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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Global observations of tropospheric BrO columns using GOME-2 satellite data" *by* N. Theys et al.

N. Theys et al.

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Nicolas Theys: Author response to referees comments

The authors gratefully thank all the reviewers for their interesting comments which did contribute to improve the manuscript.

Referee #1 comments (comments received and published: 22 December 2010)

This paper reports on application of a stratospheric BrO climatology to the determination of background tropospheric BrO columns. It appears to be a carefully done piece of work, and the manuscript is well written. A very useful result of this work is represented in Figure 14, i.e. latitude and seasonal dependence of the tropospheric BrO columns from GOME-2, amounting to, on average, about 1.5x10ËĘ13 cmËĘ-2. This is

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high quality work, and it is very timely, as there is currently substantial interest in this topic. The paper concludes that the tropospheric "hotspots" seem to correlate with low tropopause heights, but that they cannot be completely accounted for on that basis. As far as can be determined from reading the paper, the methodology is rigorous and represents the current state of knowledge. I believe this paper should be published, but only after correcting a number of significant problems. Specifically, I find that the authors draw some definitive conclusions that are not supported by the data presented in the paper. Most importantly, the paper concludes that they can confirm that the blowing snow hypothesis can account for some of the large tropospheric BrO columns. Indeed, on page 22 it is stated that "... the results of Fig. 13 confirm the existence of the mechanism of bromine release from blowing snow events,...". However, I do not believe this is the case in any way. Figure 13 compares the TOMCAT model with tropospheric BrO retrievals, when the TOMCAT model incorporates a blowing snow mechanism. This then runs the risk of having a model that is highly parameterized to support a particular mechanism, without all the details of the chemistry and meteorology to properly assess that mechanism. Since TOMCAT includes a blowing snow parameterization that results in reactive bromine release, it is not too surprising that the results are consistent with this hypothesis. It is very important to be circumspect about the blowing snow hypothesis. Surface observations show high BrO levels and ozone depletion events when the surface is thermodynamically stable, and with radiation present. In contrast, during blowing snow events, there would be enhanced vertical scale turbulence, and decreased radiation, both of which should slow bromine photochemistry. The paper should discuss if indeed the observations are consistent with stable air AFTER a blowing snow event, when presumably the surface is more saline, as discussed in the Jones et al. paper. While the authors refer to "BrO emissions", BrO is not emitted, but is photochemically produced in a process that is believed to be propagated by the BrO + BrO reaction. This turbulent mixing should substantially slow the process. The paper should state how TOMCAT parameterized BL turbulence and BL structure around the lows. Does TOMCAT parameterize both emission of sea salt, and

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appropriate BL turbulence and reduced radiation during the blowing snow events, and then do detailed chemistry? If so, knowing those details would make the paper more interesting, and also make this result more believable. This relates to the fact that there is very sparse evidence for the blowing snow mechanism, and that evidence does not include in-situ measurement of sea salt aerosol or BrO, or BrO precursors. Regarding what was discussed in Figure 13, we do not even know that the enhanced BrO observed by GOME-2 is in the boundary layer! It stated on page 22 that "The results of Figure 12 provide a strong indication that the release of bromine by blowing snow events is probably playing an important role in the bromine explosion phenomenon,...". But, in fact, Figure 12 says nothing whatsoever about blowing snow. Thus the authors statement of confirmation of the hypothesis is troubling. What would "confirm" the hypothesis would be observations of enhanced BrO at the onset of, or immediately after, a blowing snow event, along with observations of enhanced SSA (or enhanced salty surface snow). At the top of page 13, the authors say that "the results presented here call for further modeling developments...". Actually, what they call for, if anything, is in-situ measurements during blowing snow events. However, in their defense, the Conclusions are indeed much more circumspect and, I think, appropriate, stating that "...no firm conclusions can be drawn..." about this mechanism, only referring to it as plausible. Thus the Conclusions are a bit in contrast to or in contradiction with the text, and the latter should be tempered.

Reply: We agree with the referee that the findings of Section 5.2 on the mechanism of bromine release during blowing-snow events go beyond the facts, and we also come to the conclusion that parts of the discussion should be tempered (see below), especially the ones speculating over the frequency and importance of blowing snow-sourced bromine. We have of course no means to prove that blowing snow-events produce a majority of the observed polar tropospheric BrO hotspots and it is anyway not what we believe. Although one needs to be cautious considering the bromine source from blowing snow, there are nevertheless accumulating evidences in the literature for the existence of enhanced tropospheric BrO and coincident blowing snow events. We think

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it is fair to say that several elements of our study can reasonably be explained by the blowing snow mechanism. We provide specific replies to the comments raised by the referee:

- "during blowing snow events, there would be enhanced vertical scale turbulence, and decreased radiation, both of which should slow bromine photochemistry" We think this concerns mostly the Jones et al mechanism. The blowing snow mechanism (implemented in pTOMCAT) originally described in Yang et al., 2008, suggests that bromine comes from the sea salt produced through sublimation process. As mentioned by the authors, the naked sea salt will not form within the blowing snow layer (due to saturation conditions), but likely formed at the top of the layer or above it. The resulting fine sea salt might then be transported on long distances, vertically lifted, get acidified and eventually this results in bromine release. According to this blowing snow mechanism, we consider the enhanced turbulence and decreased radiation (occurring in the blowing snow layer) not as an issue. Note that, in reality, the radiation at the top of the layer might even be enhanced instead of being attenuated (as a result of enhancement of diffuse light that balance the attenuation of direct radiation).

