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Atmospheric Chemistry and Physics Discussions

Interactive comment on "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.

Anonymous Referee #1

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The authors present an analysis of satellite BrO data, time series of surface ozone and air temperature measured at three Arctic locations (Barrow, Alert, and Ny-Alesund), and aircraft BrO and ozone sonde measurements during the ARCTAS and ARCPAC campaigns. These measurements are very heterogeneous regarding their temporal and spatial coverage. Nevertheless, the authors use correlation between the different measurements in an attempt to characterize conditions and properties of springtime ozone depletion events in the Arctic. Any analysis of correlations between different observed species must be done with great care. The authors present some new ways of

performing such correlation analysis, which may be helpful to better understand some of the processes relating the activation of reactive bromine and the depletion of ozone in the springtime boundary layer of the Arctic. Therefore, this subject is well suited for publication in ACP. However, several major issues remain before the manuscript will be in a publishable form. One major issue concerns the determination of tropospheric BrO columns, which recently became the issue of a scientific debate. Not being an expert in the field, I feel quite uncomfortable with the way this is handled in the manuscript. In fact, the manuscript makes this issue even more confusing instead of clarifying it. In addition, the authors draw several conclusions from their analysis, which in my opinion are not warranted and which also neglect results from previous publications. In contrast, I believe that some issues related to the processes during the depletion of ozone may be better addressed with the available data set. Further details and some suggestions are given in the major comments below.

Major comments:

The authors calculated six different versions of the tropospheric BrO columns using two different satellite products (OMI, GOME2) and three different stratospheric BrO columns (called 20th, SCIA2ND, RAQMS). I assume that these multiple calculations were caused by the ongoing scientific debate of how to extract tropospheric BrO columns from the satellite products that deliver only total BrO columns. I further guess that these multiple calculations were performed to avoid getting dragged into this debate and to demonstrate that the determination of the tropospheric BrO column is not a critical issue. However, the presentation of the results is rather confusing to me. I admit that I am neither an expert in the field of satellite data retrieval nor in stratospheric BrO. The brief presentation of the RAQMS approach (stratospheric columns are too low and are scaled using zonal mean values from the 20th method) and the neglect of the RAQMS products in the further data analysis lead me to the conclusion that the RAQMS stratospheric BrO columns are almost useless. If that is the case, why are they presented at all? A quick search on publications regarding the compar-

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ison of BrO columns from OMI and GOME2 delivered no real result, but rather some statements in the internet that they agree quite well. Accordingly, the authors present in Fig.2 the monthly average for April 2008 of the tropospheric BrO distribution from GOME2-SCIA2ND, which in fact compares well with the OMI-SCIA2ND shown in Fig. S5 as also stated by the authors. If however the OMI and GOME2 BrO columns agree well, what is the use in using these two different satellite products? Of course, if the total BrO columns are similar and the same stratospheric BrO columns are subtracted, they should give the same tropospheric BrO distributions and the same results in the further correlations. Interestingly, the correlation coefficients between surface ozone at Alert and Zeppelin and the tropospheric BrO shown in Fig. 3 are markedly different for GOME2-SCIA2ND and OMI-SCIA2ND. There are also almost always large differences between GOME2-20th vs. OMI-20th and GOME2-RAQMS vs. OMI-RAQMS as shown in Figs. S1 to S4. What is the explanation for this difference? Do only the monthly averages agree but not the daily maps, which are used in the correlation analysis? If the two satellite products are similar and one of the methods to obtain the stratospheric BrO columns is useless, the six possible products melt down to only two independent tropospheric BrO distributions. If the two satellite products are not similar this number increases to four, but it would require a thorough discussion how and why the OMI and GOME2 BrO columns differ.

In the first paragraph of chapter 3.1.2 and in Fig. 2 the authors present the monthly average for the tropospheric column of BrO for April 2008. In Fig. 2 they also show a map of first- and multi-year sea ice suggesting a relationship between the ice properties and the BrO columns. Such a relationship could be tested since satellite data of BrO are available since the 1990s (By the way, references to publications on this subject are completely missing!) and could be used to detect if trends are in line with the modified sea ice properties of the Arctic Ocean. However, such an analysis is missing and likely beyond the scope of the manuscript. Since the authors do not refer further to the relationship of sea ice properties and BrO and since it is not used for further analysis I recommend to delete this part because it remains to superficial.

