

Review for the manuscript entitled: "Characteristics of tropospheric ozone depletion events in the Arctic spring: Analysis of the ARCTAS, ARCPAC, and ARCIONS measurements and satellite BrO observations" by J.-H. Koo et al.; MS No.: acp-2012-359

The manuscript describes a comprehensive set of ozone measurements in the Arctic and correlates them to BrO data. Also a rather extended discussion of satellite-derived tropospheric BrO measurements is given. The manuscript contains valuable information on both, tropospheric O₃ and BrO and is thus within the scope of ACP.

However, there is a fundamental issue that has to be resolved before the manuscript can be published in ACP: In this manuscript 6 new tropospheric partial column BrO "products" are introduced, none is validated and the products differ very substantially from each other. Before any conclusions can be drawn where satellite-derived tropospheric BrO partial columns are involved (and the majority of the conclusions in this manuscript are based on BrO tropospheric partial columns) these products must be validated and the authors must settle on a single product. This will require a thorough discussion on the relative merits of the different products. Another solution could be using an established, validated product instead of 6 new ones, for instance the BrO product developed by Choi et al. (2012, see literature list in the manuscript). In fact, according to the acknowledgement Sungyeon Choi was involved in analyzing the satellite data, why not using that BrO-product? Alternatively tropospheric BrO data from satellite and the discussion based on the data (correlation analyses) could be removed from the manuscript.

[Main response]

We thank the reviewer for the review. We are fully aware of the need for validating tropospheric BrO products derived from satellite measurements. It is an issue that the whole community has been and is currently struggling with. The problem is that there are no adequate validation measurements to evaluate the satellite products during the ARCTAS-ARCPAC experiments. We will provide the details in the latter part of this discussion.

Sungyeon Choi was a graduate student in Y. Wang's group until about 2 years ago. She worked with the products in this paper initially and then worked on the products in her paper a few months before she left our group. After she moved to Goddard, she decided to limit her paper to 1 set of products, which did make that paper easier to understand. In her paper, the stratospheric BrO was estimated by scaling to GEOS-5 model simulated CFC-12 and 7 ppt of BrO was added to represent the injection of VSL (very short lived) bromine species into the stratosphere. Choi et al. (2012) discussed the large uncertainty of the VSL BrO value. A photochemical steady state model was then used to estimate stratospheric BrO distributions. More detailed description can be found in that paper.

The paper by Choi et al. (2012) is very good since the uncertainty associated with each retrieval step is described (although they cannot be quantified). Keeping in mind that among the figures in that paper, only Figure 6b showed a "good" comparison between in situ BrO measurements from DC8 and OMI tropospheric BrO columns, and Figures 9b

and 10b showed more problematic comparison between WP-3B and OMI tropospheric BrO columns. Those are case studies we mentioned in section 4 of this paper. More quantitative values were given in Tables 3 and 4 of that paper, even though the tables did not give the correlation coefficients as we did in this paper. It is unfortunate that there was no detailed discussion of the implications of the two tables in that paper. Table 3 showed reasonably good agreement between the tropospheric BrO columns estimated using DC-8 in situ measurements and from satellite measurements. Table 4, on the other hand, showed large disagreement between the tropospheric BrO columns estimated using WP-3B in situ measurements and from satellite data. The large differences between OMI and GOME2 derived BrO columns are also obvious in this table.

We stated in section 4 of this paper “During the ARCTAS experiment, BrO measurements were available in only two flights on April 16 and 17. Previous studies (Choi et al., 2012; Liao et al., 2012) showed good correlations between satellite retrieved column BrO and in situ observations. Although we did not use the same satellite BrO product in this study, we showed similar results for the 3 products we chose to use in this study (Fig. S1 in the Supplement). In contrast, neither Choi et al. (2012) nor this study found significant correlation between satellite retrieved tropospheric column BrO and in situ observations from 5 ARCPAC flights (April 12, 15, 18, 19, and 21). The reason is unclear. We note that there are 4 different estimates of stratospheric column BrO and two satellite total column measurements by combining Choi et al. (2012) with this study, which captures a reasonable range of stratospheric column BrO variation estimates.” The above statements summarized the agreement between this paper and that by Choi et al. (2012). It was not stated in the paper by Choi et al. (2012) that the OMI and GOME2 are validated in the sense that the products are the best to use. The reason is that good agreement was found in only **two** DC-8 flights with BrO measurements but not in **five** WP-3B flights with BrO measurements. We further stated in the same paragraph of section 4 “Without additional BrO measurements, a true validation study based on in situ BrO measurements is therefore infeasible.”