- "Does pTOMCAT parameterize both emission of sea salt, and appropriate BL turbulence and reduced radiation during the blowing snow events, and then do detailed chemistry?" For more detailed information about the physical and chemical aspects of the model, see related papers by Yang et al. (2005, 2008, 2010) and references therein. The emission of sea salt is indeed parameterized, no treatment is applied for BL turbulence (see comment above). The bromine release from sea salt is not photochemistry dependent, but highly described based on the observed data (Sander et al., 2003). Finally, a detailed chemical scheme for the photochemical recycling of inorganic bromine is implemented (see Yang et al., 2010).

- "The authors refer to "BrO emissions", BrO is not emitted, but is photochemically produced". We fully agree. To make this clear, we have changed "BrO emissions" by "BrO precursors emissions" in the text.

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- “The paper should discuss if indeed the observations are consistent with stable air AFTER a blowing snow event, when presumably the surface is more saline, as discussed in the Jones et al. paper” Regarding pTOMCAT, the model does not include snow process. Further, pTOMCAT, like most of other models, has limited ability in simulating very stable polar boundary layer. However, the model is able in some instances to simulate high BrO concentrations and complete O3 removal for stable boundary layer (low wind speed) indicating transport effect from the (non-local) blowing snow source (see Yang et al., 2010, or we can provide material if needed). Regarding the observations, we don’t have enough elements to address the referee’s point and we believe it goes well beyond the scope of the paper. We agree with the later referee’s comment that “What would "confirm" the hypothesis would be observations of enhanced BrO at the onset of, or immediately after, a blowing snow event, along with observations of enhanced SSA (or enhanced salty surface snow)”. Currently we do not have these data to validate our mechanism.

- Regarding Fig. 13: It has already been proven that pTOMCAT CTM is able to reproduce some of the elevated tropospheric BrO column peaks measured by GOME-1 (Yang et al., 2010) when (and only when) the blowing snow mechanism (described in Yang et al., 2008) is included in the simulations. Therefore we still believe that the fact that both measured (GOME-2) and modeled independent data sets, capture the generation of BrO plumes in Arctic and Antarctic (Fig.13), makes the blowing snow mechanism a plausible explanation for the two case studies displayed, and raises the question on how important the latter mechanism is for the polar spring bromine emissions in general.

- Regarding Fig. 12: We admit Fig. 12 can not be related to the blowing snow mechanism. It shows the (apparently) strong relation between elevated tropospheric BrO and the tropospheric dynamics (e.g., as in Begoin et al, 2010) and/or dynamically driven bromine production mechanisms (blowing-snow being one of them). The fact that a similar behavior is seen between GOME-2 and pTOMCAT doesn’t enable us to say

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that blowing snow bromine production is important or even if it exists. This might be due to one or more processes (including or not blowing snow). However, it makes the snow-sourced bromine a potential contributor to elevated tropospheric BrO in polar region.

Instead of adding extended and possibly cumbersome details on the blowing snow mechanism and on how it is treated in pTOMCAT, we propose to adapt/temper parts of the text (in bold):

-(Abstract) "...While some satellite observed plumes of enhanced BrO can be explained by stratospheric descending air, we show that most BrO hotspots are of tropospheric origin, although they are often associated to regions with low tropopause heights as well. Elaborating on simulations using the p-TOMCAT tropospheric chemical transport model, this result is found to be consistent with the mechanism of bromine release through sea salt aerosols production during blowing snow events. No definitive conclusion can be drawn however on the importance of blowing snow sources in comparison to other bromine release mechanisms."

-(Section 5.2, Page 28658) "The results of Fig. 12 provide an indication that the release of bromine by blowing snow events might play a role in the bromine explosion phenomenon, in both the Arctic and Antarctic. However, one should be cautious with this interpretation since other dynamically driven bromine production mechanisms may possibly lead to similar behaviour. It is also worth adding that in another recent study, Begoin et al. (2010)..."

-(Section 5.2, Page 28659) "Although the results of Fig. 13 can be reasonably well explained by the mechanism of bromine release from blowing snow events, they provide no indication on the precise magnitude of this blowing snow source compared to other processes."

-(Section 5.2, Page 28659) "Nevertheless, the results presented here call for further modelling developments supported by satellite BrO measurements and in-situ mea-

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surements during blowing snow events in order to better assess the relative contributions of bromine sources in the polar troposphere."

1. The end of the first paragraph of the Introduction should cite Salawitch et al., 2010.

Reply: A reference to Salawitch et al. (2010) has been added.

2. You might consider citing Sirois and Barrie, JGR, 1999 regarding inorganic bromine seasonal cycles in the Arctic at the bottom of page 2.

Reply: A reference to Sirois and Barrie (1999) has been added.

3. The last paragraph of the Introduction section is unnecessary.

Reply: This paragraph has been withdrawn from the Introduction section.

4. Are brackets needed in the numerator in Equation 1?

Reply: We think brackets in the numerator in Equation 1 are not really needed.

5. I think some discussion about the VSL bromine species referred to at the bottom of page 7 is needed. If indeed there is an important contribution from such VSL species, and they are indeed very short lived, then they must be highly spatially variable, depending on where there is deep-convective injection of tropospheric air into the stratosphere, and thus there must be a great deal of uncertainty and variability in this component (which hasn't been measured). How does this translate into uncertainties in the stratospheric climatology?

