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.

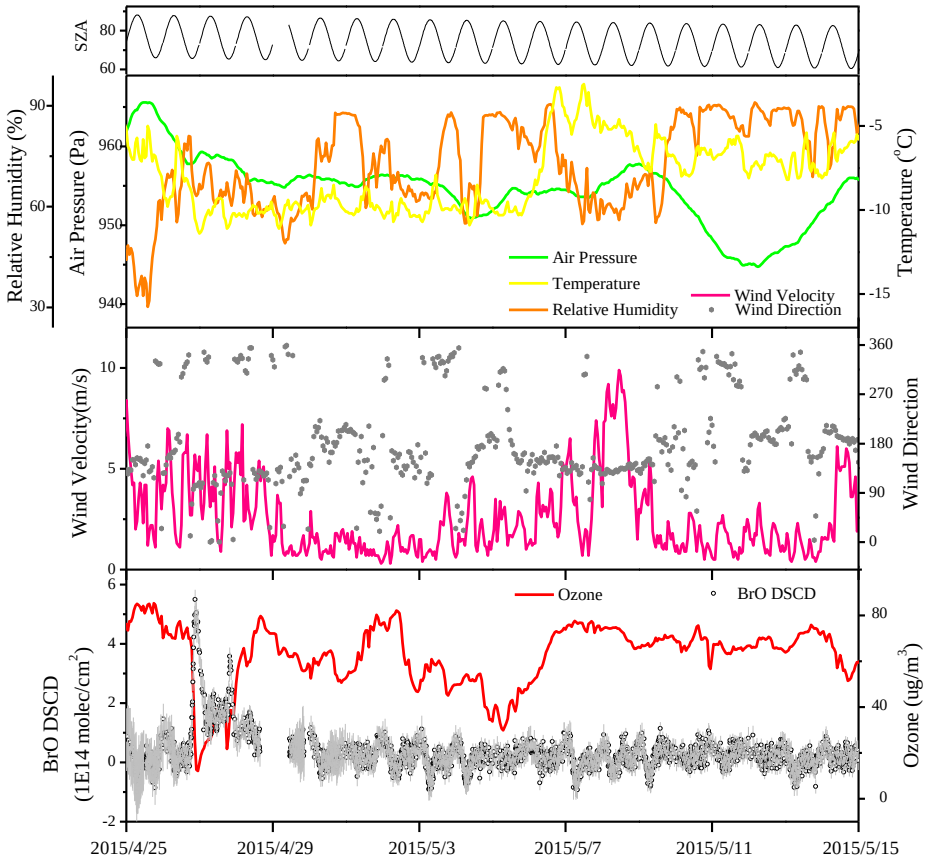
BrO VCD map from GOME-2 measurements from 20 April to 13 May 2015 are shown in Fig. 10. BrO clouds existed at two main periods: coastal North America and Chukchi Sea during 22-23 April and North of Siberia during 08-11 May 2015. Both of the BrO clouds lasted about three to four days, the first of which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

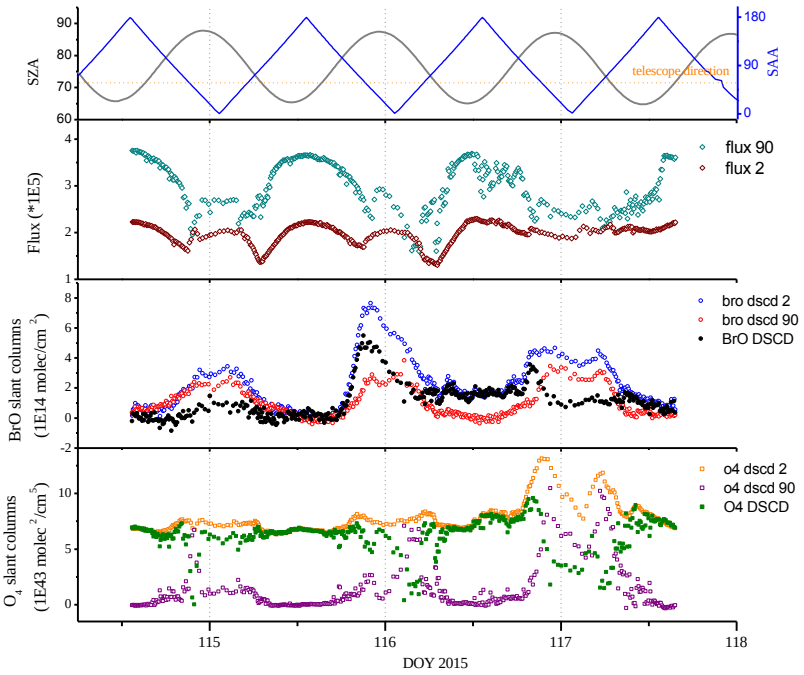
Thanks to the referee's suggestion. The time series of BrO DSCDs of 2 elevation angle are calculated by subtracting the zenith BrO dSCDs. The figure 5 has been revised. The enhancement of troposphere BrO during 26-27 April is still very clear with the highest value of 5.6×10^{14} molec/cm^2.



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."

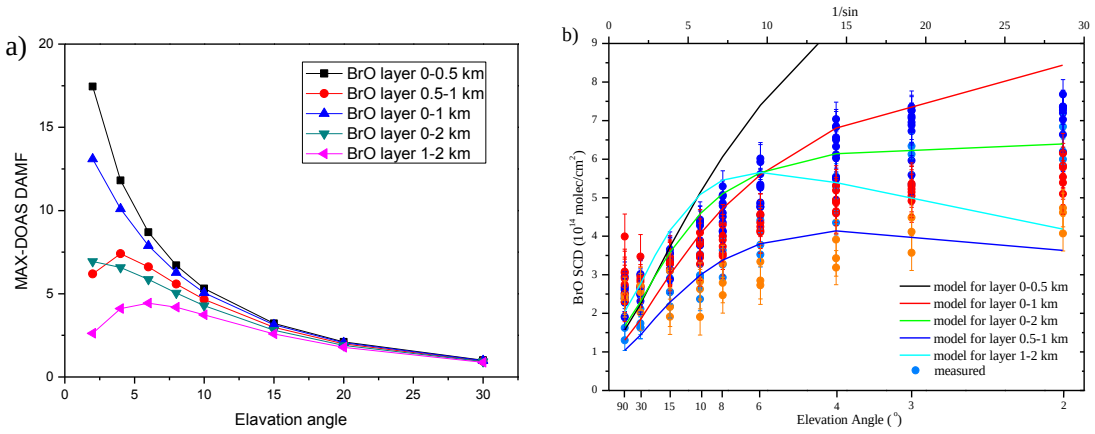


Fig. 5 The modeled DAMF (a) and BrO slant columns (b) using radiative transfer modeling simulation. DAMF are the differences of AMF for low elevation angles and zenith direction. The models are performed assuming a clear sky condition with no aerosol. In part b, the tropospheric BrO VCD is 5×10^{13} 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.

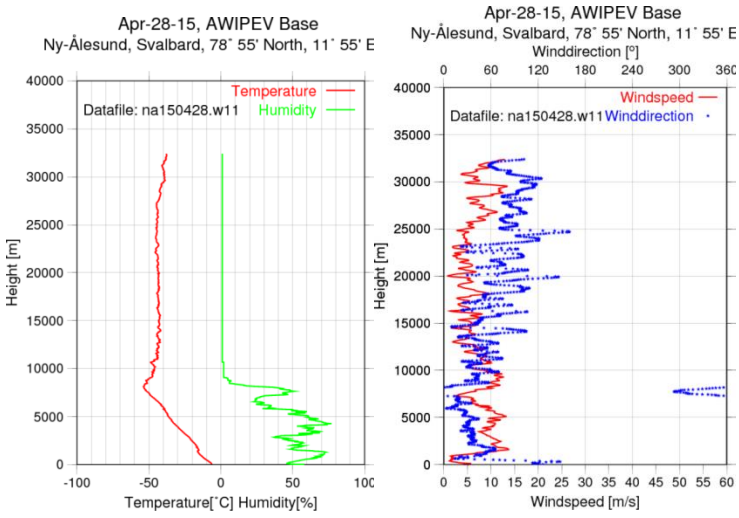
Author's Response: The BrO VCD from GOME-2 has been removed from Fig.6.

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?