Because of the very limited BrO measurements, we then stated in section 4 “One approach is to focus on correlation analysis between tropospheric column BrO and other related in situ observations. The measurements of Br₂+HOBr were reported for 7 ARCTAS flights and 5 ARCPAC flights (Neuman et al., 2010; Liao et al., 2012) and soluble bromide measurements were also available in the ARCTAS flights (Liao et al., 2012). These measurements were more abundant and had more data points above the detection limits than BrO measurements.” And further, “In Fig. S2-4 in the Supplement, we showed that the 3 satellite products we selected are consistently correlated with these in situ measurements of bromine compounds for both ARCTAS and ARCPAC flights. Obviously these data cannot be used to evaluate the magnitude of estimated tropospheric column BrO.”

To sum up the long discussion above, there are only very limited in situ BrO measurements from ARCTAS and ARCPAC and they showed inconsistent results when compared to satellite-derived tropospheric BrO columns. The additional correlation analyses with Br₂+HOBr and soluble bromide measurement were meant to supplement

the correlation analysis with in situ BrO measurements; they were not meant to replace the analysis with in situ BrO measurements.

We stated in section 2.2.1 “Retrievals of tropospheric BrO columns from satellite measurements are quite uncertain, particularly in the estimate of stratospheric BrO columns (e.g., Choi et al., 2012). During our analysis period, in situ BrO observations are too limited and they do not provide enough quantitative constraints to validate satellite tropospheric BrO column products (the details will be discussed in section 4).” These statements reflect the discussion above.

There is not a single “validated” tropospheric BrO product. The question is if we can still use satellite BrO measurements to understand better the characteristics of ODEs. Please note that the goal of this paper is to understand ODEs. The goal is not to find the best tropospheric BrO column estimates, which cannot be done without additional observation constraints on stratospheric BrO (such as BrO from VLS Bry) and tropospheric BrO distributions. We then stated in section 2.2.1, it is possible to improve the understanding of ODEs using satellite data, “This lack of quantitative validation, however, does not imply that satellite BrO measurements do not provide useful information in the analysis of the ODE characteristics. For example, if ODEs were driven by BrO chemistry, we expect that the air mass of an ODE had encountered high BrO previously. The question to analyze is therefore if there is an enhancement of BrO along the back trajectory of the ODE air mass. A key point here is that the enhancement can be relative to BrO measurements in other regions. We do not necessarily need the absolute magnitude of BrO column or concentration. The statistical method to use is correlation analysis between BrO along the air mass back trajectory and ozone. In correlation analysis, it is the variation not absolute magnitude that matters.”

We then justified the reason to use three different estimates of stratospheric column BrO in section 2.2.1, “In order to take into account of the uncertainties in the estimates of stratospheric BrO vertical columns, we take the approach of using three different estimate methods. These methods give different estimates of latitudinal/longitudinal variations in stratospheric column BrO and consequently in tropospheric column BrO. Most importantly, the estimated stratospheric BrO columns using these methods do not introduce in the resulting tropospheric BrO columns an unphysical correlation with tropospheric ozone. Therefore the uncertainty in the retrieval method can reduce or even eliminate the (anti)correlations between ozone and BrO, but it should not produce false correlations consistently.” The key point here is that we do not need to differentiate the satellite products for the analyses we did in this paper.

We re-emphasized this point in section 2.2.1, by stating “If we can establish consistent (anti)correlations between ozone and time-lagged tropospheric BrO, we should be able to learn the characteristics of ODEs from the correlation information without the need to know if the magnitudes of tropospheric BrO columns are correct. In fact, even the values of (anti)correlations between ozone and BrO are not that important. It is the change of the (anti)correlation between ozone and BrO with time or altitude that provides useful

information on the importance of in situ chemistry relative to transport and on the vertical extent of bromine-driven ozone loss.”