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In several cases the authors discuss correlations between in situ measurements (surface ozone, ozone sondes, BrO, Br2+HOBr, soluble bromide) with tropospheric BrO columns. The in situ aircraft measurements are averaged into altitude bins. Nevertheless, the in situ observations and the columns are completely different quantities and can only be compared under certain assumptions. In the case of BrO, in situ concentrations and tropospheric column should only correlate if changes in the column are related to changes in the specific altitude bin. On the other hand, high concentrations in a certain altitude range could show up in the in situ measurements, but could be masked in the tropospheric column if at the same time the BrO in a different altitude range decreases by the same (or larger) amount. Therefore, calculating correlations between in situ BrO and tropospheric BrO columns implies strong hypotheses about the tropospheric BrO distribution with high concentration close to the ground and low and constant BrO concentrations throughout the troposphere. In fact this assumption is probably well justified for Arctic springtime conditions, but they should be discussed in detail in the manuscript before presenting the correlations. In the case of Br2+HOBr and soluble bromide the authors claim to test if the observed quantities "capture to some extent the distribution of lower tropospheric BrO" (page 8). But why should these compounds correlate (besides the implied assumption about the vertical distribution like in the case of BrO)? According to the chemical mechanism the BrO maximum does not occur simultaneously with concentrations of HOBr, Br2, or HBr (included in soluble bromide) (e.g. Lehrer et al., 2004). So, the absence of a significant correlation makes the result ambiguous: the mechanism and the BrO columns are both correct or they are both incorrect. I recommend to delete this part. The most complex case is probably the comparison of in situ ozone with the BrO columns. Again, in my opinion all comparisons are based on the assumption that the relationship between ozone and BrO is restricted to the boundary layer and that other layers remain constant in ozone and BrO. On page 11 and in Fig. 3 the authors describe a stronger anti-correlation for Alert and Zeppelin without a time lag or with a delay of only 1 day. For Barrow, the anti-correlations are strongest with time delays of 1 to 3 days. The authors conclude

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that at Alert and Zeppelin local processes are responsible, while at Barrow transport is more important for low ozone values. I believe that this interpretation is an over-simplification. I agree with the conclusion that if along the back trajectories in the last 0 to 3 days BrO columns are high, surface ozone concentrations will probably be low (or lower than background). By the way, can these results be exploited to determine how fast ozone is removed? However, there is also the possibility that air masses with low ozone concentrations persisted for longer periods (i.e. longer than the backward trajectories), which were than transported to the observational sites. In fact, Bottenheim et al. (2010) and Jacobi et al. (2010) presented surface ozone time series form the Arctic Ocean indicating periods of longer than 5 days with low ozone concentrations. Thus, it could well be possible that air masses depleted in ozone were transported to the coastal station without enhanced BrO concentration along 5-day back trajectories. Such events have the potential to mask correlations between ozone and BrO. I assume that with the available data set these processes can probably be tested in more detail.

Third paragraph on page 11: In characterizing the different source regions of ozone-poor air the authors refer to Fig. 2 and describe the Chukchi Sea, “where tropospheric BrO columns are high”, the Beaufort Sea, “where we did not find the enhancement of tropospheric BrO”, and the area northwest of the Zeppelin Station, “where there is moderate increase of tropospheric BrO”. By looking at Fig. 2 I would say that average concentrations over the Chukchi Sea, the Beaufort Sea, and in the area northwest of the Zeppelin Station were approximately 6*10ˆ13, 5*10ˆ13, and 5*10ˆ13 molecules/cm2. Therefore, the Beaufort Sea can not be considered as a region with low BrO columns. This needs to be corrected affecting also some of the conclusions.

Chapter 3.1.3: The entire discussion of the relationship between the temperature and the occurrence of low ozone is not at the current state of knowledge. Several previous publications have shown that low ozone has been observed at temperatures above -20 °C. Some authors also have suggested that the relationship observed between temperature and ozone in many cases is not related to the chemical mechanisms, but

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rather to the meteorological conditions (e.g. Jacobi et al., 2010). Moreover, if the authors conclude that for Barrow low ozone is rather related to transport processes than to local chemistry, what does the temperature measured at Barrow as used in Fig. S9 tell about the conditions during the ozone depletion? I still believe that lower temperature favor the halogen activation making the chemical depletion of ozone more efficient. However, data to prove this effect is difficult to obtain. Maybe the authors can again find information on this using their aircraft data?

Minor comments:

P. 4, l. 13: . . . taking into account the uncertainties in . . .

P. 12, l. 14: . . . does not contribute . . .

P. 12, l. 21: The influence of temperature on ODEs

P. 12, l. 24: . . . 2 April 2008 in the Amundsen Gulf . . .

P.12, l. 25: They found a general correlation . . .

P. 25, l. 12: Pu??te?

Fig. 1: For which days are the solar elevations at the three locations?

Fig. 4: The large letters do not do a good job in indicating the locations of the stations.

Fig. 5: Explain how the 2-day back trajectories were split into three periods.

References

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