Reply: We agree with the referee's comment in that the VSL bromine species are likely highly variable in space and time. Despite its importance in determining the stratospheric bromine budget, measurements of this variability have indeed (to our knowledge) not been reported in the literature. Conversely this issue is the focus of several recent modeling studies and observation campaigns (a number of them being part of the SHIVA EU FP7 project). Unfortunately, the BASCOE stratospheric chemical transport model (used to generate our BrO climatology) is unable to treat the level of details

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associated to deep convection events and the resulting impact on the stratospheric bromine budget. Instead we have implemented a single source, effective for all short-lived bromocarbons, in the form of CH2Br2 leading to a contribution of 6 pptv to the total stratospheric Bry loading (the latter value being in agreement with the latest estimate from the 2010 Ozone Assessment Report, Chapter 1). We recognize that this approach has limitations but it has the merit to be pragmatic for the present application (namely, the retrieval of tropospheric BrO columns from satellite nadir observations) in the sense that the BrO output data from BASCOE is highly consistent with available stratospheric BrO observational data set (details in Theys et al., 2009b). This being said, we have considered the referee's concern on the uncertainties in the stratospheric climatology due to deep convection events, and we firmly believe these uncertainties are quite small for the present application, essentially because deep convection systems are predominantly present in the tropics and are rather localized systems. Let us consider the deep-convective injection of a given air mass from the troposphere into the (tropical) lower stratosphere. By the time the air reaches the mid- and high-latitudes (the main regions of interest of our study), the bromine source and product gases (presumably present) will be strongly diluted by atmospheric winds. Therefore it is reasonable to say that the impact of a particular deep convection event on the stratospheric BrO column outside the tropics is negligible. Now let us focus on the tropical region itself and consider the extreme case where a deep convection system with a scale of the order of a satellite pixel ($\sim$3200 km^2), brings 8 pptv directly in the form of Bry (a value that corresponds approximately to the surface total Br abundances) in the first km above the tropopause (17-18 km layer). If we further consider a ratio BrO/Bry of about 0.5 typical for the tropics at noon (Theys et al., 2009b), this will translate to an increase of about 1.3 x 1012 molec/cm^2 in BrO vertical column and of 2.6 x 1012 molec/cm^2 in BrO slant column (AMFstrato$\sim$2), i.e. a value one order of magnitude smaller than the scatter in BrO slant column for individual satellite measurements in the tropics. We safely conclude that it is undetectable. As the uncertainty on the stratospheric BrO column due to deep-convection events lies within the overall uncertainty

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on the stratospheric climatology as presented in Theys et al. (2009b), we propose not to further discuss this aspect for the sake of concision.

6. There should be a brief explanation of how/why NO2 is an indicator of BrO/Bry, or provide a reference.

Reply: The link between NO2 and the ratio BrO/Bry is due to the fact that (under usual conditions) bromine nitrate (BrONO2, formed by the reaction BrO+NO2) is the main lower stratospheric bromine reservoir. Since this aspect is extensively detailed in our last paper to which we refer in Section 3.2 (Theys et al., 2009b) and in order to keep the paper as short as possible, we prefer to simply add a reference to the work of Lary (1996).

Lary, D.J.: Gas phase atmospheric bromine photochemistry, J. Geophys. Res, 101, 1505-1516, 1996.

7. At the bottom page 18, it is stated that it is assumed that the BrO/O3 regression lope is fully controlled by the stratospheric component. But, the large offset between the stratospheric and total BrO regressions makes one wonder if this is a valid assumption. There should be a discussion of the impact of that assumption.

Reply: We agree that, at first glance, Fig. 3 might be in contradiction with the assumption that the BrO/O3 regression is fully controlled by stratospheric BrO. Our assumption is that the variations in stratospheric Bry are controlled by dynamics in a way that matches closely the O3 fluctuations (this was clearly established in Theys et al. (2009b) and further demonstrated by Salawitch et al. (2010)). The part of the column that does not correlate with ozone is assumed to be in the troposphere. In fact, the text (page 9) states that the correction uses a slope adjustment but leaves unchanged any possible offset between modeled and measured total BrO VCD, in order to preserve the information on the BrO background presumably present in the free-troposphere. This is the main message of Fig. 3. In order to clarify the assumption of the correction, we have changed the sentence (page 8) “Here the correction is based on the observed

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correlation between O3 and BrO vertical columns (see e.g., Salawitch et al., 2010)" by the following sentence (we believe is more precise) "Here the correction is based on the fact that the variations in stratospheric Bry are controlled by atmospheric dynamics in a way that matches closely the O3 fluctuations, as clearly established by Theys et al. (2009b) and further demonstrated by Salawitch et al. (2010) using measured O3 and BrO vertical columns". We also changed the sentence (Page 9) "Hence it preserves the information on the BrO background presumably present in the free-troposphere." by "Hence it preserves the information on the BrO background (not correlated with ozone) presumably present in the free-troposphere".

8. The units for the weighting function in Equation 2 should be stated. It is cmËĘ2?

Reply: We agree that the sentence following Equation 2 is misleading. The weighting function (also often called 'box-air-mass-factors') has no unit. To make this clearer, we suggest to modify the sentence by: 'In this expression, N(z) is the concentration profile of the atmospheric species of interest normalized by the corresponding vertical column and WF(z) is the so-called weighting function (no unit) that contains the dependences on all the parameters influencing the AMF, except the vertical profile of the species N(z)'.

