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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "First-year sea-ice contact predicts bromine monoxide (BrO) levels better than potential frost flower contact" *by* W. R. Simpson et al.

W. R. Simpson et al.

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In the "General" section of the review, the referee brings up three main criticisms with the manuscript.

a) The referee suggests that the data are "rather limited and correlations appear to be not significant". We stand by the data as significant and not limited, and the other review concurrs. Our data are the peak ODE season. At earlier times, there is very little sunlight with which to measure BrO, and later there is melt, which is likely to change the surface salinity and thus a different situation. Therefore, we have selected the main 40 days of the ODE season, but which carries essentially the whole year's data for 2005. Our correlations are clearly significant. We report a R-squared of 0.55,

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for the correlation of BrO with FYI. That is a very significant correlation, particularly based upon other things not dealt with in this very simple analysis (i.e. boundary layer height, temperature, etc.). As a point of reference, the article of Zeng et al. [GRL, 2003] reports correlations between ozone and a model of R = 0.58 (R-squared = 0.33) for Barrow data, and a lower correlation for Alert data. Their data are over the period DOY 60-120, which is quite close to the time period of our study, where we examine DOY 80-120. Therefore, the literature clearly accepts R-squared values significantly smaller than our report's value. The intercept at zero FYI contact is essentially zero BrO, which is what one would expect if the FYI areas are bromine sources. The R-squared for correlation between BrO and PFF, however is very small and not significant. Additionally, the correlation line predicts maximal BrO when PFF is zero, which is a clear problem with the theory that PFF produces BrO. Therefore, our point is that PFF is a much worse correlate than FYI. However one does the statistics, we see no way that PFF would be able to explain these data better than FYI. It is later suggested by the referee that temporal autocorrelation could be affecting the statistical analysis. We have considered this suggestion and find that autocorrelation is not responsible for the high correlation between FYI and BrO, as discussed in the section below.

As to the question of whether Barrow is general, we have added many comments in the text that these data pertain to airmasses impacting Barrow, Alaska. It is a future question to the community to see if what we have observed during the 2005 ODE season in Barrow applies to other locations. The point of our paper is that we have tried the PFF method to see if it is able to predict BrO impacting Barrow. The novel finding is that PFF is incapable of predicting BrO impacting Barrow, which is different than what would be expected by the published literature. This is a very significant finding that needs to be reported in the literature. We also find that FYI is capable of predicting a great deal of the variance in BrO, which points to alternative hypotheses for the origin of bromine and are discussed in the paper.

b) The referee says that ‘‘a good theory has to explain the BrO distribution observable by satellite sensors". It is beyond the scope of our paper, which is about whether FYI or PFF can explain a ground-based data set of BrO measurements in Barrow, to explain satellite BrO data. We don't even have access to these BrO data. We are making a significant point – that PFF does not predict Barrow BrO data as well as does FYI. Our data use ground-based BrO measurements. We prefer these measurements because they allow hourly (instead of daily) measurements of BrO and have reduced issues with regard separation of stratospheric and tropospheric BrO, and, to some extent, reduced issues with respect to cloud-top reflection. They are observed at Barrow, and we discuss that this observation is specific to airmasses impacting Barrow. Other locations may have different behavior, as pointed out in the manuscript, and we would encourage the community to make measurements at other locations with this sort of analysis to see if what we find for Barrow is relevant to other locations. It is possible, which we discuss in the manuscript, that locations near and downwind of polynyas might have BrO sourced from those locations. We note that airmasses impacting Barrow typically are far downwind of polynya impact, which leads to the very low PFF contact durations. However, it is important to note that the BrO levels we see here are as high as are seen in other locations around the Arctic, and thus there must be a strong source of BrO in airmasses impacting Barrow. The correlation analysis shows that FYI contact rather than PFF contact is that source for these airmasses. As far as explaining satellite remote sensing data, we would encourage the community to attempt a correlation similar analysis and show that PFF has a statistically significant correlation with satellite-derived BrO. The analysis reported in Kaleschke et al., [2004] shows case studies where there is a spatial correlation, but not an objective view over a long time-series, as reported here. Kaleschke et al., 2004 did not apply a blind statistical analysis to show that their correlation is significant, as we have done here. Therefore, our study is advancing the study of halogen activation.