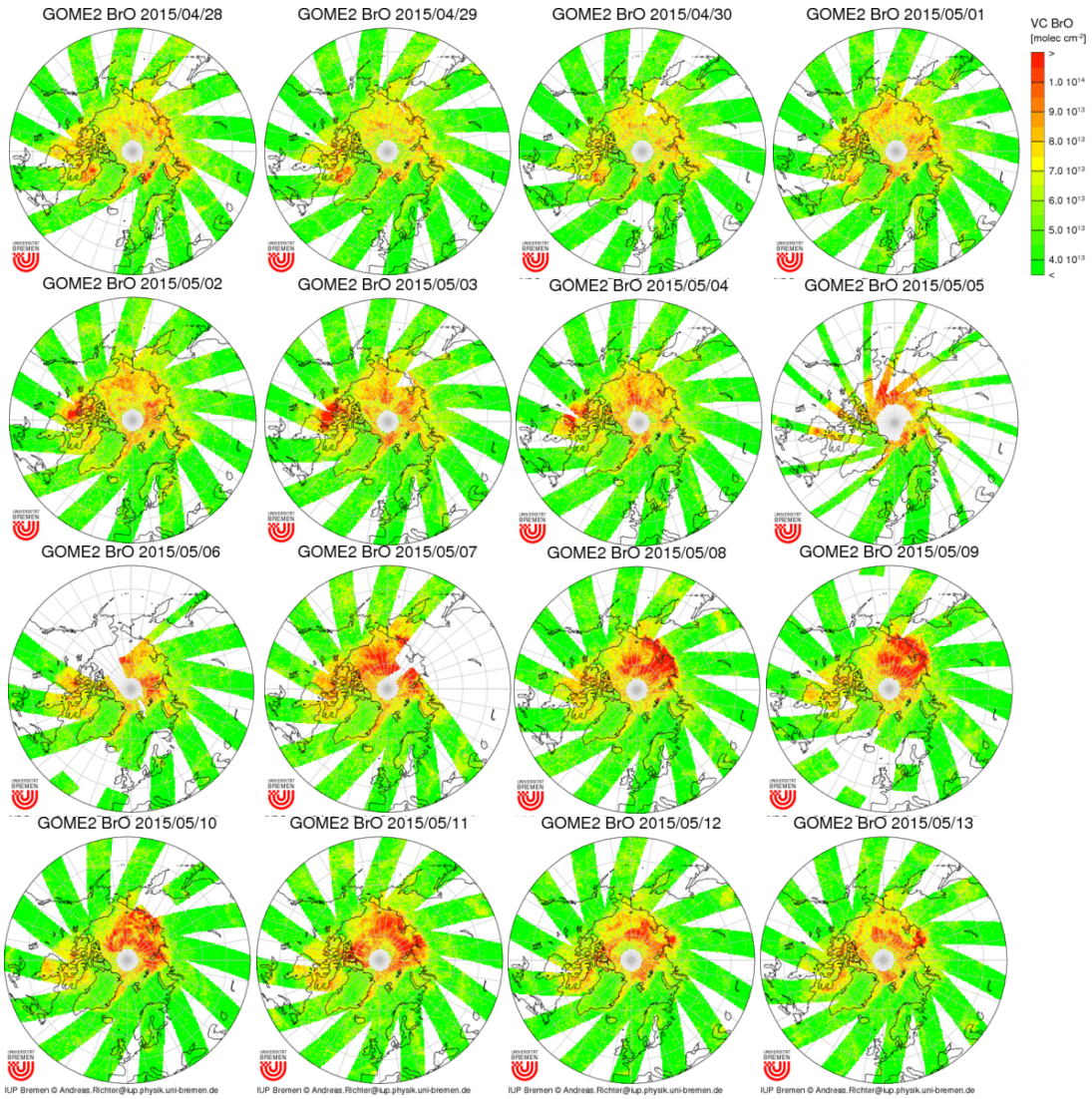
Author's Response: Revised.

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.



Response to Anonymous Referee #2

Anonymous Referee #2 General Comments:

Ozone and mercury depletion events are recurrent phenomena characterizing the atmospheric chemistry of both polar regions during springtime. Despite more than 30 years of studies of such events, major gaps still exist in our knowledge on processes, necessary conditions, and amplitude of such events. One of the major difficulties is related to the fact that observed decreases in ozone and mercury concentrations can be caused by local chemical processes as well as the advection of already depleted air masses. Luo et al. report here new measurements of BrO concentrations performed at Ny-Ålesund during a period of approximately three weeks in late April/early May 2015 with an episode of elevated BrO, which is one of the reactive species involved in the chemical destruction of ozone and the oxidation of mercury. Observed ozone and mercury concentrations show strong decreases parallel to the enhancement of BrO. After evaluating meteorological conditions and remote sensing data, the authors propose that this is one of the rare cases with in situ observations of local processes leading to the depletion of ozone and mercury. While such a conclusion appears possible, I'm less convinced than the authors that the available data and analysis allows a firm decision about the influence of local chemistry versus atmospheric transport. I suggest a more extensive discussion of the limitations of the available data and potential scenarios with the corresponding pros and cons, so that each reader can form her/his personal opinion. Below I describe in more detail my major concerns that should be discussed in a revised manuscript.

Author's Response:

We sincerely appreciate the referee for the conscientious and responsible comments, which greatly contribute to improving the quality of this manuscript. The source of BrO is the pivotal of the discussion. Following the referee's suggestions, more information and analyses have been included in the manuscript. Please find the point-by-point responses listed below, highlighted in blue and the changes in the manuscript in orange.

Major comments

The authors claim that according to the trajectories in Fig. 9 the increase of BrO cannot be explained by the transport since all air masses do have the same origin. Nevertheless, the trajectory close to sea level arriving at the beginning of the BrO episode (18:00; 26/04) travelled closest to the northern coast of Greenland. However, some of the other trajectories shown in Fig. 9 originated from areas close to the North Pole. I believe that this can indicate different origins of the air masses. Moreover, reanalysis data (e.g. NCEP) show that the synoptic situation on that day was characterized by a strong high above Greenland and a large, but weaker low over Siberia. As a result, it appears possible that air masses traveling close to Greenland and influenced by the high may have had different properties and composition compared to those stemming from the North Pole and related to the low. Even

stronger differences are visible in the backward trajectories at 3000 m altitude. (By the way, it remains unclear why these trajectories are shown.) Therefore, the statement that the "trajectories followed similar pathways, which indicate a stable circulation pattern . . ." (page 6, line 27) appears to overly simplifying the meteorological conditions. A more detailed analysis of the mesoscale situation could confirm (or not) the hypothesis of the authors.

Author's Response:

In this paper, we have preliminarily analyzed the source of BrO according to the HYSPLIT model and satellite products. Although the temporal resolution of the satellite measurement is one or two overhead data per day, we still can get a clue of the tropospheric BrO distribution. The GOME-2 BrO maps from Uni Bremen showed there is high level of BrO at the North of Greenland as well as Siberia from the mid to late April. However, what we found by ground-based MAX-DOAS just lasted for several hours, which is at different time scale. 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 in a short period of time. Thereby, before, during and after the BrO enhancement episode at the night of 26/04, the air mass of Ny-Ålesund has the similar background level. The back-trajectories showed the air almost come from the same altitude, which means there was no air turbulence at vertical direction during the episode. The back-trajectory at 3000 m has been removed.

According to the referee's suggestions, we add some detail description of the synoptic situation of the observation site in the revised manuscript. We consider that air masses transported from high Arctic might have an impact. But in an hourly time scale, the sea ice occurred in the Kings Bay, exactly the same period the enhanced BrO observed are more likely reason of this event.

Moreover, the BrO map for 26/04 in Fig. 8 demonstrates enhanced concentrations close to Greenland and probably lower concentrations further north (but due to the lack of data this remains speculative). It appears possible that the elevated concentrations are related to the transport of air masses enriched in BrO (or at least air masses enriched in BrO precursors) and already depleted in ozone and mercury. To my knowledge, the most exceptional case of transport-related changes in ozone was presented by Morin et al. (Geophys. Res.Lett., 32, L08809, doi:10.1029/2004GL022098) demonstrating that ozone concentrations can vary on the time scales of minutes due to transport.

Author's Response:

The referee thought the BrO map is the indicator of the transport of the air masses. But if you look carefully at the map, you can find that in 27/04 BrO concentration at east side rather than west side of Svalbard archipelago, where Ny-Ålesund located, is at high value. Then, we can take a look at the sea ice distribution on that day. The

west side of Svalbard is ice free ocean, while the east part is still sea ice covered. You can find the same situation at east side of Greenland. Therefore, the local sources from sea ice surfaces are more likely reason of enhanced BrO in this case.

As for the depleted ozone and mercury, there were many earlier studies indicated that they were not always in coincidence with the enhancement of BrO. In some cases, when ozone was only partially depleted and the anticorrelation between BrO and ozone was disappeared, it was possibly caused by the presence of aged air masses already depleted in ozone and mercury (Friess et al, 2011). But in this case, the ozone and mercury concentrations rapidly and synchronously dropped to a very low level, which was more likely caused by a process of reaction in participation with BrO.

The BrO map as well as the BrO VCD further manifests an additional counter-argument of local chemistry driving the ozone and mercury depletion: The Ny-Ålesund area is not part of the area with elevated BrO concentrations. In previous studies claiming local chemical processes (e.g. Jacobi et al. 2006) the measurement sites were located at least close to the area with enhanced BrO. I understand that the authors claim that differences between the satellite and ground measurements of BrO can occur (page 6, line 4ff), but in my opinion such differences, their origin, and potential consequences should be discussed in more detail.

Author's Response:

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. Besides, the coastal zone is considered as the most difficult area for satellite retrieving because of its complex underlying surface. Therefore, satellite measurements are far from enough to evaluating the local chemical processes of regional area, like Kings Bay area.

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 effective light path of the ground-based MAX-DOAS is about 10 km (@360nm). The observation direction can cover the central area of the fjord.

Besides, the time resolution of GOME-2 is one or two data per day, while the ground-based MAX-DOAS can provide results every few minutes. Therefore, the ground-based MAX-DOAS measurements are more precise and convincing.

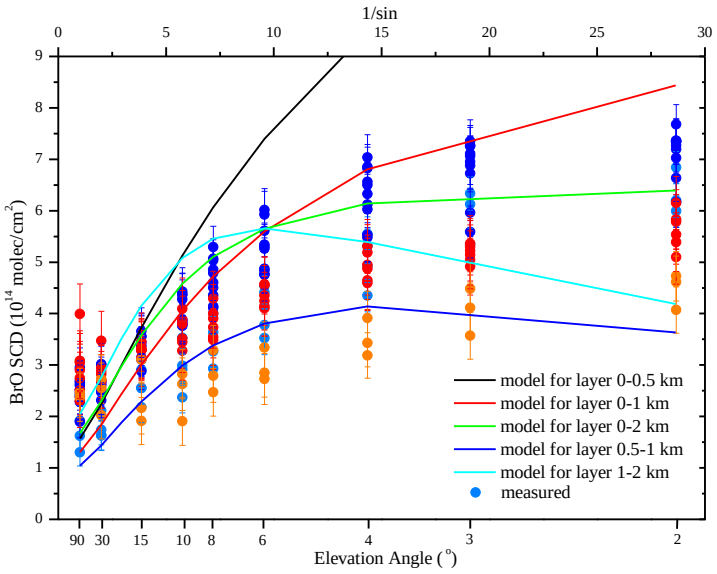
According to the referee #1 suggestion, BrO VCD data in Fig.6 has been deleted in the revised manuscript.

