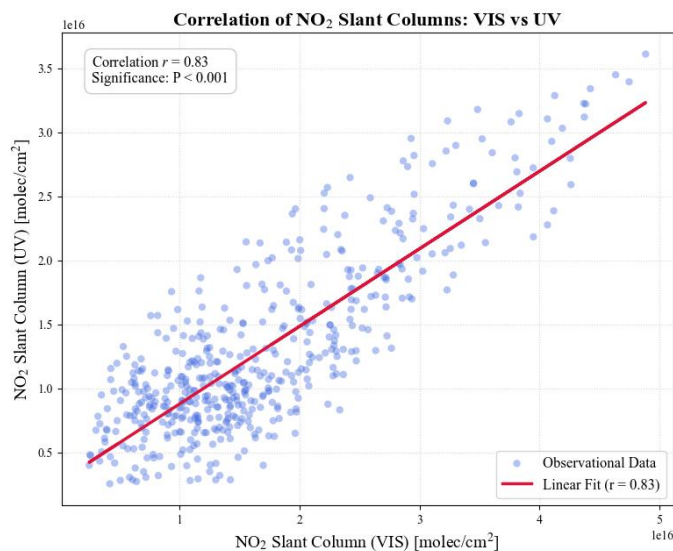


Figure R2. Correlation analysis of NO<sub>2</sub> DSCDs retrieved from the UV (335-370 nm) and visible (460-490 nm) fitting windows.

Table R1. Retrieval settings of IO, BrO, HCHO, and NO<sub>2</sub>

Parameter	Reference	Fitting intervals (nm)
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		NO <sub>2</sub>	HCHO	BrO	IO
Fitting wavelength		338-370	336.5-359	346-358	416-439
NO <sub>2</sub> (298K)	(Vandaele et al., 1998)	√	√	√	√
NO <sub>2</sub> (220K)	(Vandaele et al., 1998)	√	√	√	√
HCHO (298K)	(Meller and Moortgat, 2000)	√	√	×	√
HONO (296K)	(Stutz et al., 2000)	×	×	√	√
O <sub>3</sub> (243K)	(Serdyuchenko et al., 2014)	√	×	√	√
O <sub>3</sub> (223K)	(Serdyuchenko et al., 2014)	√	×	√	√
O <sub>4</sub> (293K)	(Thalman and Volkamer, 2013)	√	√	√	√
BrO (223K)	(Fleischmann et al., 2004)	√	√	√	×
H <sub>2</sub> O	(Rothman et al.2009)	×	×	×	√
IO	(Carlos Gómez Martín et al., 2005)	×	×	×	√
Ring	Calculated with QDOAS	√	√	√	√
Polynomial degree		5th order	5th order	5th order	3rd order
Intensity offset		Constant	Constant	Constant	Constant

Bösch, T., Rozanov, V., Richter, A., Peters, E., Rozanov, A., Wittrock, F., Merlaud, A., Lampel, J., Schmitt, S., de Haij, M., Berkhout, S., Henzing, B., Apituley, A., den Hoed, M., Vonk, J., Tiefengraber, M., Müller, M., and Burrows, J. P.: BOREAS - a new MAX-DOAS profile retrieval algorithm for aerosols and trace gases, *Atmospheric Measurement Techniques*, 11, 6833-6859, <https://doi.org/10.5194/amt-11-6833-2018>, 2018.

De Laat, A., Van Geffen, J., Stammes, P., Van Der A, R., Eskes, H., and Veefkind, J. P.: The Antarctic stratospheric nitrogen hole.: Southern Hemisphere and Antarctic springtime total nitrogen dioxide and total ozone variability as observed by Sentinel-5p TROPOMI, *Atmospheric Chemistry and Physics*, 24, 4511-4535, <https://doi.org/10.5194/acp-24-4511-2024>, 2024.

