Response to Anonymous Referee #1

Anonymous Referee #1General Comments:

The paper describes an interesting event of enhanced tropospheric BrO concentrations at Spitsbergen. During that event very rapid decrease of O3 and mercury was observed. In my opinion this is a very interesting case study and should finally be published in ACP. However, in its current form, the paper has a few major and many minor problems. They need to be addressed before acceptance.

Author's Response:

We thank the referee for the positive comments for this study and appreciate for all the valuable comments that have improved this manuscript. Please kindly find our point-to-point response to the problems/comments below in blue and the change of the manuscript in orange.

Major problems

A) The introduction is not very clear. Please put your study in a better context of existing studies. For example, please make the following points more clear: - what are important current open research questions - what does this study contribute to answer these questions

Author's Response:

Thanks for the referee's advices. We have rewritten the introduction part following your suggestions.

"Bromine monoxide is one of the key reactive halogen species which have profound impacts on the atmosphere chemistry of the polar boundary layer (PBL), especially the oxidative capacity of the troposphere (Saiz-Lopez and von Glasow, 2012). The presence of reactive bromine (in some situations "bromine explosion") is considered as the main cause of the depletion of boundary layer ozone, called "ozone depletion events" (ODEs) (Platt and Hönninger, 2003). Furthermore, halogens can efficiently oxidize gas-phase mercury, which can lead to a decrease of gaseous mercury, called "atmospheric mercury depletion events (AMDEs)" (Ariya et al., 2002;Ariya et al., 2004;Lindberg et al., 2002;Lu et al., 2001;Steffen et al., 2008).

Enhanced BrO was firstly detected by Long Path Differential Optical Absorption Spectroscopy (LP-DOAS) observations (Platt, 1994). Satellite measurements confirmed that the phenomenon of bromine enhancement covers larger area of polar regions by deriving daily global BrO map (Richter et al., 1998;Wagner and Platt, 1998;Wagner et al., 2001;Sihler et al., 2013). The primary source of reactive bromine has been explained by a series of photochemical and heterogeneous reactions at the surface of frozen ocean during polar spring (Fan and Jacob, 1992). A typical heterogeneous reaction model between gaseous and condensed phases was shown in Fig.1. Bromine is released from salty ice surfaces to the atmosphere in an autocatalytic chemical mechanism that oxidizes bromide to reactive bromine. The

reaction of HOBr in aerosol is proposed to be the pivot to explain the recycling reaction, which is an acid-catalyzed reaction (Simpson et al., 2007). Sea-ice (first year) surfaces, brine, and frost flowers have been considered as possible source of bromide aerosols (Kaleschke et al., 2004; Lehrer et al., 2004).

However, the true circumstance is that the ODEs and BrO enhancement are not always in consistency. There are only few reports of Arctic ODEs that are assumed to have been observed primarily as a result of local-scale chemical mechanism (Bottenheim et al., 2009; Jacobi et al., 2006). As the photochemical reactions are quickly happened and the lifetime of the intermediate products, e.g. the reactive bromine radicals are quite short, more accurate data with higher time resolution are needed to analyzing chemical process in PBL and investigating source of bromine.

MAX-DOAS (Multi-AXis Differential Optical Absorption Spectrometer) technique has the advantage of being able to separate clearly the tropospheric and stratospheric portions of the atmospheric column, and even derive a crude vertical profile (Frieß et al., 2011). When pointing to a direction slightly above the horizon, high sensitivities for the trace gases close to the ground can be obtained due to the long light path through the trace gas layers. It is also an important calibration of satellite observations (Platt and Wagner, 1998). In the Arctic area, ground-based MAX-DOAS long term observations have been made at Barrow, Alaska (71 °N, 157 °W), Alert, northern Canada (82.5 °N, 62.3 °W) and Ny-Ålesund, Svalbard (78.9 °N, 11.8 °E)(Tab.1). Besides, air-borne (Neuman et al., 2010;Pöhler et al., 2013) and ship-borne measurements (Bottenheim et al., 2009;Jacobi et al., 2006;Leser et al., 2003;Wagner et al., 2007) are important supplements for the analysis and modelling of bromine chemistry.