The observations of BrO, ozone, and mercury were not obtained at the same altitude. The authors claim that a large fraction of the enhanced BrO was located close to sea level. First, I agree with referee 1 that the observations in Fig. 7 rather seem to indicate that the highest BrO concentrations were actually at higher altitudes. This needs to be clarified. Second, ozone and mercury were measured at the Zeppelin Station and, thus, at around 480 m a.s.l.. Air masses at Zeppelin Station often represent tropospheric air from higher altitudes and are regularly decoupled from the boundary layer at Ny-Alesund. Thus, the authors need to demonstrate that during the

observed event, such a decoupling between Ny-Alesund and Zeppelin did not occur. Corresponding vertical profiles of meteorological data should be available for example from the French-German AWIPEV Station. Third, the vertical extent of ODEs and elevated BrO can be constrained to only a few hundred meters (e.g. Friess et al., JGR 116, D00R04, doi: 10.1029/2011JD015938). Therefore, the authors need to demonstrate why during this event the observations at sea level and the observations at higher elevations were directly linked. Finally, if the event was local and started at sea level I would expect a delayed response in ozone and mercury at 480 m altitude. However, the time series shown in Fig. 6 suggest either a concomitant increase in BrO and decrease in ozone and mercury or even an onset of the decrease in ozone and mercury before the increase of BrO. This should be clarified. Only if the authors can confirm that increase in BrO and the decrease in ozone occurred in the same air mass, a kinetic analysis as presented in chapter 4.3 is useful (see below).

Author's Response:

We perform the RTM simulations to get BrO slant columns 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. The modeled and measured BrO SCDs during the event showed that BrO layer 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 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 later 4 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 where ozone is still present. We modified the corresponding parts of the manuscript.



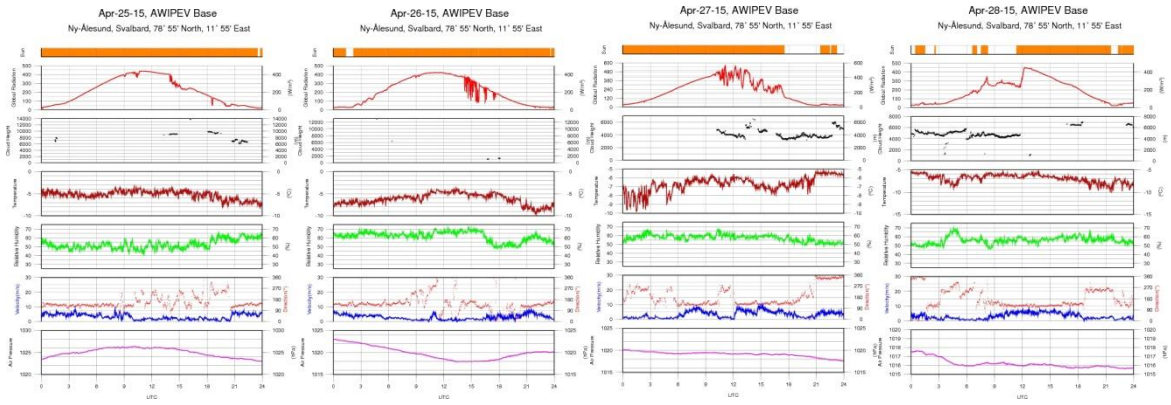
(The tropospheric BrO VCD is 5×10^{13} molecules/cm^2)

According to the area of sea ice in Kings Bay and the light path of the MAX-DOAS instrument, the range of this BrO enhancement is about 20 km radius area. The

horizontal distances between measurements location of BrO and ozone/mercury is less than 2 km. The model indicated that BrO is distributed at the layer of 0-1km. The ozone and mercury is measured at 480 m a.s.l.. So it is reasonable to explain the good anticorrelation between BrO dSCD and ozone/mercury.

The elevated BrO can also be several hundred meters (e.g. Wagner et al, ACP-7-3129-2007). As demonstrated in previous part, BrO was distributed at level of 0-1 km. The measurement data themselves are the best prove of the source of this BrO enhancement event.

The meteorology data from AWIPEV Station from 25/04-28/04 2015 are shown:



The authors state that the sea ice shown in Fig. 10 suddenly appeared in the fjord (page 7, line 5f). They further propose that the sea ice is the source of the reactive BrO. This hypothesis seems to be based on previous studies claiming that freshly formed sea ice or first-year sea ice are major sources of reactive bromine. However, the sea ice shown in Fig. 10 does not resemble freshly formed ice. The photograph rather shows crushed pieces of ice stemming from older floes and submerged in sea water. It appears that this sea ice was not formed in the fjord, but rather transported into the fjord by wind and wave actions as mentioned by the authors. Why this type of sea ice should lead to a sustained formation of reactive halogens remains, thus, unclear. I'm also convinced that the claim of the authors that this sea ice type fosters the formation of acidic sea salt aerosols is not warranted (page 7; line 8ff). Although air temperatures are low, the temperature of the crushed ice floes is probably close to the temperature of the water in the fjord, which can only be as low as ~-2◦C. As a result the claimed precipitation of calcium carbonate supporting the acidification of the aerosols formed on the observed sea ice (or even sea water as claimed by the authors; page 7, line 9f) is not likely. In any case, a more detailed description of the ice conditions and how they developed during the days before the event would be necessary and useful.

Author's Response:

Low temperature is an important prerequisite for the enhancement of BrO. A correlation between high BrO and ozone depletion with low temperatures was already found in the past researches (e.g. Tarasick and Bottenheim, 2002; Bottenheim et al., 2009; Pöhler et al.,2010; Friess et al, 2011), and was attributed to the temperature

dependence of the thermos-dynamical properties of the ice surfaces, such as the conditions of the quasi-liquid layer and the increase in uptake of HOBr by saline surfaces. Furthermore, model calculations predict that the precipitation of calcium carbonate from sea ice, which occurs 80% below 265 K, is an important prerequisite for the release of BrO since this process facilitates acidification (Sander et al., 2006). So we think the sea ice in the Kings Bay might be the crushed sea ice floating in the bay and transformed to the ice-water mixture in the fjord when it came across sharply dropped temperature.

The maximum Br concentrations derived from the kinetic analysis are higher than the BrO concentrations derived from the DOAS measurements (~45 pptV vs. 15 pptV). First of all, such a kinetic analysis can only be done if it is assured that the measurements concern the same air masses, which is not obvious with the different altitude of the observations (see above). In any case, is this a realistic result? Is the calculated Br too high or the observed BrO too low? This can also be interpreted that such a fast ozone decrease cannot occur due to local chemical processes, but only due to transport.

Author's Response: We disagree that. Firstly, the model indicated that BrO is distributed at the layer of 0-1km. The ozone and mercury is measured at 480 m a.s.l.. So it is reasonable to derive the kinetic analysis. Secondly, the kinetics is analyzed assuming the catalytic reactions are dominated by Br+O3→BrO+O2 in a homogenously PBL. It is obviously far from the true situation. Thus, the calculated Br is more likely the sum of all the bromine species, which is larger than the BrO value for sure.

In the introduction the authors claim that "the mechanisms and environment implications of ozone depletion and gaseous mercury deposition are discussed." A serious discussion of these topics is missing. Is such a discussion at all possible with the presented data?

Author's Response: We have removed this part.

Minor comments:
Page 1, line 16f: ". . .the boundary layer ozone and gaseous elemental mercury. . .": Measurements at the Zeppelin Station do not correspond to the boundary layer.
Author's Response: We think it is within the boundary layer range (~1000 m).

Page 1, line 27f: ". . .ozone dropped from typical levels (about 30 ppbv) to few ppbv. . .": And even below 1 ppbV: see e.g. Helmig et al., JGR 117, D20303, doi: 10.1029/2012JD017531.
Author's Response: Revised.

Page 2, line 1f: ". . .considered as possible source of bromide aerosols. . ."
Author's Response: Revised.

Page 2, line 4: ". . .transported over land by monsoon or air turbulence." Already mentioned by referee 1, monsoon and air turbulence are not the correct terms. Why only over land?
Author's Response: Revised.

Page 2, line 5: ". . .it is difficult to make detailed chemical observations in source area, . . ." I would say it is not more difficult to make these measurements compared to NyAlesund, but the access to the source area especially in spring is very limited.
Author's Response: This sentence has been revised.
"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 temporal resolution are needed to analyzing chemical process in PBL and investigating source of bromine."

Page 2, line 6: A few more studies in the sea ice area exist. For example, see Jacobi et al., JGE 115, D17302, doi: 10.1029/2010JD013940, 2009; Halfacre et al., ACP 14, 4875-4894, 2014.
Author's Response: Thanks a lot. Correlated references have been added.

Page 2, line 23f: "One of the reasons is that influenced by the North Atlantic Warm Current (NAWC), the near surface air temperature and sea surface temperature (SST) of East Greenland and North of Europe are relatively high. . .": This statement is unclear.
Author's Response: The sentence has been revised.
"However, recently the Arctic sea ice coverage has dramatically reduced, especially at East Greenland and North of Europe. 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)."