9. Re the first sentence in section 3.3.3, you might cite Neuman et al., ACP, 2010.

Reply: A reference to Neuman et al. (2010) has been added.

10. Bottom of page 13 - make it clear that those uncertainties are absolute uncertainties, not relative. I also think it is always better to use the word uncertainty, as the word "error" implies a systematic uncertainty.

Reply: We agree. To make it clearer we have changed the sentence (bottom of page 13) "The latter input parameter uncertainties are taken as follows..." by "The latter input parameter absolute uncertainties are taken as follows...".

11. The first sentence of Section 4 is a strange way to begin a section, as it reads as

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if it is a conclusion. The word "verified" is a poor word to use, as it implies some sort of correctness. It would be better to just say that a comparison with SCIA has been done and here you discuss the results. Along these lines, at the end of this section, the paper refers to the agreement as "satisfactory". That is a fully subjective term that depends on your criteria, and it should be changed. The discussion in section 4.2 also contains some subjective comments, such as "the agreement between GOME-2 and ground-based data is generally good...". The average reader has no idea what that might mean in quantitative terms. It would be best if the subjective evaluations are removed, and they are simply replaced with quantitative comparisons. For Figure 7, it might be more interesting/useful to discuss the times when the two are systematically different, in quantitative terms.

Reply: We agree that several parts of section 4 are rather vague. The first sentence of the section has been changed by: “In this section, the reliability of the GOME-2 BrO columns is assessed through comparisons with SCIAMACHY satellite nadir observations (total BrO columns) and independent ground-based observations (stratospheric and tropospheric BrO columns)”. At the end of Section 4.1, we have withdrawn the last sentence “Therefore we consider the agreement obtained satisfactory for all conditions”.

In Section 4.2, we have added values for the differences between the satellite and ground-based BrO columns:

- “In general, climatological BrO stratospheric vertical columns are found to be in good agreement with the stratospheric columns inferred from the ground-based observations, in terms of mean level and seasonal variation (with a tendency to produce lower values by 0.15 ± 0.5 1013 molec/cm^2 on average).” (Page 15)

- “For Southern hemisphere winter time, the stratospheric climatology has however a tendency to produce slightly higher values than the ground-based data (by $\sim$ 0.5 x 1013 molec/cm^2).” (Page 16)

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- “The agreement between GOME-2 and ground-based tropospheric columns is generally also good, except from mid-April to end August 2008 where the GOME-2 tropospheric BrO columns (green line) are systematically higher than the values retrieved from the ground-based observations (mean bias: 0.7 x 1013 molec/cm^2) ” (Page 16)

- “If one assumes a tropospheric BrO profile shape peaking at 8 km rather than 6 km, the agreement between satellite and ground-based data significantly improves (with GOME-2 being lower than the ground-based data by 0.13$\pm$0.7 1013 molec/cm^2 on average).” (Page 16)

12. Mid page 14 - delete the "scientific product".

Reply: done

13. Section 4.2 - describe the sites discussed, in terms of local characteristics. For the last paragraph in this section, it would be helpful to remind the reader about the time of day for the satellite-ground comparisons.

Reply: We have added the following sentence on the sites: “Both stations belong to the Network for the Detection of Atmospheric Composition Change (NDACC) and are remote sites not influenced by local pollution sources.” We have changed the last paragraph of Section 4.2 by “From Figs. 6 and 7, we conclude that both ground-based and satellite observations are consistent with a tropospheric BrO column of $\sim$1.5 x 1013 molec/cm^2 for morning conditions ($\sim$09:30 solar local time), ….”.

14. On page 17 and on page 20 the text refers to "BrO emissions". It is important that both the authors and the readers are aware that BrO is not emitted; rather, precursors, like Br2 or organobromine compounds are emitted, and then photolyze. There is considerable scientific interest in the drivers of those emissions! The top paragraph on page 17 refers to correlations of BrO with the coast lines of the Arctic and the Antarctic, and sea ice. However, it is clear in Fig. 8 (and in other places in the literature) that the enhanced BrO in the Arctic does not follow the coast lines. It is also the case that the

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last sentence of this paragraph is not in any way supported by the data presented! Just compare March and April for the Arctic in Figure 8. In both cases the areas in red are well into the ice covered region. There is much more to the story than just BrO following the ice retreat.

Reply: We fully agree with the referee in that BrO is not "emitted". To make this clear, we have changed "BrO emissions" by "BrO precursors emissions" on pages 7, 17 and 20. We agree with the referee that the first paragraphs of Section 5 (page 17) are not well formulated. Obviously, Arctic tropospheric BrO does not strictly follow the coast lines. Therefore, we suggest that the sentence "The regions with enhanced tropospheric BrO columns exhibit an excellent correlation with the areas of sea ice, located along the coast lines of the Arctic and Antarctic." simply becomes "The regions with enhanced tropospheric BrO columns exhibit an excellent correlation with the areas of sea ice." We also have to admit that the last sentence of the paragraph stating that the month-to-month variation of tropospheric BrO can be linked to the sea-ice retreat is simply incomplete. We prefer to withdrawn this sentence from the text.

15. Mid page 18 and Fig. 10 - it seems from looking at Fig. 10 that the tropospheric (rather than stratospheric) columns may correlate better with tropopause height; however, staring at the plots is not the best way to decipher correlations. Can you be more quantitative about the correlations?