Luo, Y., Si, F., Zhou, H., Dou, K., Liu, Y., and Liu, W.: Observations and source investigations of the boundary layer bromine monoxide (BrO) in the Ny-Ålesund Arctic, *Atmospheric Chemistry and Physics*, 18, 9789-9801, <https://doi.org/10.5194/acp-18-9789-2018>, 2018.

Meinander, O., Kontu, A., Lakkala, K., Heikkilä, A., L, Y., and Toikka, M.: UV albedo of arctic

snow in spring, *Atmospheric Chemistry and Physics Discussions*, 8, <https://doi.org/10.5194/acpd-8-4155-2008>, 2008.

Perovich, D., Roesler, C., and Pegau, W.: Variability in Arctic-sea ice optical properties.: *Journal of Geophysical Research*, 103, 1193-1208, <https://doi.org/10.1029/97JC01614>, 1998.

Wagner, T., Ibrahim, O., Sinreich, R., Frieß, U., von Glasow, R., and Platt, U.: Enhanced tropospheric BrO over Antarctic-sea ice in mid-winter observed by MAX-DOAS on board the research vessel Polarstern, *Atmospheric Chemistry and Physics*, 7, 3129-3142, <https://doi.org/10.5194/acp-7-3129-2007>, 2007.

Wagner, T., Ibrahim, O., Shaiganfar, R., and Platt, U.: Mobile MAX-DOAS observations of tropospheric trace gases, *Atmospheric Measurement Techniques*, 3, 129-140, <https://doi.org/10.5194/amt-3-129-2010>, 2010.

Warren, S. G.: Optical properties of ice and snow.: *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences*, 377, <https://doi.org/10.1098/rsta.2018.0161>, 2019.

Xing, C., Xu, S., Song, Y., Liu, C., Liu, Y., Lu, K., Tan, W., Zhang, C., Hu, Q., Wang, S., Wu, H., and Lin, H.: A new insight into the vertical differences in NO<sub>2</sub> heterogeneous reaction to produce HONO over inland and marginal seas, *Atmospheric Chemistry and Physics*, 23, 5815–5834, <https://doi.org/10.5194/acp-23-5815-2023>, 2023.

Line 199 and 203: References such as this should be formatted as Wagner et al. (2010).

Re: Thank you for this comment.

We sincerely appreciate the reviewer's professional and constructive feedback. The citation in the relevant section has been corrected to Wagner et al. (2010). Furthermore, we have performed a comprehensive line-by-line audit of the entire manuscript to ensure that all in-text citations strictly adhere to the journal's formatting guidelines.

*The following content has been added:*

Details of this method are provided in Wagner et al. (2010). Radiative calculations in this study were conducted with the atmospheric radiative transfer model SCIATRAN 2.2 (Rozanov et al., 2005).

Line 284: Refers to chapters. Is this a carryover from a dissertation format? Please update to the proper terminology.

Re: Thank you for this comment.

We thank the reviewer for identifying this terminological inaccuracy. The term has been standardized as "sections" throughout the revised manuscript. Furthermore, we have performed a meticulous audit of the entire text to ensure consistent nomenclature when referring to the various components of the paper.

*The following content has been added:*

The relationship between IO and chlorophyll-a concentrations will be analyzed in depth in subsequent sections, incorporating synchronously observed marine ecological data (see Section 3.3.1 for details).

Line 296: This line needs a break after 'excluded'. Something is missing in the structure of the sentence, please revise.

Re: Thank you for this comment.

We are grateful to the reviewer for identifying the significant lapses in scientific logic and sentence structure. To address the problematic phrasing, we have rectified the sentence by incorporating an explicit causal connective ("due to") and refining the punctuation to ensure improved syntactical clarity and logical flow.

*The following content has been added:*

To ensure data reliability, satellite products with high cloud contamination (effective cloud fraction > 0.4) and poor retrieval quality (relative error > 100%) were excluded. This filtering is necessary because cloud particles significantly interfere with ultraviolet-visible radiation transmission, altering the optical path length and leading to biases in trace gas retrieval.