However, recently the Arctic sea ice coverage has dramatically reduced, especially at East Greenland and North of Europe. As influenced by the North Atlantic Warm Current (NAWC), the near surface air temperature and sea surface temperature (SST) are getting higher at North Europe (Fig.2). In recent years, Kings Bay in Ny-Ålesund even has ice-free open water all year round, which is a unique character comparing with other parts at the same latitude in Arctic. Therefore, it is critical to have a better understanding of the possible reactive bromine source and the impact of the halogen activation on PBL ozone depletion and mercury deposition under a rapidly change Arctic.

In this study, we have caught a unique process of enhanced bromine and depleted ozone in Ny-Ålesund in late April. The key role of bromine was confirmed by ground-based MAX-DOAS measurements. This event provides a rare opportunity to investigate the source of bromine and process of ozone depletion at this area. Kinetic studies of ozone depletion and gaseous mercury deposition are discussed afterwards."

B) The discussion of the role of long range transport is not clear. In my opinion, from the data you present (trajectory and satellite data), long range transport of air masses enriched in bromine can not be excluded. This should be clearly stated in the paper. Nevertheless, from other findings, I think you can very well conclude that this is probable a local event: -the sea ice occurred only for a very short period close to the

measurements -exactly during this period, the enhanced BrO is observed. Both findings indicate that the enhanced BrO is caused by a local source (connected to the sea ice). Here, it would be very important to have more information: -how large was the area in which the sea ice appeared? -how does this area compare to spatial scale determined by the wind speed (and direction) and the duration of the ozone destruction? -how long have the air masses been in contact with the sea ice before they reached the measurement site? -I think it is in general very important here to discuss the importance of transport compared to chemical processes.

Author's Response:

We agree reviewer's opinion that this BrO enhancement is a local event.

Kings Bay is an inlet on the west coast of Spitsbergen, one part of the Svalbard archipelago in the Arctic Ocean. The inlet is 26 km long and 6 to 14 km wide. The BrO map and the BrO VCD in Fig. 6 are both origin from GOME-2 satellite measurements, with a ground-pixel size of 80×40 km^2. According to the light path of the MAXDOAS instrument, the range of MAX-DOAS measurement is about 10km radius area, which covers the central area of the fjord.

The GOME-2 BrO product from University of Bremen showed there is high level of BrO at the North of Greenland as well as Siberia from the mid to late April. The NCEP reanalysis data showed a strong High above Greenland resisted for several days (from 23/04 to 27/04), which indicated the similar conclusion that the transport of the air masses is not within a short period of time. However, what we found by ground-based MAX-DOAS just lasted for several hours, which is at different time scale.

We added some descriptions in the manuscript part 4.1.

"Possible sources of reactive bromine are newly formed sea ice and frost flowers which can provide highly concentrated saline surfaces, thereby adequate sea salt aerosols. Another important source is the transport of the air masses which already contain elevated BrO and depleted ozone. Therefore, we investigate the history of the air masses arriving at measurement site using backward trajectories. Furthermore, the sea ice distribution (Fig.2) and the satellite BrO maps (Fig.10) are important instructions as well.

72-hour backward trajectories at Ny-Ålesund (10, 500, 1000 meters a.s.l.) from 26 April (0600 UTC) to 27 April (1800 UTC) were calculated every 6 hours (Fig.9). From the map of three altitudes, air masses turned from northwest direction, which is origin from North America to the middle of Arctic Sea. From the vertical distribution of air masses, before noon of 26 April, the air masses came from low boundary layer, while after 18:00 26 April, from the upper troposphere.