Page 2, line 29f: ". . .high level of troposphere BrO can be detected much more frequently in East Arctic (coastal area of north Asia and North America). . .": In my opinion this statement is not in agreement with the typical springtime BrO distribution in the Arctic. For example see Theys et al., ACP 11, 1791-1811, 2011.
Author's Response: This sentence has been removed.

Page 5, line 10f: I checked the indicated web page for the photographs and was not able to find anything resembling Fig. 10. On the webpage is a folder "Webcam", but the first photos are from 19 May 2015. In the folder "OldWebcam" a photo for 26 April 2015, 22:22:01 (UTC) is available, but with a resolution too low to identify sea ice on the fjord. In the folder "Panorama" photos for the period 22 to 29 April appear to be missing. The authors should verify the source of the used photographs.

Author's Response: It is a pity that only OldWebcam can be seen before 19 May 2015.

Page 5, line 25f: "The occurrence of depleted troposphere ozone and enhanced BrO appears to be unpredictable in May." This statement is unclear.
Author's Response: This sentence has been revised.
"During 4-5 May, partial ozone (not to near zero level) was depleted in the absence of BrO."

Page 6, line 17 (and throughout the manuscript): Precipitation of mercury is not the correct term.
Author's Response: Revised to "deposition".

Chapter 4.4: In the current form this chapter presents rather limited novelty. I believe it can be deleted or some parts may be merged with previous chapters.
Author's Response: This part has been merged with previous chapters.

The maps in Fig. 8 were apparently downloaded from the University of Bremen webpage, but the source is not mentioned in the manuscript.
Author's Response: Revised.

Observations and the source investigations of boundary layer BrO in Ny-Ålesund Arctic

Yuhan Luo[1], Fuqi Si[1], Haijin Zhou[1], Ke Dou[1], Yi Liu[2] and Wenqing Liu[1]

[1]Anhui Institute of Optics and Fine Mechanics, ~~Key Laboratory of Environmental Optics and Technology,~~ Chinese Academy of Sciences, Hefei, 230031, China

[2]National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, 230027, China

Correspondence to: Yuhan Luo (yhluo@aiofm.ac.cn) and Fuqi Si (sifuqi@aiofm.ac.cn)

Abstract. During polar spring, the presents of reactive bromine in polar boundary layer are considered as the main cause of the ozone depletion and mercury deposition. But many uncertainties still remain in understanding the mechanisms of the chemical process and the source of bromine. As the Arctic sea ice has dramatically reduced recently, it is critical to investigate the mechanism using more accurate measurements with higher temporal and spatial resolution. In this study, a typical process of enhanced bromine and depleted ozone in late April, 2015 in Ny-Ålesund boundary layer was observed applying ground-based Multi Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS) technique. The results showed that there were as high as 5.6×10^{14} molecular cm^{-2} BrO slant columns above the Kings Bay area in 26 April. Meanwhile, the boundary layer ozone and gaseous elemental mercury (GEM) was synchronously reduced by 85% and 90% respectively. Considering meteorology, sea ice distribution and air mass history, the sea ice in the Kings Bay area, emerged only for a very short period time when the enhance BrO was observed, was considered as the major source of this bromine enhancement event. The kinetic calculation showed that the ozone loss rate is 10.3 ppbv h^{-1}, which is extremely high compared to other area. The GEM loss rate is about 0.25 ng m^{-3} h^{-1}. The oxidized GEM may directly deposit to snow/ice and thereby influence the polar ecosystem.

1 Introduction

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);(Platt and Wagner, 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~~occurred over the~~ 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 temporal 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, which has lower spatial and temporal resolution compared with ground-based measurements. In the Arctic area, ground-based MAX-DOAS 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. 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 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.

2 Instruments and methods

2.1 Instrument setup

The MAX-DOAS measurement site is located at Yellow River Station (78°55´30”N, 11°55´20”E) at Ny-Ålesund, west coast of Spitsbergen. The observation position is shown in Fig. 3. To have a rough idea of the climate condition, monthly mean sea ice concentrations anomalies and air temperature anomalies in April 2015 are demonstrated in Fig. 2. The observations were carried out from 25 April to 15 May 2015. Due to the wavelength adjustment, no data is available during a short period from 28 to 29 April.

The MAX-DOAS instrument operated at Ny-Ålesund consists of indoor and outdoor parts. The telescope receiving scattered sunlight from multi angles is controlled by a stepper motor to adjust elevation angles from horizon (0 °) to zenith (90 °). The field of view of the telescope is about 1 °. The scattered sun light is imported through the quartz fiber with numerical aperture of 0.22 into the indoor spectrograph (Ocean Optics MAYA pro) with a one dimensional CCD (ILX511 linear array CCD) containing 2068 pixels. The wavelength range of the spectrograph is from 290 nm to 420 nm, thus enabling the analysis of trace gases including O_3, NO_2, BrO, OClO, HCHO, and O_4. The spectral resolution is about 0.5nm (FWHM). The CCD detector is cooled at -30 ℃ while the whole spectrometer is thermally stabilized at +20 ℃ using a thermal controller. A computer sets the configuration of the system and controls the automatic measurements. 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. The standard mercury lamp is used for spectra calibration. Calibration measurements of dark current and offset are performed after each measurement.

The telescope is pointed towards Northeast direction, which covers the Kings Bay area (Fig.3). 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 range of MAX-DOAS measurement is about 10km radius area, which covers the central area of the fjord. The sequence of elevation angles is 2 °, 3 °, 4 °, 5 °, 6 °, 8 °, 10 °, 15 °, 30 °and 90 °above the horizon.

2.2 Data evaluation

The spectra measured with the above described setup are analyzed using the well-established DOAS retrieving method (Platt, 1994). The wavelength calibration was performed using the QDOAS software developed by the Belgian Institute for Space Aeronomy (BIRA) by fitting the reference spectrum to a high resolution Fraunhofer spectrum (Kurucz et al., 1988). The spectral analysis of BrO is performed at 340-359 nm, encompassing three BrO absorptions

bands, which improves the accuracy of the inversion. O_3 (223K, 243K) (Bogumil et al., 2003;Vandaele et al., 1998), NO_2 (298K, 220K) (Vandaele et al., 1998), O_4 (Hermans et al., 2003), BrO (228K) (Wilmouth et al., 1999), OClO (233K) (Kromminga et al., 2003), and Ring Structure (Chance and Spurr, 1997) are involved in the inversion algorithm. The O_4 retrieval is performed using the same set of cross sections as for BrO but in the wavelength interval at 340-370 nm. The high resolution cross sections were convoluted with the instrument slit function determined by measuring the emission line of a mercury lamp. A fifth order of polynomial was applied to eliminate the broad band structures in the spectra caused by Rayleigh and Mie scattering. Furthermore, a nonlinear intensity offset was included in the fit to account for possible instrumental stray light. A wavelength shift and stretch of the spectra was allowed in the fit in order to compensate for small changes in the spectral adjustment of the spectrograph.

The fit procedure yields differential slant column densities (dSCD) using noon time zenith sky measurements as Fraunhofer reference for the analysis. An example of the fit result of BrO and O_4 is shown in Fig.4. The spectrum was recorded on 26 April, 2015 19:59 UTC (SZA=86 °) at the elevation angle of 2 °. The BrO dSCD is 5.10×10^{14} molecular cm^{-2}. The residual root mean square is 4.59×10^{-4}, resulting in a statistical BrO dSCD error of 1.63×10^{13} molecular cm^{-2}. The DSCDs of BrO at elevation angle 2 ° were obtained by subtracting 90 °of each sequence, which eliminate the influence of stratosphere BrO change.

Since DSCDs are dependent on the light path, wavelength and observation geometry, DSCDs are then converted to vertical column density (VCD) by dividing the differential air mass factor (DAMF), which is the averaged light path enhancement for solar light traveling through the atmosphere compared to a straight vertical path.

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.

2.3 Complementary data

Ny-Ålesund is a science community hosting over fifteen permanent research stations. Atmospheric measurements have been measured continuously at Zeppelin Station, Ny-Ålesund since 1990. Located on Zeppelin Mountain with altitude 474 meters a.s.l., it is a background atmosphere observatory operated by NPI (Norwegian Polar Institute) and NILU (Norwegian Institute for Air Research) , which are part of the Global Atmosphere Watch (GAW) Framework.

Surface ozone was measured by UV photometry. Gaseous mercury in air was measured using Tekran mercury detector. Hourly Surface Ozone and gaseous mercury data are downloaded at EBAS database (Tørseth et al., 2012).

Meteorology data including temperature, air pressure, relative humidity, wind direction and velocity, and global radiation are recorded by AWIPEV Atmospheric Observatory in Ny-Ålesund. 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 at Ny-Ålesund.

Webcam on the 474m Zeppelin Mountain records the sea ice change of Kings Bay and the cloud situation of Ny-Ålesund. (https://data.npolar.no/_file/zeppelin/camera/)

In order to get a rough idea of BrO distribution, BrO maps of northern hemisphere by GOME-2 product are downloaded from http://www.iup.uni-bremen.de/doas/scia_data_browser.htm. Stations overpass BrO vertical column densities for MetOp-A (GOME-2A) and MetOp-B (GOME-2B) in Ny-Ålesund, Arctic are downloaded from https://avdc.gsfc.nasa.gov/index.php?site=580525926&id=97.

Using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model via the NASA ARL READY website (http://www.ready.noaa.gov/ready/open/hysplit4.html) (Draxler and Rolph, 2013;Stein et al., 2015), back trajectory analyses were carried out to find the history of air masses. 72-hours ensemble back trajectories were driven by meteorological fields from the NCEP Global Data Assimilation System (GDAS) model output.