Reply: We have calculated the correlation coefficients between the tropopause heights and the columns as depicted in Figure 10: the stratospheric columns and tropopause heights have a correlation factor of -0.7, while the tropospheric columns and tropopause heights have a correlation factor of -0.35. We would prefer not to add these numbers in the text, as they only bring little to the discussion. However, we want to avoid that the reader has a false impression in that the tropospheric (rather than stratospheric) columns may correlate better with tropopause height. Following a suggestion of Anonymous Reviewer #2, we have inverted the color scale of the 'Tropopause height' plots of Fig. 10 and it actually facilitates the visual comparison

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to the BrO columns shown.

16. The statement on page 19 that (for the Hudson Bay) "...one can see that the retrieved tropospheric BrO columns rarely exceed the surrounding tropospheric background by more than this limit" (later defined as 3.5x10ËĘ13) is very odd and unsupportable for two reasons: a) there are only three cases presented. So, what does "rarely" mean? And, b) in every case presented in Figure 10 that limit is exceeded, for at least part of Hudson Bay! From the data one can only conclude the opposite of what was stated.

Reply: We agree that the word “rarely” is not appropriate here. Nevertheless we could still identify in Fig 10 (Hudson Bay region) cases where that limit is not exceed. We propose to adapt the text with the following sentence “By inspecting the results of Fig. 10 over the Hudson Bay region (55-70°N, 70-96°W) in conditions of very low tropopause heights, one can see that the retrieved tropospheric BrO columns in some instances do not exceed the surrounding tropospheric BrO background by more than this limit.” The referee also mentions that Figure 10 only shows three cases, so it is difficult to draw conclusions (based on Fig. 10 solely) on how often ‘hotspots’ over the Hudson Bay area can be explained by stratospheric BrO or not. This is precisely why we have Fig. 11 where we investigate the frequency of occurrence of such features for the entire spring season over the Hudson Bay area and for the Northern high latitudes in general.

17. Top of page 20 - I simply cannot see how the data presented in Figure 11 could in any way "confirm the effect of a weather pattern specific to this area". That sentence should be deleted.

Reply: ‘Weather pattern’ is maybe not the right expression but from Figure 11 one can see that the conditions of low altitude tropopause (and high O3 column) are more frequent (in %) over Hudson Bay than for the Northern high latitudes in general. We agree to delete the sentence “This confirms the effect of a weather pattern specific

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to this area and responsible for low tropopauses (Salawitch et al., 2010).", as it is not crucial for the reader.

18. Figure 15 is a very nice representation of the impact of the dependence of tropospheric column BrO on cloud top pressure, and is a convincing case for the determination of tropospheric background BrO.

Reply: Thank you for this positive comment.

19. Figure 4 and caption - did you plot Air Mass Factors, or are they weighting functions, as indicated in the caption?

Reply: Weighting functions are plotted in Figure 4. The ambiguity comes from the label of the x-axis: 'Air Mass Factor'. It has been changed in 'Weighting function'.

20. Figures 6 and 7 - it is hard to tell the difference between black and green.

Reply: We have changed the green lines in blue lines. We believe it leads to a better color contrast.

Referee #2 comments (comments received and published: 17 January 2011)

The manuscript presents the derivation of tropospheric observations of bromine monoxide from the GOME-2 instrument, drawing on techniques previously by the same group for removing stratospheric BrO loading from total column measurements. The paper is well written and the approach is fundamentally sound. The overall quality conforms to the high standards we have come to expect from the BIRA group. The topic of tropospheric BrO loading is important, and the manuscript is timely, particularly in light of recently published work regarding stratospheric bromine loading. It is well suited for publication in ACP. In general, there is little to be found at fault with the manuscript, aside from the overinterpretation of snow-blowing events. This as already been addressed by Anonymous Reviewer #1, and I second that criticism. In addition, I want to point out that Figures 8 and 13, particularly where they show monthly averaged GOME-2 BrO in the Antarctic during October 2007, seem to fail to support the snow-

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blowing hypothesis: Strongly elevated BrO in the observations is almost entirely limited to coastal and off-coastal areas, while p-TOMCAT results show no such localization. If snow-blowing events were an important contributor to elevated BrO, would one not expect a more even distribution between on- and off-shore regions around the coast or sea ice edge?

Reply: For the discussion on the blowing-snow mechanism, please refer to the replies to Referee #1 comments. It is true that one should expect elevated BrO columns to be localized over coastal and off-shore areas if blowing-snow were an important contributor to elevated BrO. We were really puzzled to see that pTOMCAT behaves differently. Therefore, we went through the different possibilities that may cause the model predicting more BrO over inland than in reality (model resolution, treatment of snow salinity, bromine depletion factor, etc. see Yang et al., 2010). After several sensitivity tests, we identify an error in the calculation of the tropospheric BrO columns from the modeled output BrO profiles (this error is thus not related to any model settings): the BrO column was estimated by integrating the BrO profiles down to the sea level rather than down to the surface altitude. This affects mainly the results over Greenland and Antarctic inland (high altitude plateaus), with pTOMCAT overestimating the tropospheric BrO column by 1-3 x 1013 molec/cm^2 (in case of non-zero surface BrO concentrations). We have updated the figures (Figs 12 and 13) showing the pTOMCAT results and we found that the changes were small and do not affect the conclusions of the paper. Therefore and since the error we found is not related to the model itself, we propose to simply update the figures (12 and 13) in the revised version of the paper. We thank the referee for his useful comment.