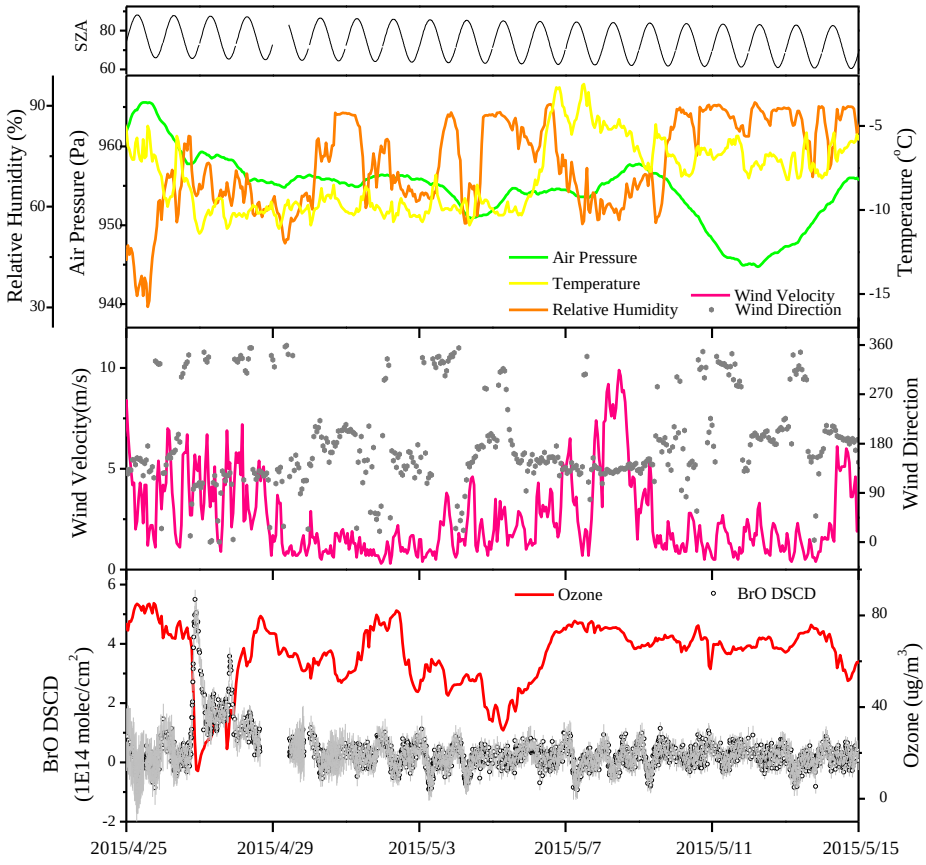
BrO VCD map from GOME-2 measurements from 20 April to 13 May 2015 are shown in Fig. 10. BrO clouds existed at two main periods: coastal North America and Chukchi Sea during 22-23 April and North of Siberia during 08-11 May 2015. Both of the BrO clouds lasted about three to four days, the first of which was occasionally at the same period with the Ny-Ålesund BrO enhancement event. However, what we

found by ground-based MAX-DOAS just lasted for several hours, which is at different time scale. Thereby, air masses transported from high latitude of Arctic from 22 April might have an impact on BrO enhancement in Ny-Ålesund, but not the most critical reason."

C) You use a fixed Fraunhofer reference spectrum. In my opinion this is not a good strategy here, because you are interested in tropospheric BrO DSCDs. I strongly suggest to use a sequential Fraunhofer reference. The QDOAS software which you use offers this option. Alternatively, you could subtract the BrO DSCDs from the 90◦ measurement of each elevation sequence from the BrO DSCDs at low elevation angles.

Author's Response:

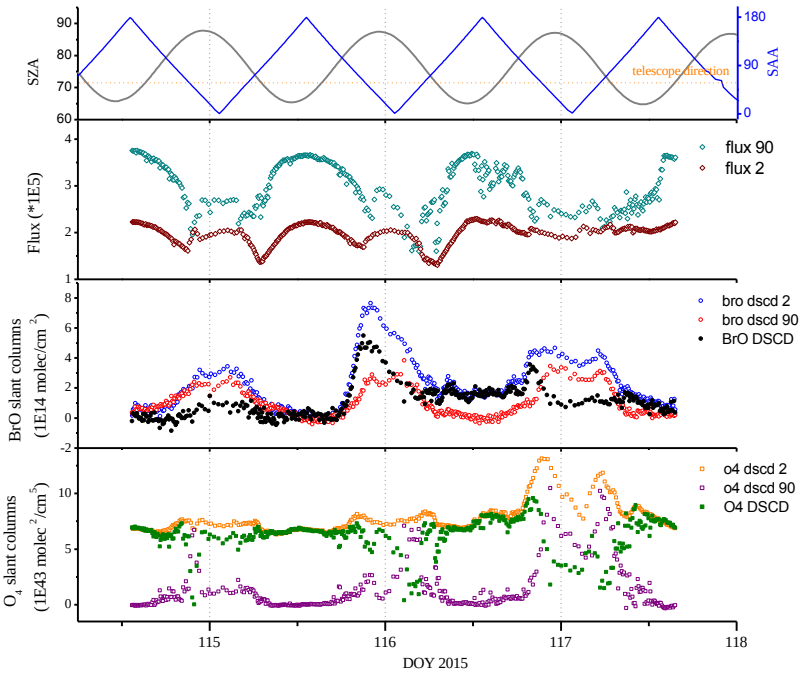
Thanks to the referee's suggestion. The time series of BrO DSCDs of 2 elevation angle are calculated by subtracting the zenith BrO dSCDs. The figure 5 has been revised. The enhancement of troposphere BrO during 26-27 April is still very clear with the highest value of 5.6×10^{14} molec/cm^2.