We selected three products in the analysis. The difference between OMI-SCIA2ND and GOME2-SCIA2ND products represents the difference between the two satellites. GOME2-20th products used a different estimate of stratospheric column BrO, which is not dependent on SCIAMACHY measurements. The three products are all observation based. If the correlation analyses of ozone and these products show similar ODE characteristics, we are confident that the analysis results are not due to choosing OMI or GOME2 in the analysis or using a specific estimate method of the stratospheric BrO columns. We used in situ observations of BrO, Br₂+HOBr, and soluble bromide in the selection. If we only used DC-8 BrO (2 flights), the result is the same. As we stated before, there are more data of Br₂+HOBr, and soluble bromide. The correlation results of Br₂+HOBr, and soluble bromide are in qualitative agreement with using DC-8 BrO alone. The usage of Br₂+HOBr, and soluble bromide provides additional support to choosing the three products.

This is not to say that differentiation of satellite products is not important. We will discuss here briefly what will be needed in such an analysis. The reasons for product difference could be the instrument error, retrieval algorithm, cloud interference, and the estimates of the stratospheric BrO columns. It will take more than a devoted paper to make a statement that satellite X is better than satellite Y. We have no observation constraints to do it for BrO. The retrieval algorithm depends on the a priori profiles used. Choi et al. (2012) already discussed the difference of the BrO profiles observed between DC-8 and WP-3B. Because of high surface brightness, we do not have good information on clouds (amount or altitude). The retrievals were done assuming no cloud presence in Choi et al. (2012) as well as in this paper. Lastly the stratospheric BrO columns are obviously different from different methods. For example, the stratospheric BrO columns used by Choi et al. (2012) were based on a model simulation. In this paper, we used the RAQMS simulation. The Bry profiles used in the two models are probably different, the simulated BrO/Bry ratios are also probably different, and RAQMS did not include VSL Bry. However, we have no measurements of stratospheric Bry (either correlated with CFC-12 or from VSL bromine species) or BrO during the ARCTAS/ARCPAC period to know how and why one model result is better than the other. Again, how to differentiate the different products is an important question that we cannot answer since we do not have adequate measurements to evaluate these estimates. We reiterate the previous point that there are only very limited in situ BrO measurements from ARCTAS and ARCPAC and they showed inconsistent results when compared to satellite-derived tropospheric BrO columns. (Correlations with Br₂+HOBr and soluble bromide only provide qualitative constraints.)

The approach we used in the paper was finalized after carefully considering available data and measurements and doing tedious analysis work in the past several years. It may not be the perfect solution but we believe it is the best that one can do with available measurements. The approach works because the error added from each process is not correlated with tropospheric ozone as we stated previously. In other words, the

processing uncertainties only added white noise with respect to the correlation with tropospheric ozone.

The evaluation of satellite products is a complex problem. If the reviewer has further questions, we will try to answer in the interactive review process. We do not, however, believe that such detailed discussion on the validation of satellite BrO derived tropospheric columns (particularly with respect to the paper by Choi et al. (2012)) belongs to this paper. What we stated in section is adequate.

Detailed additional comments:

Page 16230, Lines 13-24: Are the diurnal variations average variations of all days during April 2008? What exactly is the meaning of a diurnal variation in the 10th percentile (i.e. values that are exceeded 90% of the time) of an average (?) diurnal variation. This needs through discussion.

[Response]

In the month of April, we have 30 data points for each hour (1 data point per day). We calculate the 10th percentile value based on these 30 data points (yes, the values will exceed 90% of the time on average) for each hour. The profile is generated by plotting the 24 hourly values. We will add this explanation in the text.

Figure 2 and Page 16231 lines 8ff: Only one of the 6 satellite BrO – retrievals is shown (GOME2-SCIA2ND), in the suppl. Material two more are shown (OMI-SCIA2ND, GOME2-20th) of which the latter (GOME2-20th) deviates significantly from the other two. What about the remaining three evaluations (see p. 16228, lines 18, 19)?

