

Review #1

This is an excellent paper on the chemistry of BrCN, which previously has never been reported to be present in the atmosphere. Detected by two chemical ionization mass spectrometers during the ATom flights, this molecule appears to form in regions where active bromine chemistry is especially prevalent, i.e., in the polar springtime boundary layer when ice/snow is present. The paper presents the measurements, does an excellent job at working through likely BrCN formation and loss pathways, and is well written.

An interesting observation is that high amounts of CHBr₃ (relative to CH₂Br₂) correlate with BrCN. Given that HOBr is believed to form CHBr₃ from reactions with DOM, this is indirect support for abiotic formation of BrCN via the multiphase reaction of HOBr with HCN. This makes sense given that this reaction (Reaction S4) has such a large rate constant (close to diffusion limited) in water. HCN is also measured to help constrain the chemistry but an open question, as usual, is the pH of the surface where the multiphase chemistry is occurring. The paper also lays open the potential for there being a biotic source of BrCN (and HOBr).

The main point raised in the paper is that HOBr/Br- chemistry is required for bromine recycling and so, if HOBr is instead reacting to form BrCN, the ozone and mercury loss chemistry shuts down. To my knowledge, this is a new suggestion.

The vertical gradient of the BrCN mixing ratio implies a fairly short lifetime in the atmosphere on the order of days, which is argued to be due to some type of aerosol loss process. Given the high reactivity of BrCN with a range of organic functional groups, it is not unreasonable to hypothesize that complex organobromine compounds are forming as a result.

[We thank the Reviewer for the positive comments, and wish to answer the questions and comments as directly as possible.](#)

Questions:

1. Were the calibrations for both CIMS instruments performed with mixing ratios close to the ambient values? That point said, a factor of two agreement between different instruments, ionization schemes, and calibration procedures is pretty darn good for a molecule of this type.

[1. The NOAA ToF I-CIMS was calibrated at mixing ratios in the range of 18 - 68 ppbv, and the CIT-CIMS was calibrated for BrCN over the range of 3 - 130ppbv. Both instrument responses](#)

were found to be linear over these ranges. These aspects will be added to the Experimental Methods section.

2. Has anyone ever reported measurements of cyanide ion in ice/snow?

2. We are not aware of any CN^- measurements snow or ice in background polar regions. Conversations with researchers experienced in snow measurements in polar regions (J. Dibb, personal communication, 2023) and a literature search has revealed only reports of contamination of urban snow by ferrocyanide additives used in de-icing salts. This may be because of very low values in general, or due to the fact that CN^- would represent dissolved-N available for biological use (nutrients), hence may not be stable for long periods.

3. Was there any evidence of BrCN in heavily biomass burning impacted regions, where the HCN mixing ratio would be very high?

3. There are two points of comparison that show the BrCN from WF is quite small-to-negligible: BB plumes observed either transported from Siberia (Oct 27, 2017) or off the coast of Africa during the ATom project did not show BrCN above detection limit. Measurements with the same I-CIMS in WF plumes encountered on Aug 3, 2019, during FIREX-AQ (Warneke et al., 2023) showed BrCN to be at most 1 pptv, barely above detection limit ($\text{DL} \cong 0.3 \text{ pptv}$ during FIREX-AQ) in 1 min averaged data. These observations were in the middle of plumes in which HCN was over 40 ppbv (measured by the same CIT-CIMS).

4. It is reasonable to assume that HCN is the reactive species for this multiphase chemistry. That said, is it possible that acetonitrile may also be reactive? Probably not, but just wondering.

4. A cursory literature search reveals numerous papers in which reactions of HOBr/Br₂ with organic species were carried out in acetonitrile solution. We deduce from this that acetonitrile is essentially inert with respect to reaction with these active Br compounds.

5. My main question: The paper presents data of active bromine species, such as BrCl and BrO. Presumably the CIMS also measured signals for HOBr and Br₂. Why were those signals (even if not calibrated) not shown? It would have been interesting to see HOBr/BrCN correlations.

5. Unfortunately, we have found that HOBr and Br₂ measurements are not reliable due to interconversion on our inlet (Neuman et al., 2010), and have stated this (lines 184-185, original paper). But we will show the HOBr and Br₂ signals for the 5/19/18 flight in our revised manuscript as described in more detail as a response to Reviewer 2.

6. We know from (unpublished) experience that the AMS shows signal for aerosol bromine during ozone depletion events in the Arctic. To my knowledge, these signals have never been calibrated, but it might nevertheless be fun to look at the AMS signals to see if there is any evidence for where some of the Br is going, if indeed it is getting lost via irreversible reactions of organics with BrCN. For example, are there organo-N-Br ion fragments detected in the particles during ozone depletion events?

6. There were no apparent increases in the AMS measurement of non-refractory bromine for the periods when we saw elevated BrCN on Oct 19, 2018, and overall, the measurement was quite low, 1.4 ± 0.7 pptv equivalent mixing ratio. We are not aware of any AMS data product that encompassed organo-N-Br ions or related fragments.

My recommendation is to publish this paper after the authors decide whether they want to address the above questions.

We have chosen to address the Reviewer's questions as best we can.

References:

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- Warneke, C., Schwarz, J. P., Dibb, J., Kalashnikova, O., Frost, G., Al-Saad, J., Brown, S. S., Brewer, W. A., Soja, A., Seidel, F. C., Washenfelder, R. A., Wiggins, E. B., Moore, R. H., Anderson, B. E., Jordan, C., Yacovitch, T. I., Herndon, S. C., Liu, S., Kuwayama, T., Jaffe, D., Johnston, N., Selimovic, V., Yokelson, R., Giles, D. M., Holben, B. N., Goloub, P., Popovici, I., Trainer, M., Kumar, A., Pierce, R. B., Fahey, D., Roberts, J., Gargulinski, E. M., Peterson, D. A., Ye, X., Thapa, L. H., Saide, P. E., Fite, C. H., Holmes, C. D., Wang, S., Coggon, M. M., Decker, Z. C. J., Stockwell, C. E., Xu, L., Gkatzelis, G., Aikin, K., Lefer, B., Kaspari, J., Griffin, D., Zeng, L., Weber, R., Hastings, M., Chai, J., Wolfe, G. M., Hanisco, T. F., Liao, J., Campuzano Jost, P., Guo, H., Jimenez, J. L., Crawford, J., and Team, T. F.-A. S.: Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ), *Journal of Geophysical Research: Atmospheres*, 128, e2022JD037758, <https://doi.org/10.1029/2022JD037758>, 2023.