3 Results

Time series of BrO DSCDs at 2 °, surface ozone concentrations, solar zenith angle (SZA), air pressure, air temperature, relative humidity, wind velocity and wind direction from 25 April to 15 May are presented in Fig.6. Starting from late afternoon in 26 April, BrO DSCDs clearly exceeded the background levels and peaked at 5.6 $\times 10^{14}$ molecular cm^{-2}. 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. During 4-5 May, partial ozone (not to near zero level) was depleted in the absence of BrO.

Time series of BrO dSCDs from 26 April to 28 April in every elevation angle (2 °, 3 °, 4 °, 6 °, 8 °, 10 °, 15 °, 30 °) are

plotted in Fig. 7. Results of different elevation angles distinguished obviously during the BrO enhancement period. But the differences of the BrO dSCDs ≤4° are very small, indicating that the highest value of BrO is probably not above the surface. In order to have a better understanding of the vertical distribution of reactive bromine at Arctic boundary layer, comparison between the measured BrO SCDs from MAX-DOAS measurements with the modeled ones from SCIATRAN model are performed (Fig.5). BrO layer height between 0-1 km is considered as the most possible distribution of BrO layer, which is compatible with the measurements. BrO dSCDs distributed from 0-1 km to more likely at 0.5-1 km along with time. This could be explained by that Br/BrO photochemistry reactions are taking place from the boundary layer to the free troposphere where there is enough ozone to react.

Sunshine duration, global radiation, SZA, BrO DSCDs from MAX-DOAS at 2° elevation angle, BrO volume mixing ratio, surface ozone and gaseous mercury from 26-28 April are plotted in Fig. 8. The BrO VMRs were calculated assuming a 0-1 km layer of BrO profile. The highest BrO VMR is about 15 pptv during the ODE. Ozone as well as gaseous mercury dropped extremely fast right after the enhancement of BrO. But there seems not sufficient reactive bromine presented locally in the boundary layer since the ozone turned to slowly increase just four hours later (at 23:00 26 April). Afterwards, both ozone and mercury has a slowly recovery with a fluctuation in the 27 afternoon.

4 Discussions

In this research, high concentration of troposphere BrO has been detected using the ground-based MAX-DOAS technique. As high as 5.6×10^{14} molecular cm^{-2} BrO column has been detected above Kings Bay, Ny-Ålesund. The retrieval shows that the enhancement occurred accompanied with severe ozone depletion and mercury deposition. This enhancement event is a good opportunity to investigate the source of BrO and the impact on the environment of Arctic boundary layer. The following parts are discussed in detail from air mass history, sea ice distribution, and ozone loss and mercury deposition.

4.1 History of air masses

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. Additionally, the transport air masses might be the reason of the slowly back BrO concentrations to normal values until 3 May.

4.2 Sea ice distribution

According to the observation of sea ice concentration from AMSR-E and Zeppelin webcam, Kings Bay is ice-free water area during the measurement period. However, large amount of sea ice appeared at Kings Bay on 26 April (Fig.11), floating from the bay entrance by both wind and tidal and lasted for few hours. The shape of sea ice was broken ice pieces with irregular border. The ice–sea water mixture was filled in the gaps, which was salty-enriched.

The efficient ozone loss is consistent with the temperature decline (Fig.12). The meteorology data shows that on 26 April air temperature continually goes down and reaches bottom of -11.4^{o}C at 22:00. According to the precipitation curve of calcium carbonate, more than 80% of carbonate precipitates below 265K. This process will provide acid aerosol from alkaline sea water, which triggers the transformation of inert sea-salt bromide to reactive bromine (Sander et al., 2006). Although the sun radiation intensity is not strong at that time, the heterogeneous reactions can still happen under the twilight.

Thereby, this BrO enhancement event is more likely a local process, mainly influenced by underlying surface change and local environment. The surface ozone concentrations increased along with the melting of sea ice, which indicated that the life span of BrO radicals are very short. When sea ice disappeared, the reaction immediately ended and reactive bromine radicals gradually transformed to soluble bromide (e.g. HOBr), which explained the sink of it (Fan and Jacob, 1992).

4.3 Kinetic analysis

What makes this case very special is that the increasing rate of BrO and the depletion rate of boundary layer ozone are

really fast. The surface ozone reduced by 85% within 4 hours. The ozone loss rate is as high as 10.3 ppbv h^{-1} or 248 ppbv d^{-1}, which is extremely high compared with previous studies in Polar Regions (Tab. 2). The deposition of gaseous mercury occurred concurrently with tropospheric ozone depletion, as well as the enhancement of BrO (Fig. 14), which indicated that the oxidation of GEM by reactive halogen species (Br atoms and BrO radicals) is considered to be the key process of mercury depletion. The GEM decreases from ~2 ng m^{-3} to lower than 0.3 ng m^{-3} during the BrO enhancement event. The mercury loss rate is about ~0.25 ng m^{-3} h^{-1} or 6 ng m^{-3} d^{-1}. The oxidized GEM may directly deposit to snow/ice or associate with particles in the air that can subsequently deposit onto the snow and ice surfaces, and thereby threaten polar ecosystems and human health.

The chemical kinetics of bromine enhancement and ozone decay are analyzed assuming that the catalytic reactions are dominated by reactions showed in Fig.1. A first-order loss of ozone is due to reaction $Br+O_3 \rightarrow BrO+O_2$ resulting in the rate law:

$$r = -\frac{d[O_3]}{dt} = k_1 \cdot [O_3] \quad \text{(Eq. 1)}$$

$$[O_3] = [O_3]_0 \cdot \exp(-k_1 \cdot t) \quad \text{(Eq. 2)}$$

$$\ln\frac{[O_3]}{[O_3]_0} = -k_1 \cdot t \quad \text{(Eq. 3)}$$

$[O_3]_0$ is the ozone concentration at the beginning of decay determined from the measured mixing ratio of 74.72 ppbv. $\ln\frac{[O_3]}{[O_3]_0}$ versus time are showed as hollow square in Fig. 13a.

According to the method by Jacobi et al. (Jacobi et al., 2006), the first order rate constant k_1 can be determined as follows:

$$\frac{d(\ln\frac{[O_3]}{[O_3]_0})}{dt} = -k_1 \quad \text{(Eq. 4)}$$

The measured decrease of $\ln\frac{[O_3]}{[O_3]_0}$ versus time was fitted by:

$$\ln\frac{[O_3]}{[O_3]_0} = -\exp(b \cdot t + a) \quad \text{(Eq. 5)}$$

$$\frac{d(\ln\frac{[O_3]}{[O_3]_0})}{dt} = -b \cdot \exp(b \cdot t + a) \quad \text{(Eq. 6)}$$

$$\ln(-\ln\frac{[O_3]}{[O_3]_0}) = b \cdot t + a \quad \text{(Eq. 7)}$$

$$k_1 = b \cdot \exp(b \cdot t + a) \quad \text{(Eq. 8)}$$

$\ln(-\ln\frac{[O_3]}{[O_3]_0})$ versus time are plotted as black dots in Fig. 13a. The coefficients a and b are obtained from the linear fit in plot.

The ozone loss begins relatively slow and accelerates with time, which is consistent with the process of bromine explosion.

Assuming that the first order decay is dominated by the reaction $Br+O_3 \rightarrow BrO+O_2$, we are able to calculate the Br

concentrations as follows:

$$k_1 = k_{Br} \cdot [Br] \quad \text{(Eq. 9)}$$

$$k_{Br} = 1.7 \cdot 10^{-11} \cdot \exp(-\frac{800}{T}) \quad \text{(Eq. 10)}$$

k_{Br} is a constant depending on temperature (Fig. 13b). Thereby, the calculated Br concentration increases from 1.1×10^7 to about 1.2×10^9 atoms cm^{-3} (corresponding to 44.8 pptv) (Fig. 13c). Considering the assumption that the halogens are homogenously distributed in the PBL, the concentrations of Br at sea surface layer in the bromine explosion could be even higher.

5 Conclusions

Typical process of enhanced bromine and depleted ozone in Ny-Ålesund boundary layer was observed using ground based MAX-DOAS techniques in late April, 2015. As high as 5.6×10^{14} molecular cm^{-2} BrO DSCDs were detected on 26-27 April. Meanwhile, severe ozone depletion and mercury deposition occurred under BrO VMR of 15 pptv. The model showed enhanced BrO distributed at 0-1 km above the sea surface. By analyzing the air mass history and sea ice conditions, this BrO enhancement event is more likely a local process. The underlying sea ice and low temperature provide acid aerosols, which are prerequisites for the formation of BrO radicals. The kinetic analysis shows that the ozone loss begins relatively slow and accelerates with time, which is consistent with the process of bromine explosion. The ozone loss rate is as high as 10.3 ppbv h^{-1}, which is much higher than previous studies in Polar Regions. GEM loss rate is about ~0.25 ng m^{-3} h^{-1}. This study is a pivotal complement for BrO research in Arctic BL. Further observations and analysis are required to identify the chemical mechanisms.