D) You apply the method of Sinreich et al. (2013). However, this method should be applied to the tropospheric DSCDs, for which the stratospheric part was already removed (both BrO and O4), see the point above. In the current form, the derived O4 light paths include the light paths in the free troposphere and stratosphere, which are misleading for your study.

Author's Response:

Thanks to the referee for pointing this mistake. As shown above, tropospheric BrO has been calculated by subtracting 90 ° dSCDs of the same sequence. However, when calculating O_4 DSCD, we find large inconsistency of O_4 dSCDs between 2 and 90 elevation angles results, leading to miscalculated results of O4 DSCDs. From the figure below, we can find that the solar zenith angles are from 65 ° to 88 ° at the observation site. As given in Y Wang et al, the rapid method should be applied for SZA<70 ° and RAA>50 ° to ensure that the uncertainties are mainly< 20%. So this method might not very suitable at high latitude polar regions. Therefore, we remove the part of light path calculation and calculate the BrO VMR assuming a homogeneous BrO layer of 1 km thickness at the surface.



E) From the dependence of the BrO DSCDs on elevation angle you conclude that the highest BrO concentration is located at the surface. If this was the case, then the differences of the BrO DSCDs for the low elevation angles should be much larger. In my opinion, the highest BrO concentrations are probably not located directly at the surface. To clarify this important point I suggest to perform one of the following tasks: a) perform RTM simulations (for different assumed BrO profiles) and compare the RTM results to your measurement results. Then you can derive more robust conclusions about the BrO profile shape. b) it would be even better to perform a full profile inversion.

Author's Response:

We perform the RTM simulations to get BrO slant columns using four different assumed BrO profiles: a. 0-0.5 km; b. 0-1 km; c. 0-2 km; d. 0.5-1 km; e. 1-2 km. The modeled and measured BrO SCDs during the event were shown in figure below. A

BrO layer height between 0-1 km can be considered as the most possible distribution of BrO layer, which is compatible with the measurements.

The color of the measured BrO dots also showed different steps of this process. The blue dots indicated data points from the first 4 hours of the BrO enhancement event in 26/04, while red and orange dots indicated 4 later hours in the morning of 27/04 when ozone was almost depleted already. The fact that enhanced BrO levels changed from 0-1 km to more likely at 0.5-1 km could be explained by Br/BrO reactions taking place from the boundary layer to the free troposphere.

We modified the corresponding parts of the manuscript.

"We perform the radiative transfer modeling (RTM) simulations using SCIATRAN (Rozanov et al., 2005) to get modeled DAMF using five different assumed BrO profiles with evenly distributed air masses: a. 0-0.5 km; b. 0-1 km; c. 0-2 km; d. 0.5-1 km; e. 1-2 km (Fig.5a). The models are performed under clear sky condition with no aerosol input. Remarkable difference exists for different input profiles. For BrO layer 0-0.5km, 0-1 km and 0-2 km, DAMFs all increase with the decrease of elevation angles. While for BrO layer 0.5-1 km and 1-2 km, the dependence on the telescope elevation angle is weaker especially at small elevation angles.

The modeled BrO SCDs for different input BrO profiles are shown in Fig.5b. The input BrO VCD is 5×10^{13} molecules/cm^2. The measured BrO SCDs from 20:00 26/04 to 05:00 27/04 are also plotted. The blue dots indicate data points for the first 4 hours in 26/04, while red and orange dots indicate later 4 hours in the morning of 27/04. BrO layer between 0-1 km can be considered as the most possible distribution of BrO layer, which is compatible with the measurements. Thereby, BrO SCDs can be converted to volume mixing ratios (VMR) assuming a homogeneous BrO layer of 1 km thickness at the surface."