[Response]

We can add the other 3 monthly distributions if the reviewer insists. They are not included now since they are not used in the paper based on the evaluations of Figures S1-S4. We are not writing an evaluation paper of column BrO products (please see the reasons given in the main response). The other three products are included to demonstrate “These methods give different estimates of latitudinal/longitudinal variations in stratospheric column BrO and consequently in tropospheric column BrO. Most importantly, the estimated stratospheric BrO columns using these methods do not introduce in the resulting tropospheric BrO columns an unphysical correlation with tropospheric ozone.” We stated previously that the three products we selected with different satellite and stratospheric column estimates are enough to show the robustness of the results. The other three products have higher noises based on the comparisons of Figures S1-S4 and are therefore not used.

Figure 3 and Page 16231 lines 23ff: The time-lagged correlations are found to be "generally consistent" between the 3 trop. BrO products. However, there are 6 trop. BrO products (see p. 16228, lines 18, 19), what are the criteria to select just these three?

[Response]

We stated in section 2.2.1 “While not quantifying the uncertainties in the derived tropospheric BrO columns, the large separation of correlation coefficients does indicate that the products have different characteristics. As discussed previously, the uncertainty of satellite retrievals can affect the (anti)correlations between ozone and BrO. We therefore chose three products (OMI-SCIA2ND, GOME2-SCIA2ND, and GOME2-20th) that show generally high correlations with in situ measurements of bromine compounds in this study.”

When the lower correlations for Alert are due to larger uncertainties in sat. products at higher latitudes, why is R for OMI-SCIA2ND so much larger?

[Response]

The R value for OMI-SCIA2ND is not very large ($|R| < 0.2$ for OMI-SCIA2ND). In general, the correlation between ozone and OMI-SCIA2ND is poor at Alert. The reviewer may be thinking of the question why the results among the three products are not as consistent in Alert as the other two sites. We think that it is a reflection of larger uncertainties in satellite data because solar zenith angle is smaller at high latitudes and the error from the estimated air mass factor is larger (please see Choi et al. (2012)).

Page 16232, para. starting in line 6: The behavior of ODE – back-trajectories and non-ODE – back-trajectories (Fig. 4) is interpreted in local chemistry or transport (or a bit of both), respectively, being dominant at the particular site. It is not explained whether this fits with the local conditions.

[Response]

Does the local condition refer to local vertical stability? The vertical stability issue was examined in section 3.2. At Barrow, we have both surface and ozonesonde measurements, so we examined how transport affects to the local ODEs at Barrow in terms of the vertical stability and the vertical profile of potential temperature (Fig. 7 and 8). ODEs at Barrows are generally associated with an inversion layer near the surface. Unfortunately, we don't have the ozonesonde measurements at the other two surface sites. We also used the analysis of diurnal profiles of ozone percentiles at the three surface sites (Figure 1) to understand the relative importance of in situ photochemistry.

Fig. 5: The (largely blue) colour code below panels (a) and (b) appears to indicate the trop. BrO columns. This should be said. Results from at least OMI-SCIA2ND (Fig. S7) are twice as high, they cannot be said to be "similar", at best one could argue that the patterns are similar.

[Response]

We will clarify the caption of Figure 5 as suggested to state that the patterns are similar. We will change “Results using OMI-SCIA2ND and GOME2-20th BrO VCDs are similar (Figs. S7 and S8).” to “Results using OMI-SCIA2ND and GOME2-20th BrO VCDs show similar patterns (Figs. S7 and S8).”

But since the trop. BrO column distributions are largely uniform this is not very meaningful. So what could be learned from Fig. 5?

[Response]

Figure 5 shows that ODEs tend to originate from (relative) high-BrO regions. As the reviewer noted earlier, SCIAMACHY based products did not remove as much stratospheric BrO as the 20th percentile method. There is a much higher “constant” background. It does not affect correlation analysis result, so we did not try to remove it. For example, based on the 2 BrO flights of DC-8 which correlates well with SCIAMACHY based products, we can compute a (positive) constant through least-squares regression. Removing the constant would bring tropospheric column BrO of SCIAMACHY based products down to the magnitude estimated by the 20th percentile method. We do not think that it can be justified given the problem with WP-3B BrO data. Doing it or not does not affect the correlation analysis with ozone. Therefore, we did not do it in this paper.

