

## Second review of Luo et al “Observations and the source investigation of boundary layer BrO in Ny-Aalesund Arctic”

In my first review, I laid out a number of major concerns. The majority of these have been addressed, and overall the authors have made improvements to their paper. An important aspect to address was the potential role of long-range transport, and the authors have significantly improved the way they address this. They have presented good evidence supporting their view that long-range transport is not responsible for the changes observed in O<sub>3</sub> and BrO.

However I still have one major concern that needs to be addressed, which was not adequately tackled in the reviewer’s responses. I will re-iterate more clearly below. My other comments are minor points of clarification.

### **Major concern:**

A key aspect of this paper is the kinetics calculation of rates of ozone loss. Whether such a calculation is meaningful rests on whether the chemical changes observed are occurring *in situ*.

In their revised manuscript, the authors continue to argue that the O<sub>3</sub> loss and BrO increase are locally-driven, and that for this reason it is possible to calculate kinetic rates of ozone loss.

However, in order to calculate meaningful rates of ozone loss, the chemical processes have to be occurring **in situ**, i.e. **actually happening during the period of observations, and at the place of the observations**. This is where I have a problem with the conclusions as currently presented.

There are various reasons why I am not convinced:

- A) I have looked in as much detail as I could at the new Figure 6 (expanding and stretching it). To me, it looks as if **every single meteorological variable** changes concurrently with the changes in BrO and O<sub>3</sub>. In particular, wind direction switches from  $\sim 350^\circ$  before the O<sub>3</sub> loss/BrO increase, to  $\sim 100^\circ$  during the period of O<sub>3</sub> depletion/BrO increase; wind speed increases from  $\sim 3$  m/s before the O<sub>3</sub> loss/BrO increase, to 6 m/s during the period of O<sub>3</sub> depletion/BrO increase. After the peak in BrO, both wind speed and wind direction return to their previous speeds/direction. **The fact that changes in all the meteorological variables are concurrent with chemical changes, strongly suggests that changes observed in chemistry are evident because of changes in transport, albeit on a small scale.** The paper would benefit from a figure that showed the range of chemical and meteorological observations – relative humidity, air pressure, temperature, wind velocity, wind direction, ozone, and BrO - from start 26<sup>th</sup> April to end April 27<sup>th</sup> to explore in detail what is happening locally. This is the critical period of observations, and none of the current range of figures presents all the information available in sufficient detail.
- B) Key information is presented in section 4.2. The authors state “It is also worth paying attention that the time period that the sea ice existed and the time BrO started to enhance as well as ozone depleted was not exactly the same. From Fig. 8 and 12, the

ozone loss started from 14:00 UTC 26<sup>th</sup> Apr. And as described upon, the sea ice existed in the fjord after 20:00 UTC 26<sup>th</sup> Apr.” Indeed, Fig 8 shows that BrO enhancement and O<sub>3</sub> depletion started at around 14:00, with Fig 12 showing that the sea ice arrived in Kings Bay around 20:00. **Observations of O<sub>3</sub> loss and BrO enhancement thus precede the arrival of ice in the Bay by around 6 hours. By definition, therefore, the observed chemical changes are not happening “in situ”, and the observations cannot be used to derive chemical rates of change.**

In particular point B) above leads me to conclude that these data cannot be used to derive O<sub>3</sub> loss rates, and that this section of the manuscript should be removed before publication. If the authors wish, they could describe why such a calculation is not feasible. Nonetheless, I believe that the paper is sufficiently interesting to publish without the derivation of O<sub>3</sub> loss rates.

#### Minor comments:

- i) It is worth saying something for Fig 5, and why the 0-0.5km layer does not best match the data; this fact also points to this not being an in situ process, local to Kings Bay.
- ii) Abstract line 1: “presents” should be “presence”
- iii) Throughout: “molecular cm<sup>-2</sup>” should be “ molec.cm<sup>-2</sup> “
- iv) Abstract line 12: “ice in Kings Bay area, **which** emerged only ...”
- v) The quality of English needs checking throughout, e.g. “in consistency” is not an English phrase and should be replaced.
- vi) Introduction: “ A typical heterogenous reaction model between gaseous and condensed phases **is** shown in Fig. 1”
- vii) Introduction: “Bromine is released from salty ice surfaces” – but Fig 1 says “aerosol”
- viii) Section 2.2 either use dSCD or DSCD but not both.
- ix) Towards the end of Section 2.2 “much attention should be paid on the large elevation angles” – define what you mean by “large”.
- x) Towards the end of Section 2.2: Change “From Fig.5b we can see obviously that the measured BrO DSCDS before midnight are in good consistence with...” to “From Fig.5b we can see obviously that the measured BrO DSCDS before midnight are **best reproduced by...**”
- xi) Towards the end of Section 2.2: “**This suggests that the** BrO layer between 0-1km can be considered as the most **likely** distribution.”
- xii) Section 2.3: “According to the **radiosonde** records of...”
- xiii) Section 2.3: “..height of the boundary layer is around 1200 meters at Ny-Alesund” – what is the range of boundary layer height, and is it possible to say what was it on 26<sup>th</sup> April at the start of the O<sub>3</sub> loss/BrO increase?
- xiv) Section 2.3: The trajectories shown are not “ensemble” trajectories – remove the word “ensemble” at the end of section 2.3.
- xv) Section 4.1, first paragraph “Then we calculated the air mass backwards trajectory ending at 18:00 (UTC) 26<sup>th</sup> April in every hour (Fig 9**b**). i.e. not Fig 9a here.
- xvi) Section 4.2 – “The ice-sea water mixture was filled in the gaps, which was salty-enriched.” – What evidence do you have that it was salty..??

- xvii) Section 4.2, second paragraph – if more than 80% of carbonate precipitates, will it make things acid, or only less alkali..?? Why should they become acid?
- xviii) Section 4.2, second paragraph – “This process will provide acid aerosol from sea water” – do the authors really mean it will produce *aerosol*..?? If so, what is the mechanism..? What evidence do the authors have that the surface is airborne..? Throughout the majority of the paper they refer to sea-ice... Which surface is the one that matters..?
- xix) Section 4.2 – If the authors still want to discuss influence of temperature with respect to ozone loss, they should refer to previous work looking at the link between these processes, e.g. Tarasik and Bottenheim, ACP 12, 197, 2002. Note that Tarasik and Bottenheim suggest -20C is the temperature able to trigger ODEs.
- xx) Section 4.2 – again, the authors write “The sea ice is not totally fresh ice but the low air and water temperature in the fjord might cause the formation of brine ice mixture which is rich in sea salt aerosols” – the brine may be rich in sea salt, but aerosol only refers to sea salt once airborne – please correct this.
- xxi) Conclusions – again, the authors refer to “low temperature provide acid aerosols” – do they really mean that the surfaces are airborne? This needs clarification or correction
- xxii) Conclusions – statements about kinetics calculations need to be removed, as per Major concern described above.
- xxiii) Fig 2 b and c – maps are poor quality and need to be improved.
- xxiv) Fig 5 – caption – The modelled DAMF (a) and BrO slant columns (b) – but (b) is now DSCD ... Also, is fig c) SCD or DSCD?
- xxv) Fig 10 – quality is somewhat improved with the large images, but they are still hard to read. Please improve, and indicate location of Spitzbergen.
- xxvi) Fig 11 – needs information on source of photo, in particular to clarify that it is not the Kings Bay web cam.