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Table 1. Comparisons of BrO mixing ratio at four main Arctic observation sites

Sites	Observation periods	BrO mixing ratio	Methods	References
Greenland ice sheet (72N, 38W, 3200ma.s.l.)	14 May-15 June 2007, 9 June-8 July 2008	3-5ppt	LP-DOAS	(Stutz et al., 2011)
Barrow, Alaska (71°19'N, 156°40'W)	26 February-16 April 2009	~30ppt	MAX-DOAS LP-DOAS	(Frieß et al., 2011)
Alert, Nunavut (82°32'N, 62°43'W)	20 April- 9 May 2000	~30ppt	MAX-DOAS	(Hönninger and Platt, 2002)
Ny-Ålesund, Svalbard (78.9N, 11.8E)	20 April-27 April 1996	~30ppt	LP-DOAS	(Tuckermann et al., 1997)

Table 2. Comparisons of BrO mixing ratio and ozone loss rate

Method	BrO mixing ratio	Typ. Rate of O3 destruction	References
Observation at PBL	up to 30 pptv	1-2 ppbv h-1	(Tuckermann et al., 1997;Hönninger and Platt, 2002)
Observation at MIZ	~63 pptv	6.7 ppbv h-1 or 160 ppbv d-1	(Jacobi et al., 2006)
Observation at salt lakes	up to 176 pptv	10-20 ppbv h-1	(Hebestreit et al., 1999;Stutz et al., 2011)
Observation at Marine BL	~2 pptv	~0.05 ppbv h-1	(Leser et al., 2003)
Model	30-40 pptv	7.6 ppbv d-1	(Lehrer et al., 2004)
Model	100 pptv	40ppbv d-1	(Fan and Jacob, 1992)
Observation at Ny-Ålesund BL	~15 pptv	10.3 ppbv h^{-1} or 248 ppbv d^{-1}	**this study**

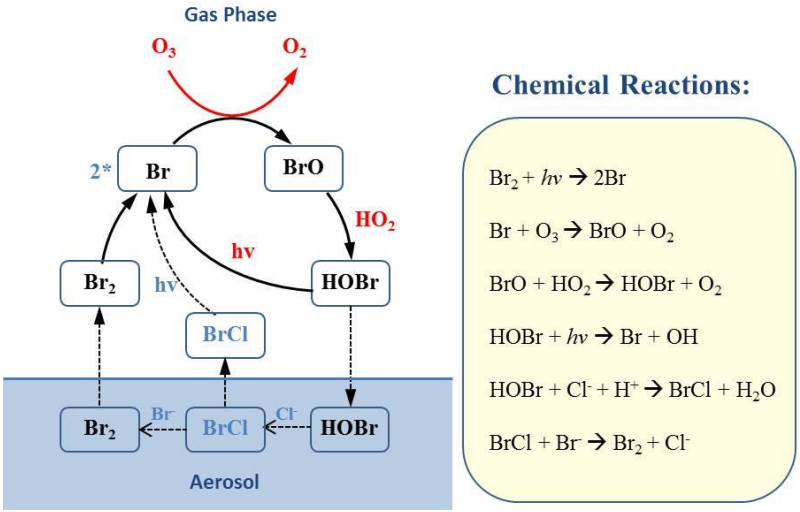

Fig. 1 Chemical reactions of BrO-Ozone cycle

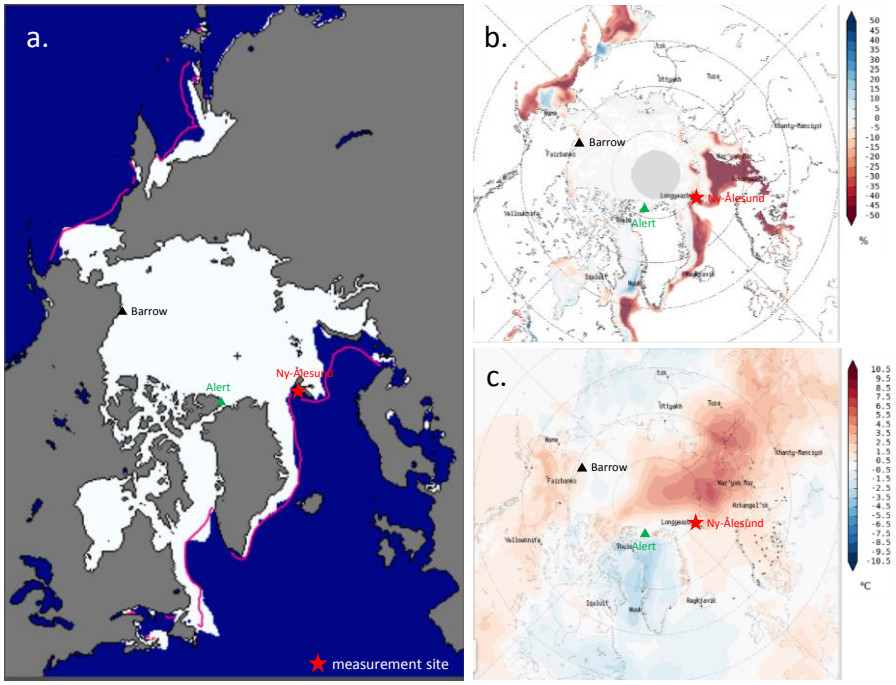

Fig 2. a. Sea ice extent of Apr 2015 in Arctic area (data from http://nsidc.org/data/seaice_index/); b. Monthly mean sea ice concentrations anomalies of April 2015 compare to averages from 1979 to 2015 ; c. Two meters air temperature anomalies of April 2015 compare to averages from 1979 to 2015 (b and c data are from http://nsidc.org/soac)

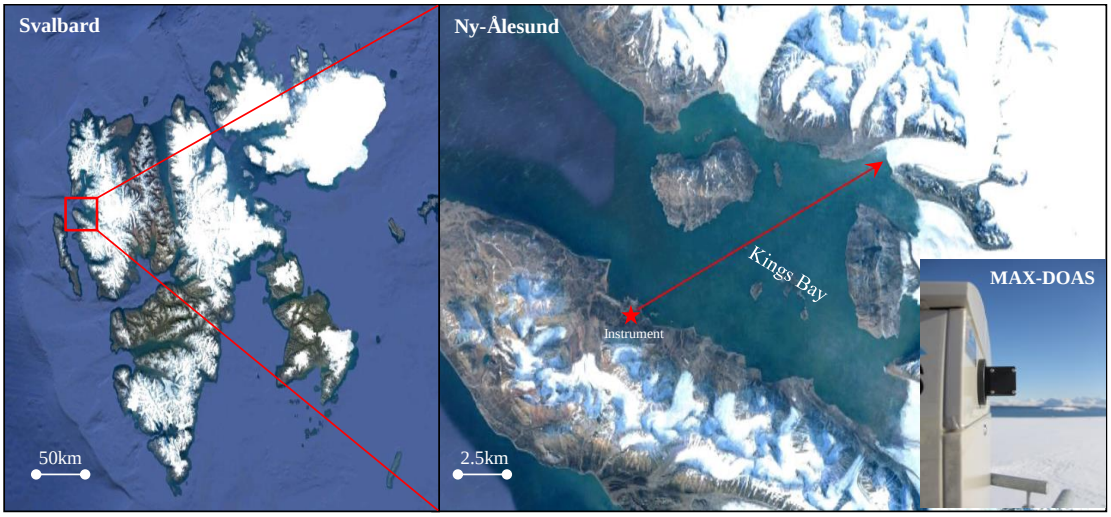

Fig.3 MAX-DOAS field observation in Ny-Ålesund, Arctic

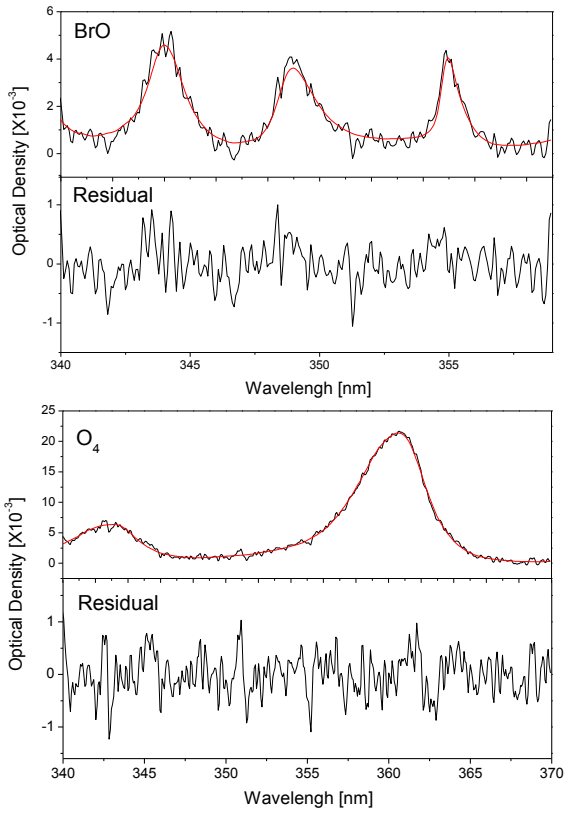

Fig.4 Examples for spectral retrieval of BrO and O4. The spectrum was recorded under clear sky conditions at 2 ° elevation on 26 April 2015, 19:59 UTC, SZA = 86 °. (Black lines: Retrieved spectral signatures fitted result for absorber; red lines: fitted cross sections)