Page 16234, lines 13 ff: A stable boundary layer not only reduces exchange of O3-depleted air masses (in other words: flow of O3 from above to the surface), but also serves to keep the level of "catalyst" (i.e. HOBr) height thus enhancing the efficiency of the "bromine explosion" mechanism.

[Response]

It could be true depending on the source of HOBr and the recycling mechanism. This paragraph is a short review of previous literature. If the reviewer knows a paper that we should cite for this mechanism, please let us know and we will add it.

Page 16235, line 10 and Fig. 7: The text refers to "the vertical profiles of ozone . . .", the figure caption to "mean profiles". How many profiles are averaged? Over which period of time? At which time of day did the launches take place?

[Response]

Ozonesonde measurements for ARCIONS were from the April 1 to 20 in 2008, once per day near local noon-time. The information on ozonesonde data was given in section 2.1.1. There are 6 ODE days at Barrow and Resolute, and 2 days at Churchill. We will add this information in the caption of Fig. 7.

The temperature "laps rate" is probably the vertical gradient of the potential temperature?

[Response]

The temperature lapse rate is dT/dz . It is defined on P. 16235, line 22.

Page 16236, line 20 and Fig. 8: The increase of the O₃-Theta correlation with altitude is an interesting finding indeed, but why does it reflect the "increasing thermal stability"? Would not higher thermal stability mean stronger increase of Theta with altitude and thus weaker O₃-Theta correlation than at the surface?

[Response]

The increase of thermal stability is shown in the lapse rate change in Figure 7. The inversion layer ($dT/dz > 0$) is most stable and tends to have the largest R values between O₃ and theta. If ODE occurs, both low ozone and low temperature would likely remain longer in a more stable layer, leading to a larger R value.

Page 16236, lines 22ff and Fig. 9: Vertical profiles of R are shown, what is the reason for the variation of r with altitude? Is there a BrO vertical profile or is BrO assumed to be constant and all variation comes from the O₃ profile? If yes it should be stated in the manuscript and then the meaning of "correlation" must be explained, is it temporal correlation? Since the nature of the correlation is not clear it is difficult to judge what a correlation might mean.

[Response]

The correlation is between the column value and O₃. So a high negative correlation would indicate the column BrO variation is similar to that of ozone. We do not know the vertical distribution of BrO and do not need to assume one either. The correlation analysis can only tell us about the variation patterns of the two parameters. The correlation at a given altitude has to be temporal. We will state it in the text.

Pages 16238 to 16240: The discussion of the trop. BrO column retrieval is not very convincing: Apparently there is little correlation between satellite BrO and in-situ data (page 16239, lines 10ff). In this situation using many different retrieval algorithms for the trop. Partial BrO column will not help since none actually correlates. The statement that 3 satellite products were selected that "showed good correlations with in situ measurements of bromine compounds (BrO, Br₂+HOBr, and soluble Br)" is cryptic in this context: The satellite instruments measure BrO and no other Br-species, also, is there correlation or not?

[Response]

Please see the main response on using satellite BrO retrievals in this analysis since that discussion is long. The selection is based on the correlation profiles with bromine species. The inconsistency of satellite derived columns between the 2 DC-8 flights and 5 WP-3B flights is unresolved. Choi et al. (2012) showed the same result.

In summary, the main difficulty with this manuscript are the not-validated tropospheric partial column BrO "products" derived from satellite data combined with the fact that the conclusion drawn from the 6 different products sometimes differ significantly. Possible solutions to this dilemma are listed above, they require major revision of the manuscript.

Please see the long explanation in the main response. It is long because we are dealing with a complex problem. We understand the desire to obtain a clear answer. In the case of retrieving tropospheric column BrO from satellite measurements, we must deal with the nuances of many unknowns. The devil is clearly in the details in this case. However, we do not think that these details affect the ODE characteristics analyses we presented and we believe that those results are robust despite of the uncertainties in the satellite retrievals. The uncertainty "baggage" does mean that it will take some effort to understand the reasons for how we did the analyses. Fortunately, general readers not interested in BrO retrievals can skip the relevant discussion easily. The reviewers obviously cannot. We appreciate the effort that the reviewer puts into this paper.