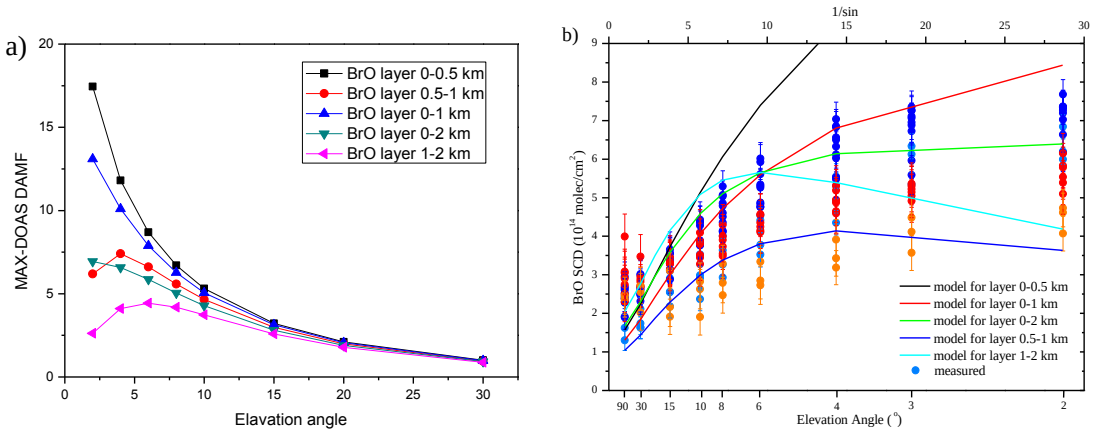


Fig. 5 The modeled DAMF (a) and BrO slant columns (b) using radiative transfer modeling simulation. DAMF are the differences of AMF for low elevation angles and zenith direction. The models are performed assuming a clear sky condition with no aerosol. In part b, the tropospheric BrO VCD is 5×10^{13} molecules/cm^2. The measured BrO SCDs during the event are also shown (solid dots). The blue dots indicated data points from 20:00 to 24:00 in the evening of 26/04. The red and orange dots indicated data points from 00:00-4:00 in the morning of 27/04.

Minor points:
Page 1, line 24: Enhanced BrO was first detected by LP-DOAS observations. Please add the respective references.
Author's Response: We add the respective reference.

Page 2, line 4: I think Monsoon and turbulence are not the correct terms here. Monsoon is a tropical to mid latitude phenomenon. Why not simply write 'wind'?
Author's Response: It has been revised.

Page 2, line 19: I don't agree with this statement for observations over bright surfaces like ice or snow. I think for such conditions a general underestimation was not reported.
Author's Response: This sentence has been revised.
"It is also an important calibration of satellite observations, which has lower spatial and temporal resolution compared with ground-based measurements."

Page 2, line 21: You write 'Long-path DOAS measurement provides regional determination of BrO in PBL.' It is not clear what exactly you want to say with this. LP-DOAS usually has light path lengths between a few and 20 km.
Author's Response: This sentence has been removed.

Page 2, line 22: you write 'but few ground-based MAX-DOAS measurement of BrO has been performed in Ny-Ålesund.' I think you can not write this. To my knowledge, University of Bremen performs MAX-DOAS measurements there since many years. (Did you compare your results with the Bremen results?)
Author's Response: This sentence has been removed. And corresponding references have been added.

Page 3, line 9: Did you perform MAX-DOAS measurements also before and after the presented period? Have you observed similar events before or after, or in other years?
Author's Response: We have carried out the MAX-DOAS measurements at Ny-Ålesund intermittently since 2010. However, the instrument began to work every year mostly from the early summer. So this is the first time we have measured BrO at this area.

Page 3, line 9: What do you mean with 'wavelength adjustment'? Why do you have no measurements during such periods of wavelength adjustment?
Author's Response: At that day, we were trying to get some IO information. So we changed another spectrometer with different wavelength range. It is a pity that we do not have continues data records.