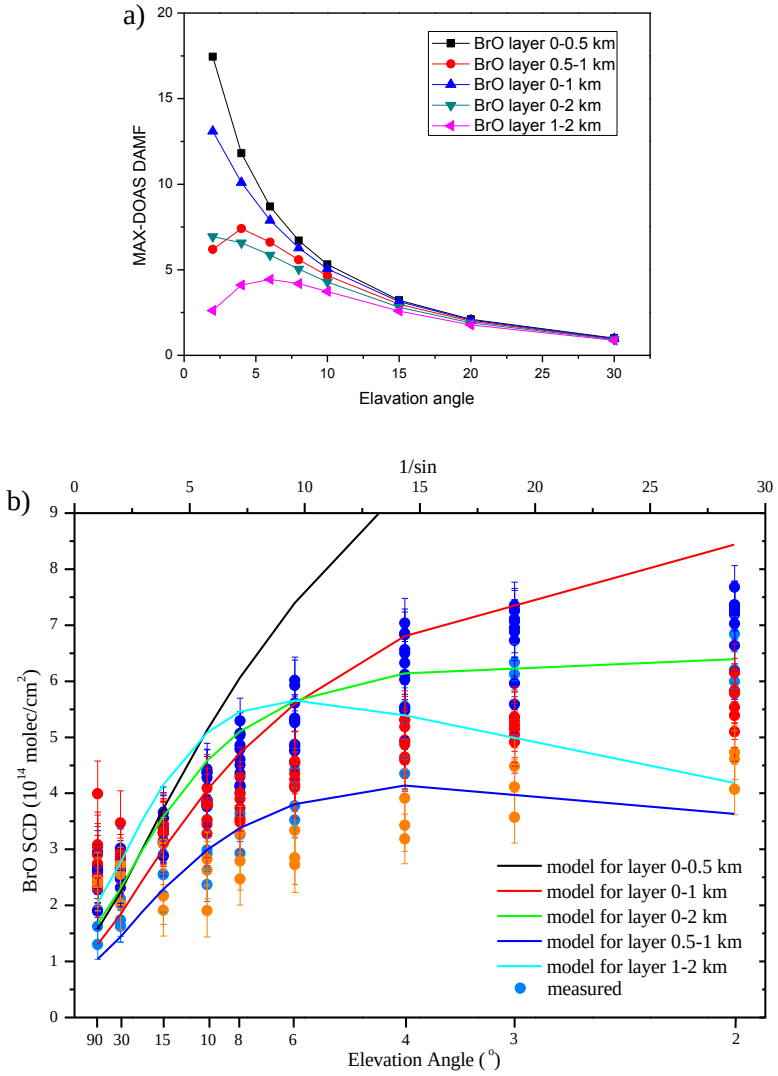

Fig. 5 The modeled DAMF (a) and BrO slant columns (b) using radiative transfer modeling simulation. DAMF are the differences of AMF for low elevation angles and zenith direction. The models are performed assuming a clear sky condition with no aerosol. In part b, the tropospheric BrO VCD is 5×10^{13} 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.

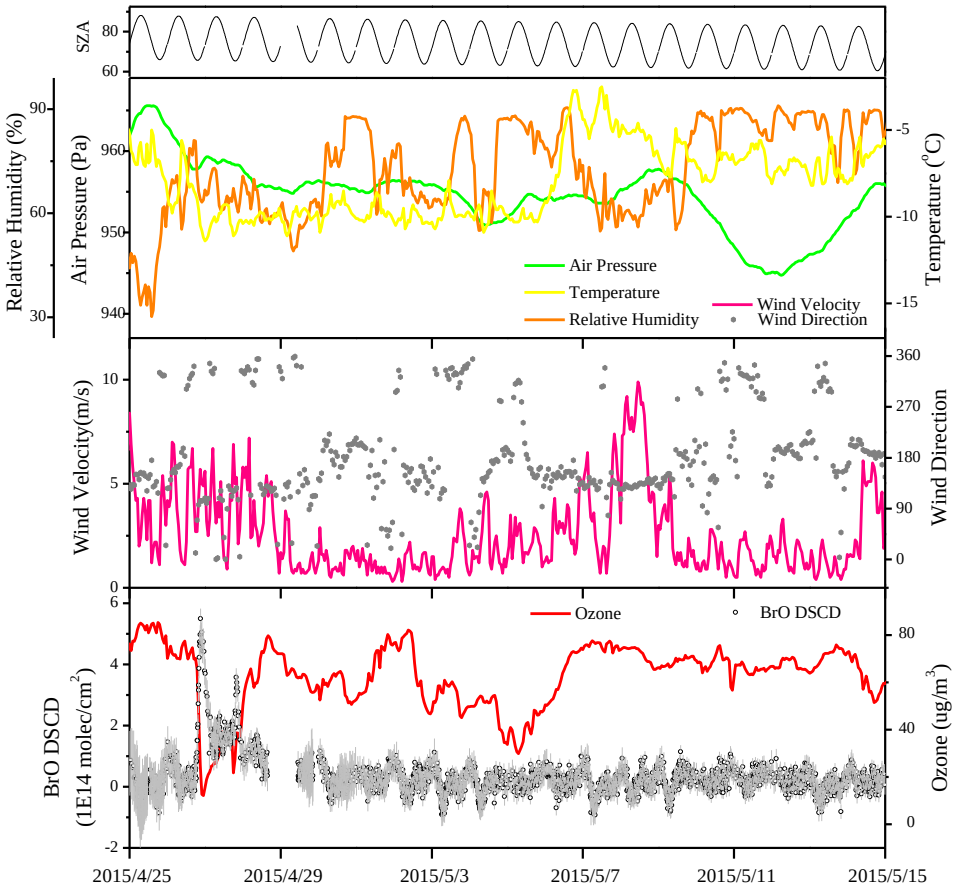

Fig.6 Time series of BrO dSCDs at 2 °, surface ozone, SZA and meteorology data during the measurement.

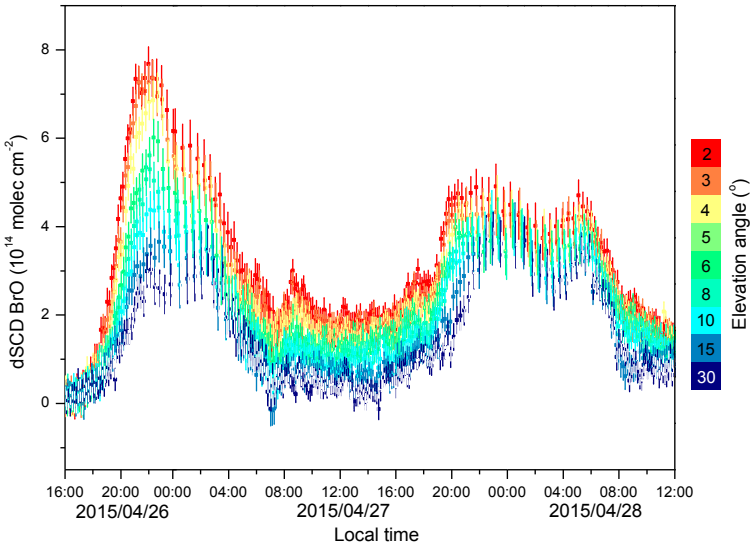

Fig.7 BrO dSCDs of different elevation angles during the enhancement period

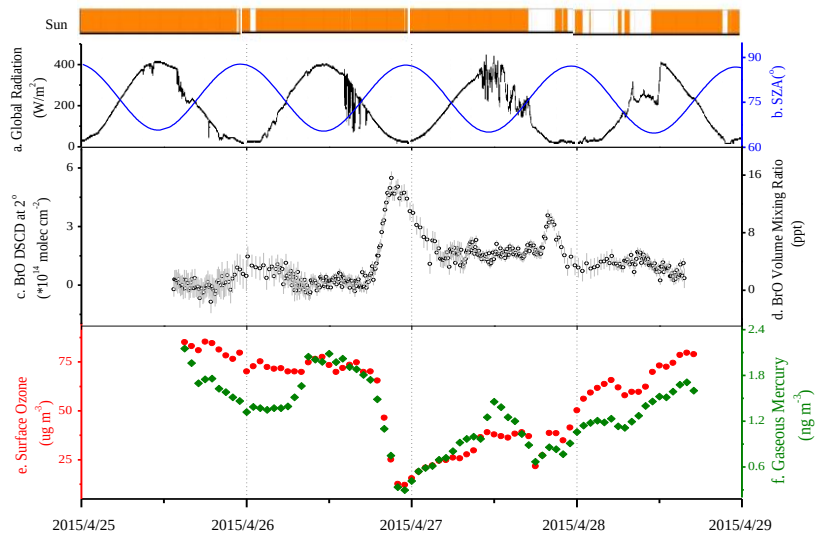

Fig.8 a. Global radiation (W/m^2) (Cited from AWIPEV database); b. SZA; c. BrO DSCDs from MAX-DOAS at elevation angle 2 °; d. BrO VMR (ppt); e. surface ozone (ug/m^3); and f. gaseous mercury (ng/m^3) from 25/04 noon to 28/04 2015. BrO mixing ratios are calculated assuming a homogeneous BrO layer of 0-1 km.

