

***Interactive comment on* “Observations and the source investigations of boundary layer BrO in Ny-Ålesund Arctic” by Yuhan Luo et al.**

Anonymous Referee #2

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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-Alesund 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

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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.

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.

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

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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.

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-Alesund 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.

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

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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).

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 $\sim -2^{\circ}\text{C}$. 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.

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 measure-

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ments 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.

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?

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.

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.

Page 2, line 1f: “...considered as possible source of bromide aerosols...”

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?

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 Ny-Alesund, but the access to the source area especially in spring is very limited.

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.

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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.

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.

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.

Page 5, line 25f: “The occurrence of depleted troposphere ozone and enhanced BrO appears to be unpredictable in May.” This statement is unclear.

Page 6, line 17 (and throughout the manuscript): Precipitation of mercury is not the correct term.

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.

The maps in Fig. 8 were apparently downloaded from the University of Bremen webpage, but the source is not mentioned in the manuscript.

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