The methods for separation of stratospheric and tropospheric BrO, as well as the spectral retrievals of BrO from GOME-2 observations are sound and accurately described. On a side note that has practically no impact on the retrievals, I would suggest to the authors to replace the Meller HCHO cross-sections with those of Cantrell scaled by 0.9. This is the current recommendation of the HITRAN advisory board, and the

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authors may find Cantrell to yield slightly lower RMS values compared to Meller. However, the impact of this change on the retrieved BrO columns is in all likelihood negligible and does not warrant a reprocessing of the data for the analysis presented in the manuscript.

Reply: We take good note of this recommendation.

Some specific comments, mainly of cosmetic nature, in the order they appear in the manuscript:

Reply: All small corrections/typos have been accounted for and changed in the text. (Points # 1, 2, 3, 4, 5, 7, 8, 9, 10, 13).

1. Page 3 Line 21: “OMI/Aura”

2. Page 5 Line 11: “poleward of $\pm 45^{\circ}$ latitude”

3. Page 10 Line 10: “smaller”

4. Page 16 Line 7: "data for southern hemisphere winter time"

5. Page 16 Line 30: "for the polar spring period"

6. Page 17, Lines 6 and following: The authors are noting the excellent correlation of elevated BrO with sea ice extent. Is it possible to provide a quantitative estimate on how sea ice edge effects contribute to bromine explosions, compared to snow-blowing events?

Reply: We are not sure what the referee means and how to make a quantitative comparison.

7. Page 18 Line 8: "can have stratospheric origin"

8. Page 20 Lines 7/8: "frequency is 20%"

9. Page 20 Line 21: "BrO production"

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10. Page 21 Line 6: "(temperature, illumination, availability of surfaces for heterogeneous reactions, etc.)"

11. Page 21 Line 21: Does the model include bromine emissions from the above-mentioned heterogeneous reactions, e.g., interactions of of ocean water with fresh ice surfaces?

Reply: Again, we are not sure what the referee means. If the question relates to frost flowers, they are not explicitly included in the model. However, the use of observed snow salinity in the parameterization implies that the effect from frost flowers is implicitly included (through their influence on snow salinity).

12. Page 22 Lines 5/6: What is "a strong indication that [snow-blowing] probably plays an important role" supposed to mean exactly?

Reply: For the discussion on the blowing-snow mechanism, please refer to the replies to Referee #1 comments.

13. Page 22 Line 12: "it can reinforce"

14. Page 22 Line 25: As it stands, Figure 13 does not "confirm the existence of the mechanism of bromine release from blowing snow events"

Reply: For the discussion on the blowing-snow mechanism, please refer to the replies to Referee #1 comments.

15. Page 38 Figure 4: What exactly is plotted, Air Mass Factor or Weighting Function? To show the vertical distribution of the response of BrO to atmospheric composition, it may be more illustrative to plot Scattering Weights which, integrated over altitude, give the AMF.

Reply: Weighting functions are plotted in Figure 4. The ambiguity comes from the label of the x-axis: 'Air Mass Factor'. It has been changed in 'Weighting function'.

16. Page 39 Figure 5: This figure wastes some real estate. I suggest limiting the y-axis

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plot range to 2-8x1013 mol/cm2 to provide more detail and dynamic range.

Reply: We agree. This has been changed.

17. Pages 40/41 Figures 6/7: If space permits, I suggest adding a panel of BrO total VCD to the comparison. This should help identify where, if any, discrepancies exists between groundbased and satellite observations that manifest in differences of stratospheric and tropospheric VCDs as shown in the two panels of the figures.

Reply: One could simply add a third subplot (on top of the existing ones) with a comparison of the total columns, but we think it will not add a lot of information. As this aspect is not crucial for the reader, we prefer to keep the figures as they are.

18. Page 44 Figure 10: The inverted color scale of the "Tropopause height" row makes the visual comparison to the BrO columns more difficult than it needs to be. I suggest either inverting the color scale or plot "Tropopause pressure".

Reply: In line with the comment 15 of Anonymous Referee #1, we have inverted the color scale of “Tropopause height” plots of Fig 10.

19. Page 45 Figure 12: The legend in the plots is too small to read. I suggest to move the legend to a separate panel below the figures, with enlarged font size.

Reply: We agree. This has been changed.

Referee #3 comments (comments received and published: 26 January 2010)

The manuscript gives a detailed description of a novel algorithm to improve the determination of tropospheric BrO column densities from UV - spectra recorded by nadir viewing satellite instruments. Some applications on GOME-2 data are presented and some interesting conclusions regarding polar BrO ‘hot spots’ and BrO in the free troposphere are drawn. The described algorithm builds on an earlier publication with the same first author (Theys et al. 2009), which describes a central part of the new algorithm, i.e. the global stratospheric-BrO climatology. Moreover, the new algorithm

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presented here appears to improve over a similar algorithm described in a very recent publication by Salawich et al. 2010 in several points, for instance it uses NO2 to correct for photochemical effects, employs a wider spectral range less susceptible to O3 interference, and it gives a convincing error analysis of the derived tropospheric BrO columns. Overall, this appears to be a very important and thorough piece of work which should be of great interest to the scientific community. There are only few major questions that should be answered by the authors before the manuscript is ready for publication: (a) A central element of the algorithm is the correlation of BrO with the total O3-column. How does strong chemical loss of stratospheric O3 (e.g. the ozone hole) affect the results? This question is not discussed in the manuscript despite its great importance for the precise determination of tropospheric BrO hot-spots, which tend to occur in nearly the same area and time as stratospheric O3 loss (polar springtime). (b) Four of the authors of the present manuscript are also co-authors on Salawich et al. 2010, however there are major differences in the approach, in particular the spectral range used for BrO evaluation in this manuscript is 332-359 nm while Salawich et al. 2010 analyse much shorter wavelengths (320-347.5 nm), moreover in the work presented here a modified DOAS approach is used. What is the rationale for such a drastic change and how does it affect the results? (in fact it is hard to believe that the choice of the spectral range should not affect the resulting BrO columns and in particular possible interferences from O3). (c) A prominent result of Salawich et al. 2010 is the possibility that short lived organic Br-species make a major contribution to BrO in the polar lower stratosphere, it would therefore be interesting to know whether the present study confirms this result.

