**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.

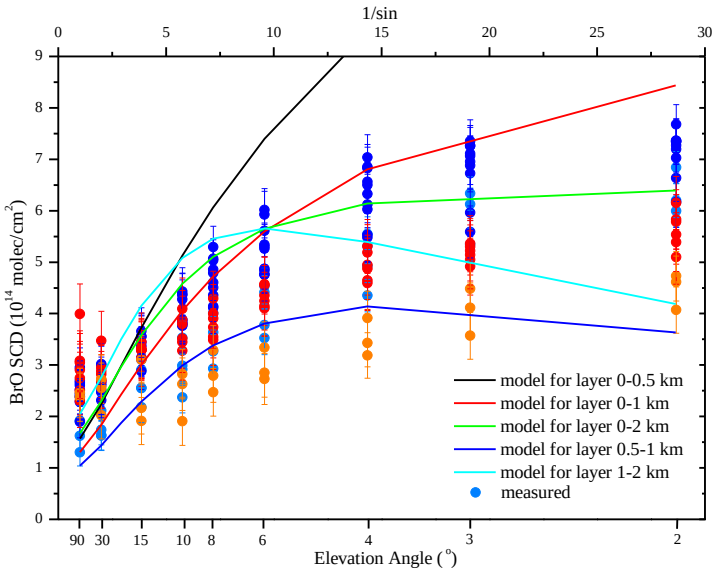
According to the referee #1 suggestion, BrO VCD data in Fig.6 has been deleted in the revised manuscript.

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.



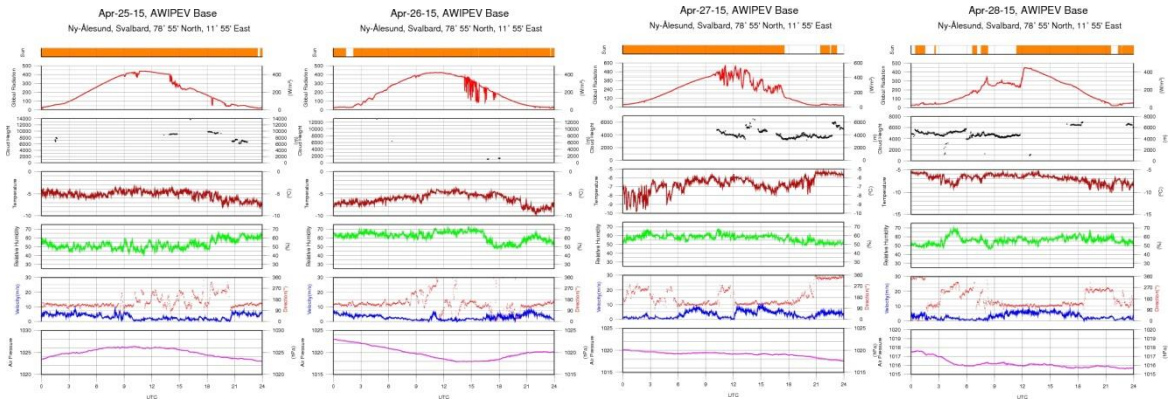

(The tropospheric BrO VCD is $5\times10^{13}$ molecules/cm$^2$)

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.