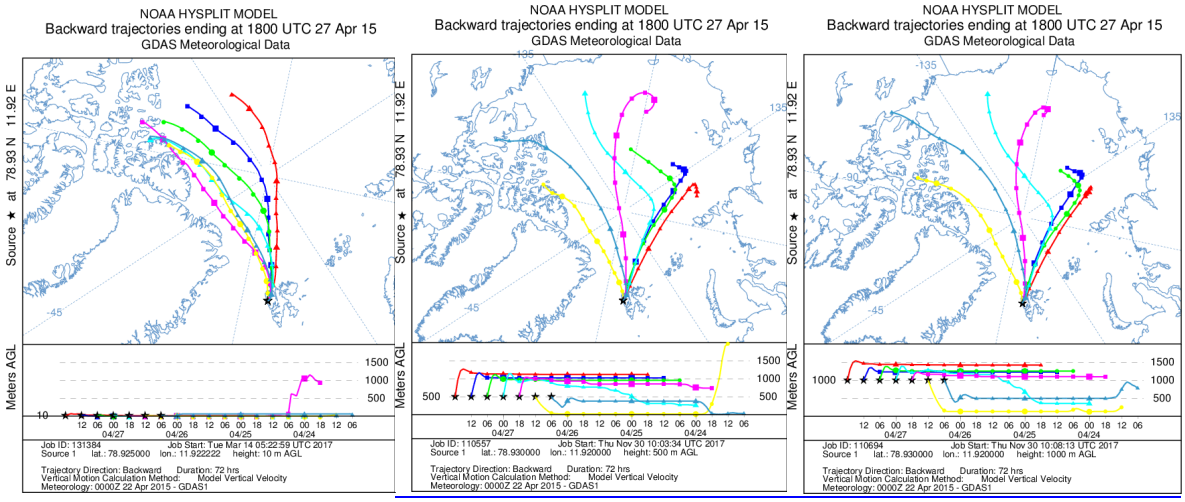

Fig. 9 Back trajectory model of air masses arriving at Ny-Ålesund from 26 April (0600 UTC) to 27 April (1800 UTC) at 10, 500, 1000 meters a.s.l.. Every 6h a new trajectory starts, each trajectory runs 72h.

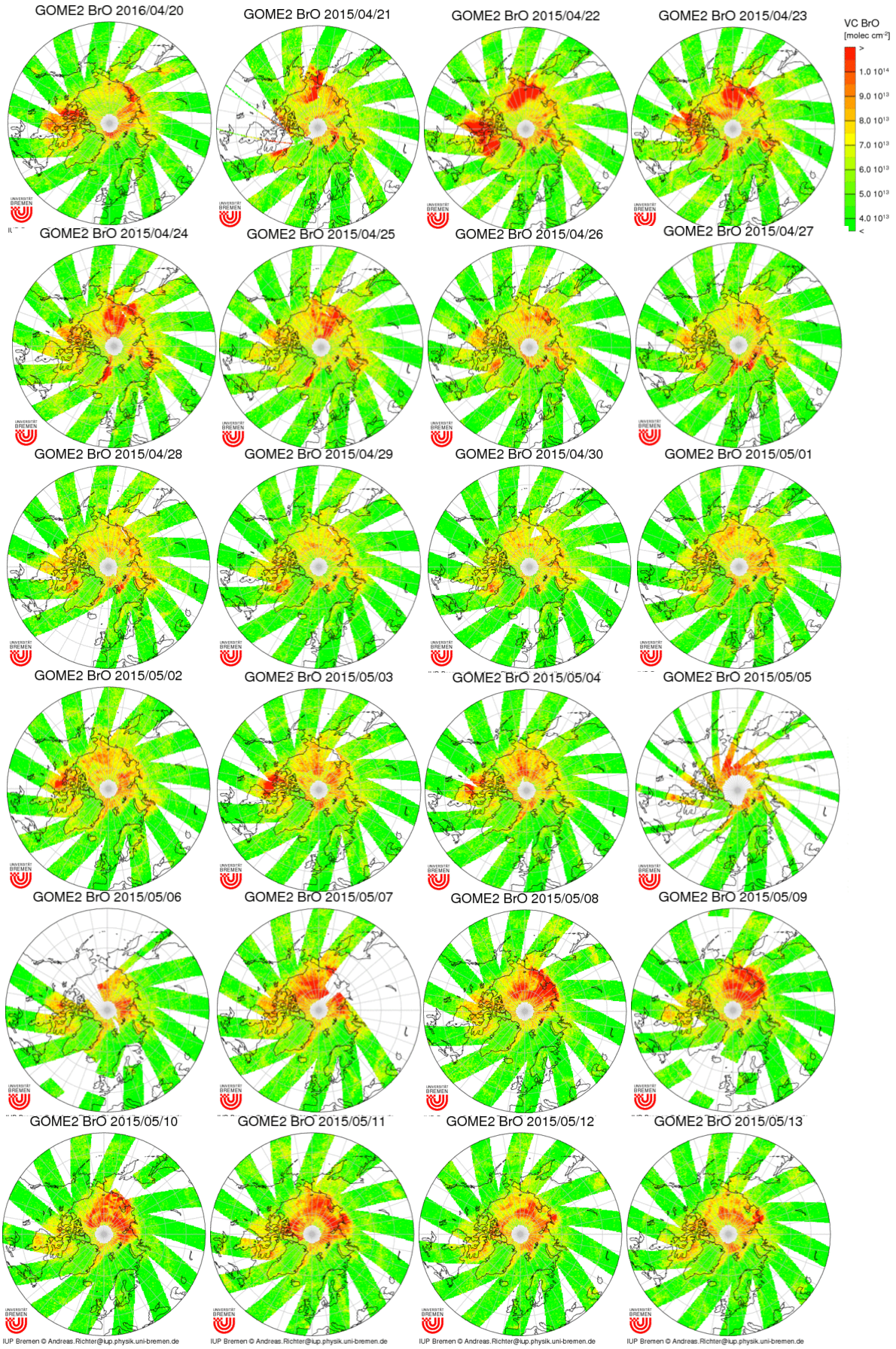

Fig.10 Map of troposphere BrO of northern hemisphere by GOME-2 product from 20 April to 13 May. (Cited from http://www.iup.uni-bremen.de/doas/scia_data_browser.htm)

5

Fig.11 Sea ice in Kings Bay, Ny-Ålesund at 22:00, 26 April 2015

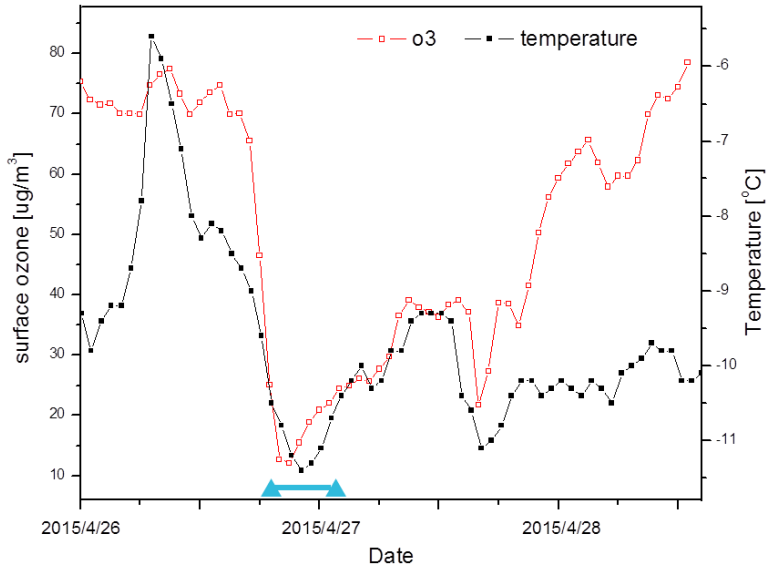

Fig.12 Time series of surface ozone and air temperature during the BrO enhancement event, blue triangles present the sea ice existence in Kings Bay

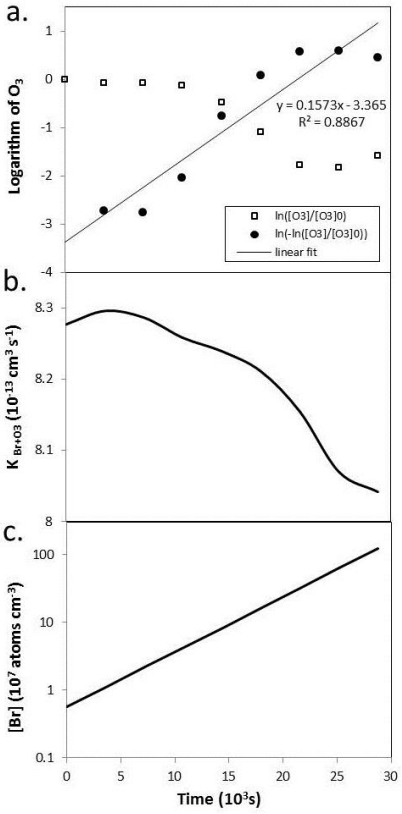

Fig.13 Analysis of surface ozone loss in 26 April 2015

a. Plot of $\ln([O_3]/[O_3]_0)$ and $\ln(-\ln([O_3]/[O_3]_0))$ versus time; b. Calculated temperature dependent reaction rate coefficients for O_3+Br; c. Calculated Br concentration.

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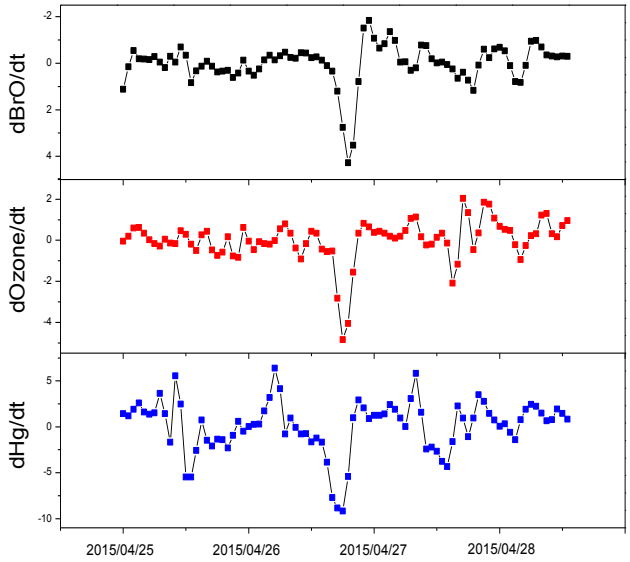

Fig.14 Time series of dBrO/dt, dO3/dt and dHg/dt during the BrO enhancement event