Reply:

(a) This question is discussed in our previous paper (Theys et al., 2009b) describing the stratospheric BrO climatology and the error associated to the parameterization of BrO columns, using O3 and NO2 vertical columns. The outcome of this error analysis is that the stratospheric BrO climatology provides reliable results with a precision better

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than 14% in all conditions. This error is included in the overall uncertainty on the stratospheric BrO correction treated in the present work.

(b) It should be said that none of the authors of the present manuscript have been involved in the development of the OMI BrO product (presented in Salawitch et al., 2010). Since the late nineties, the retrieval of BrO from space-based nadir UV instruments (like GOME-1, SCIAMACHY, GOME-2 and OMI) has historically been made using wavelength intervals lying between 336 and 360 nm (in order to avoid strong O3 absorption at shorter wavelengths). Therefore, we rather consider the improved OMI BrO product (presented in Salawitch et al., 2010) using the 320-347.5 nm range, as a drastic change with respect to (all) other satellite nadir BrO products (including the one presented here). It should be mentioned that porting retrieval settings 'as is' to a new sensor rarely work out (particularly for small absorbing species as BrO). Actually we tried to apply the OMI BrO fitting interval to GOME-2 but without success. We believe that one of the main reason why OMI is able to retrieve BrO in the 320-347.5 nm range, is because of the better OMI S/N ratio in the UV channel compared to GOME-2. The referee says that it is hard to believe that the choice of the spectral range should not affect the resulting BrO columns and in particular possible interferences from O3. We fully agree. Finding the optimal settings is usually determined empirically in an attempt to maximize the sensitivity to the trace gas and at the same time minimize interferences with other absorbers and instrumental effects. As far as this work is concerned, the BrO fit has been found to be better constrained by using 5 absorption bands (332-359 nm) rather than 4. This was only possible by treating the increasing O3 absorption (non-linear) signal with a modified DOAS approach. Note that using a short wave window as 320-347.5 nm leads to much stronger O3 interferences. For the OMI retrieval, this has been treated using a direct fitting method as explained (although briefly) in Salawitch et al. (2010). Finally, we have also compared our GOME-2 BrO total columns to the ones from OMI (not shown). The comparison exercise was over the Arctic region for two years (2007 and 2008). We found an excellent agreement (within fitting uncertainties) between both data sets. If needed, we can provide such material upon agreement with

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the OMI data provider.

(c) We think using satellite nadir BrO data to address the issue whether short lived organic Br-species make a major contribution to BrO in the polar lower stratosphere or not, is a difficult task. This is essentially because satellite nadir measurements are sensitive to both stratosphere and troposphere (albeit with different sensitivities) and that we can not exclude the existence of similar patterns in the stratospheric and tropospheric BrO columns fields. Conversely we consider that the question on the contribution of short-lived bromocarbons can be better tackled using vertically-resolved BrO observations from instruments on board aircrafts, balloons or satellites in the limb geometry (as done by many research groups) and (of course) with in-situ measurements of the short-lived bromine species themselves (in both stratosphere and troposphere). The approach we have followed to correct the total BrO column satellite observations for the stratosphere was to develop a stratospheric BrO climatology (Theys et al., 2009b) that is closely linked to an extensive set of stratospheric BrO observations from ground-based, balloon and satellite limb (SCIAMACHY) platforms. The CTM BASCOE underlying the stratospheric BrO climatology uses a bromine set-up including a short-lived bromobcarbons contribution (in the form of CH2Br2) of 6 pptv to the total stratospheric Bry loading (the latter value being in agreement with the latest estimate from the 2010 Ozone Assessment Report, Chapter 1). With this stratospheric BrO climatology, we have been able to reproduce and even correct the enhancements in total BrO column caused by increases in stratospheric BrO due to a decrease in tropopause height. We consider that result as a further indication that short lived organic Br-species make a significant contribution to BrO in the polar lower stratosphere. Our short-lived bromocarbons contribution to stratospheric Bry of 6 pptv lies at the lower end of the range of 5 to 10 pptv provided by Salawitch et al. (2010). However, given the uncertainties on the measured and modeling results of our analysis, we estimate 6 pptv as a reasonable value and we can not find an objective reason to consider a higher value. As for the question raised by Salawitch et al. (2010) whether satellite BrO 'hotspots' have a stratospheric origin, our analysis indicates (section 5.2) that

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these features are relatively infrequent, when using the definition of 'hotspot' found in Salawitch et al. (2010).

There are a number of minor questions the authors might want to consider:

1) Page 28637, lines 20-24: This sentence appears to be incomplete, also the statement made here is not in contradiction to BrO being present in the free troposphere.