We have made an open public comment on the work of Bottenheim and Chan [2006], which was unknown to us at the time of submission of this manuscript. We have added text to the manuscript specifically addressing this reference, which we believe provides

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a match between FYI and ozone depletion, reinforcing our findings in this manuscript.

c) The referee suggests that our publication needs to explain mercury deposition distributions. Although we agree that it is a goal of the study of halogen activation to be able to predict mercury deposition, we feel that the linkage between mercury deposition and halogen activation involves too many steps to be a clear marker of halogen activation. Polynyas are a major region of convective mixing, evaporation of water, and condensation of water as those wet airmasses cool. Therefore, we expect that polynyas are major regions of atmospheric scavenging. The deposition of mercury requires two things; the mercury must be oxidized, then brought to the ground. Because polynas cause vertical mixing and intense atmospheric scavenging, we argue that they may more effectively deposit mercury than the more stable, non-convective, air motion typical over unbroken sea ice. Therefore, we feel that mercury is a very indirect measure of the location of halogen activation and that high levels are likely to be caused by scavenging in the convective polynya environment. Also, we leave open the possibility that polynyas may source BrO; we simply have little polynya influence and thus cannot speak of their influence. All of these ideas; however are beyond the scope of this paper and cloud the issue that we wish to present – BrO is better predicted by FYI than PFF for airmasses impacting Barrow during the spring 2005 ODE season.

To discuss this point in the manuscript, we have added ‘‘In another Antarctic study, Bargagli et al. [2005] found that mercury deposition was enhanced near a coastal polynya, which can be interpreted as indicating that halogen activation was localized to the polynya environment. However, mercury deposition is a very indirect measure of the location of halogen activation, and the high mercury levels observed could be caused by enhanced scavenging in the convective polynya environment (Douglas et al. [2005]).”

Specific issues (replies to each point in the referee’s comments):

*** On the title: We considered removing PFF from the title but find that a title lacking

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PFF would not be nearly as accurate. The referee suggests calling the manuscript ‘‘a trajectory study”, which is true, but the same trajectories are used for both the PFF and FYI analysis, so simply using ‘‘trajectory” would not be able to express the main point of the paper – that PFF and FYI give different results. The term ‘‘potential frost flowers" must be used because there may be frost flowers not detected in PFF (discussed in the manuscript). We have added ‘‘observed at Barrow, Alaska" to the title to clarify that our publication is specifically about airmasses impacting Barrow.

*** While we concur that there is a broad spectrum between frost flowers and salty snow and division is somewhat arbitrary, we feel it is critical to understand the mechanism by which sea salts become atmospherically accessible. To simply say ‘‘sea salt" would not allow us to discuss how future climate scenarios may impact halogen activation, which is a key part of the manuscript. Specifically, we added the sentence: ‘‘These two hypotheses for how sea salt bromide becomes atmospherically accessible and chemically activated are clearly limiting endpoints of a spectrum halogen activation mechanisms and the actual process in nature is likely to involve a mixture of both processes."

*** On the trajectory passing near the polynya. The trajectory does not directly impact the polynya, as discussed in the manuscript. It is stated in the text that ‘‘the radial averaging algorithm causes overlap of the trajectory with open water shown in the vicinity".

*** The HYSPLIT model was forced by the NCAR FNL data, and this has been explicitly mentioned in the text.

*** We have changed the reference to the sea ice data to ‘‘http://iup.physik.uni-bremen.de:8084/", which is at the Institute of Environmental Physics, Bremen, as requested.

*** We have implemented rules for dispersion of the airmasses; however these rules do not affect the finding of the manuscript – that BrO is better predicted by FYI than PFF.

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Calculations without dispersion have similar PFF timeseries and no improvement in its behavior, as mentioned in the text. While it would be possible to make a much more detailed model of the complete atmospheric column involving vertical and horizontal mixing, clouds, etc., this is not our point and is beyond the scope of our manuscript. We have mentioned that these factors are likely to degrade the correlation between FYI and BrO, but we still find that a good correlation with an analysis that only includes one factor. This finding is very convincing that FYI is important. We hope that future workers develop more complex models, but it is beyond our scope. The specific modification to the text is: ‘‘Substituting this algorithm for the simple pixel-by-pixel calculation only had a minor effect on the PFF time series, smoothing some high-frequency noise, and was chosen as more realistic."