Page 3, line 19: Please give typical integration times
Author's Response: We have added this information.
"The integration time (typically from 100 ms to 2000 ms multiple 100 scan times) of

each measurement depends on the intensity of scattered light which can be influenced by cloud and visibility."

Page 4, line 17: please add information about typical uncertainties of this method, which are given in Sinreich et al., 2013. You might also have a look at the paper by Wang et al., 2015: Wang, Y., Li, A., Xie, P. H., Wagner, T., Chen, H., Liu, W. Q., and Liu, J. G.: A rapid method to derive horizontal distributions of trace gases and aerosols near the surface using multi-axis differential optical absorption spectroscopy, Atmos. Meas. Tech., 7, 1663-1680, https://doi.org/10.5194/amt-7-1663-2014, 2014.
Author's Response: We have given up using this method (see details in major point D).

Page 4, line 20: To my knowledge, the formula is only valid for the tropospheric DSCDs. That means that a) the DSCD for 90◦ elevation of the individual elevation sequence have to be subtracted from the DSCDs of the low elevation angles (for analysis with fixed reference) before the formula is applied b) or the analysis has to be performed with a sequential reference. Since you use QDOAS, I strongly recommend to use this option.
Author's Response: As shown above, tropospheric BrO has been calculated by subtracting 90 °dSCDs of the same sequence.

Page 4, line 24: In my opinion it makes no sense to apply such a correction, because of two reasons: a) the differences of the light paths for such small wavelength differences are very small b) the errors of this method (Sinreich et al) are generally rather large. Thus the uncertainties caused by the different wavelengths are negligible. I suggest to remove this part (lines 23 to 31)
Author's Response: This part has been removed.

Page 5, line 25: The results in Fig. 5 indicate that enhanced BrO (above the background) is found until 4 May 2015.
Author's Response: What the author means is that the surface ozone concentrations did not recover until 29 April. We have revised this in the manuscript.
"At the same period, surface ozone sharply decreased to several ppb and not recovered to normal value until 29 April. During this period, the wind velocity is more than 5 m/s and decreases in 29 April. Over a period of one week, elevated BrO levels went back to the detection limit in 4 May under a stable boundary layer."

Page 5, line 29: I suggest to remove the GOME-2 BrO VCDs from the figure. You show total BrO VCDs. It is unclear how they relate to the BrO mixing ratios from the MAX-DOAS. If you want to keep the GOME-2 BrO VCDs, then you should discuss, how large the stratospheric BrO VCD is. And you should indicate, above which value of the total BrO VCD you think they are affected by enhanced tropospheric BrO.
Author's Response: We have removed the GOME-2 BrO VCDs from the Fig.6.

Page 6, line 1: Since you use a fixed Fraunhofer reference, these light path lengths include the light paths in the free troposphere and stratosphere. This makes no sense here. I strongly suggest that you should use a sequential Fraunhofer reference (see major point above).

Author's Response: This part has been removed.

Page 6, line 4: at least on 27 April a slight enhancement is seen.

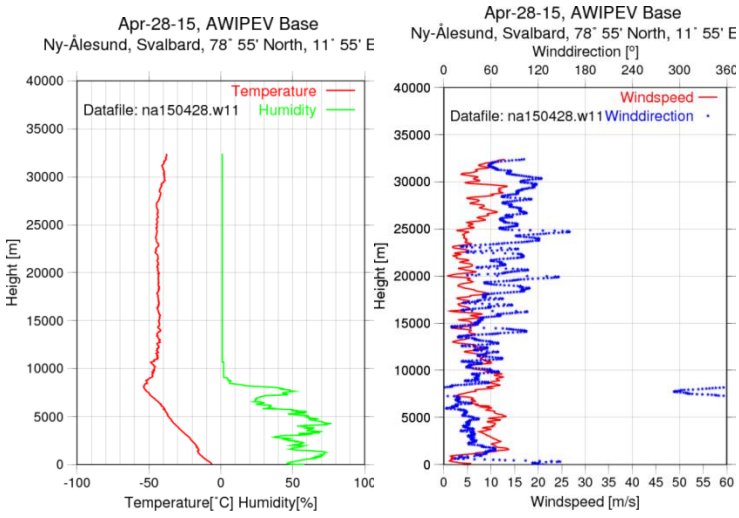
Author's Response: The BrO VCD from GOME-2 has been removed from Fig.6.