Reply: We have changed the sentence line 22 "..leads to efficient ozone depletion in the polar boundary layer.." by "..leads to efficient ozone depletion in the polar troposphere..", to be more general.

2) Page 28638, line 14: Perhaps the publication "Hollwedel, J. et al. (2004), Year-toyear variations of spring time polar tropospheric BrO as seen by GOME, Adv. Space Res. 34, 804-808." would be more easily accessible than Hollwedel 2005.

Reply: Hollwedel et al. (2004) is more easily accessible but has little to do with the context of stratosphere-troposphere separation. Therefore we prefer to keep the reference Hollwedel (2005) in the text.

3) Page 28638, line 20: What is the meaning of " ... a negligible impact of the tropospheric BrO content on the stratospheric correction ..."

Reply: In past attempts to separate stratospheric and tropospheric BrO, the stratospheric correction also accounted for a possible free-tropospheric BrO background. The focus of these studies was the polar boundary layer emissions. We believe our approach is more general as further explained in the text (Page 28638 line 22-24).

4) Page 28639, lines 2-4: Does this mean that the limb-correction approach is only applicable to tropical latitudes (where the tropopause height exceeds 15km) ?

Reply: Yes.

5) Page 28642, lines 9-11: What are the implications of this statement for the retrieval used in Salawich et al. 2010?

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Reply: (Please refer to the reply to Referee #3 major comment b) for the discussion on BrO retrieval) This statement relates only to our GOME-2 retrieval in the 332-359 nm wavelength interval. For details on OMI retrieval, please refer to the authors of Salawitch et al. (2010).

6) Page 28642, line 26: Give literature reference describing BASCOE.

Reply: We have added a reference to Errera et al. (2008) and Viscardy et al. (2010)

Errera et al.: 4D-Var Assimilation of MIPAS Chemical Observations: Ozone and Nitrogen Dioxide Analysis, Atmos. Chem. Phys., 8, 6169-6187, 2008.

Viscardy, S., Errera, Q., Christophe, Y., Chabrillat, S., and Lambert, J.-C.: Evaluation of ozone analyses from UARS MLS assimilation by BASCOE between 1992 and 1997, JSTARS 3, 190-202, 2010.

7) Page 28643, lines 1-3: Give literature references supporting this statement.

Reply: We have added a reference to Theys et al. (2009b).

8) Page 28643, line 7: Give details how is the strat. BrO profile "calculated"?

Reply: This is described in our previous paper (Theys et al., 2009b). To clarify the text, we changed the sentence "..a stratospheric BrO profile is calculated using the O3 and NO2 (stratospheric) vertical columns.." by "a stratospheric BrO profile is calculated from the parameterization using the O3 and NO2 (stratospheric) vertical columns..".

9) Page 28643, line 19: 1 PVU equals 10-6 m2 s-1K kg-1.

Reply: This has been changed in the text.

10) Page 28643, line 24: How large is the "small effect"?

Reply: Calculations show it leads to a maximum of 3% differences in stratospheric column. We have added this information in the text.

11) Page 28644, line 1: "ensure consistency" with what?

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Reply: Ensure consistency with the total column observations, as described in the rest of the section 3.2.

12) Page 28646, line 7: Give definition (formula) of capital Phi.

Reply: A definition of Phi has been added in the text.

13) Page 28648, line 5: “This pragmatic choice ...” of what?

Reply: We agree it is not clear. We changed the sentence by “The choice of a free-tropospheric BrO profile constitutes. . .”.

14) Page 28648, lines 6-9: What is the source of the surface albedo?

Reply: For the discussion on the surface albedo, please refer to sections 3.3.1. and 3.3.2.

15) Page 28649, line 16: Does “adding in quadrature” refer to sum of squares?

Reply: Yes. This has been changed in the text.

16) Section 4: What is actually gained by the comparison with SCIAMACHY results?

Reply: The overall good agreement between GOME-2 and the (widely used and published) SCIAMACHY results in terms of seasonal and latitudinal variations strengthens our confidence in our GOME-2 BrO retrieval.

17) Page 28650, Lines 1-29: this section appears to belong into the experimental section (section 2).

Reply: We disagree. Placing these lines in section 2 will not clarify the text as they strictly relate to SCIAMACHY retrieval, only used in section 4.2.

18) Page 28652, line 11: Is there snow in Lauder in winter (August)?

Reply: Occasionally, Lauder can be snow-covered in winter but certainly not winter long as for Harestua.

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19) Page 28652, lines 23-25: Is the derived tropospheric BrO column (ca. 1.5E13 cm-2) actually a significant result in view of the (1 sigma!) error amounting to (0.8-1.5)E13 cm-2?

Reply: In spite of the large errors associated to the retrieval, we consider the derived averaged tropospheric BrO column (1.5E13 cm-2) as a significant and reasonable result: it is consistent with ground-based (Figs 6 and 7) and satellite global observations for nearly clear-sky (Fig. 14) and cloudy pixels (Fig. 15).

20) Page 28653, lines 14-15: Could the sea ice effect be an effect of different albedo between ice and water?

Reply: No. In principle, the albedo effect is accounted for in the retrieval and the difference in tropospheric column between ice and water is much too strong to be explained by a possible error on the albedo values used.

21) Comment of figures: Generally the print on the axes and in particular on the colour scales (Figs 8, 9, 10, 13) is too small and therefore very hard to read. In Fig. 12 (lower panel) the lable covers part of the curves.

Reply: This has been changed.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28635, 2010.