*** The referee asks about BrO sinks. They are clearly present in the system; however we have not carried out a modeling study that could include such a BrO sink. We are simply correlating FYI and BrO. We find that BrO seems to increase with increasing FYI contact (up to three days), but this is a finding not an assumption. It is specifically mentioned that the relationship between BrO and FYI is not necessarily linear.

*** We have substituted the reference to Kwok (2004), as requested.

*** We have removed the points with the strongest ODEs because they affect the partitioning between Br and BrO. At low O3, reactive Br (sum of Br and BrO) repartitions to being mostly Br and is not visible as BrO. Therefore, at low O3, BrO becomes a poor marker of reactive bromine. Thus, we have removed these data from the correlation, as is discussed in the manuscript. We have added a sentence mentioning: ‘‘At the times when ozone is depleted $<$1 ppbv, FYI is generally elevated and PFF is low to absent, in agreement with the findings from other airmasses."

*** We have considered the idea that temporal autocorrelation could affect the ability of PFF to predict BrO or significantly decrease the ability of FYI to predict BrO and find that it is not an issue. To address this point, we have averaged our hourly data to

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daily averages. These daily data have less temporal autocorrelation. Because our and other data show significant BrO and O3 variations on hourly timescales, it is likely that daily averaged data are not temporally autocorrelated. The daily data, when analyzed for R-squared show precisely the same values as when presented in hourly averages. A figure showing these data has been included in the editor's ‘‘response” file. Therefore, autocorrelation does reduce the number of points in the scatterplot, but not the correlation coefficient. Therefore, our findings are significant whether they have some temporal autocorrelation or not. Because we have found that autocorrelation is not an issue, we have left the original analysis in the manuscript.

Further issues and suggestions:

*** We have discussed precisely what we mean by first year ice with more clarity in the introductory section. It is mentioned by the referee that there are other ways to define ice types, but we seek the simplest definition here for clarity. Defining first year ice as the ice that formed that winter is extremely effective in predicting BrO impacing Barrow. We hope that future publications address the subltles of ice types in more detail and through this analysis may be able to improve on our correlation. To clarify the text, we have added, ‘‘It is clear that this definition of contact with first-year sea ice is very crude, but as it will be shown, even such a crude definition is capable of explaining a great deal of the variance observed in BrO."

*** We have discussed Bottenheim and Chan [2006] both in the open public discussion as a comment, and in the manuscript. The ‘‘cold spots" are not related to actual temperatures in Bottenheim and Chan but to low ozone sources (and thus not ‘‘hotspots" but low level sources – ‘‘cold spots").

*** The referee mentions that PFF is relatively small in his data set for this timeperiod (March / April), which is in good agreement with our findings that there is very little PFF influence on Barrow during this time. We have added text specifically mentioning that these PFF impacts are very low.

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*** We do not have the satellite data and it is beyond the scope of this paper to try to mesh in data that are quite different is spatial / temporal coverage as well as different in the effects of clouds on the data. Therefore, we have not used satellite data in this publication. We encourage the community to carry out similar analysis to what we have done using satellite data; however.

*** There are a few other BrO data sets that are in the community, but not very many, and additionally, we do not have access to these data. Friess does have such a data set from Antarctica, but he is not a co-author. Others may have such data, but they are not co-authors. Therefore, it is beyond the scope of this paper to analyze either satellite or other station data. We would encourage the persons who have these other BrO data to make such an analysis.

*** We have discussed above that mercury deposition is an extremely complex and incompletely understood process that involves multiple steps – oxidation, scavenging, vertical transport, re-emission, etc. Therefore, it is a poor tracer of halogen activation. We have also never claimed that ‘‘first-year sea ice is the only source of reactive bromine". We leave open the possibility that there are other sources of reactive bromine at many places. Our paper is simply to say that a source recently under discussion in the literature – Potential Frost Flowers is not the only source of reactive bromine. In these data, we find that FYI appears to be a better source area.

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