Page 6, line 9: The differences of the BrO DSCDs between 2◦ and 4◦ are very small (5 to 10%). In my opinion this indicates that the highest values are probably not directly above the surface. I suggest that you should perform RTM simulations (for different assumed BrO profiles) and compare them to the measurement results. Then you can derive more robust conclusions about the BrO profile. Alternatively also a full profile inversion could be done.

Author's Response: Thanks for the referee's suggestions. We have performed the RTM simulations and compared them to the measured results. The comparison indicates that BrO is not exponentially decreased with the altitude. Please see detail in major point E and corresponding part in the manuscript.

Page 6, line 12: how high is the boundary layer? Maybe the maximum BrO concentration is on the upper edge of the boundary layer? (see e.g. Wagner et al., 2007)

Author's Response: According to the sondes records of temperature, humidity and wind speed from AWIPEV, the height of the troposphere is around 8000 meters and the height of boundary layer is around 1200 meters.



Page 6, line 28: In my opinion this can not be concluded. The trajectories pass over several regions with enhanced BrO (e.g. directly north of Spitsbergen). So, in principle air masses enriched in BrO might have been transported to Spitsbergen.

Author's Response: We have revised this part in the manuscript.

"72-hour backward trajectories at Ny-Ålesund (10, 500, 1000 meters a.s.l.) from 26 April (0600 UTC) to 27 April (1800 UTC) were calculated every 6 hours (Fig.9). From the map of three altitudes, air masses turned from northwest direction, which is origin from North America to the middle of Arctic Sea. From the vertical distribution of air masses, before noon of 26 April, the air masses came from low boundary layer, while after 18:00 26 April, from the upper troposphere.
BrO VCD map from GOME-2 measurements from 20 April to 13 May 2015 are shown in Fig. 10. BrO clouds existed at two main periods: coastal North America and Chukchi Sea during 22-23 April and North of Siberia during 08-11 May 2015. Both of the BrO clouds lasted about three to four days, the first of which was occasionally at the same period with the Ny-Ålesund BrO enhancement event. However, what we found by ground-based MAX-DOAS just lasted for several hours, which is at different time scale. Thereby, air masses transported from high latitude of Arctic from 22 April might have an impact on BrO enhancement in Ny-Ålesund, but not the most critical reason."

Page 7, line 15: The enhancement goes very slowly back to normal values (until 4 May). You might mentioned the period here.
Author's Response: It has been added in Part 4.1.

Fig. 2b: to which reference (time period) are the anomalies calculated? Please give a reference for the map.
Author's Response: Fig. 2b has the same reference as Fig. 2c.

Technical suggestions / language improvement (please note that language improvement is urgently needed; here I list only a few points)
Page 1, line 11: 'difficulty of real-time observations' What exactly is meant here?
Author's Response: This sentence has been revised.

Page 1, line 17: separately => respectively?
Author's Response: Revised.

Page 2, line 4: former => source?
Author's Response: Revised.

Page 2, line 9: If you took this scheme from another publication, please add the corresponding reference.
Author's Response: It is an original figure.

Page 4, line 18: The sentence 'The diurnal variations of the clear-sky AMFs for BrO are in accordance with O4 in the boundary layer.' is not clear to me. Please clarify.
Author's Response: This part has been removed.

Page 5, line 13: Are you sure that the BrO maps are from NASA? In Fig. 8 you show

results from Uni Bremen.

Author's Response: GOME-2 BrO maps are from Uni Bremen. Station overpass BrO VCDs are downloaded from NASA products. We have added the reference.

Page 5, line 26: unpredictable => unexpected?

Author's Response: Revised.

Fig. 5: It should be mentioned that presented BrO DSCDs are obtained from measurements at 2◦ elevation angle.

Author's Response: We have added this information in Fig.5.

Fig. 8: Not the tropospheric, but the total BrO VCDs are shown. Please correct the caption. Would it be possible to show additional BrO maps for the period after 27 April?

Author's Response: GOME-2 BrO VCDs have been removed from Fig.6.
The BrO maps downloaded from Uni Bremen for period 27/04-13/05 are shown below.