

Response to Anonymous Referee #1:

We would like to thank Anonymous Referee #1 for his/her careful reading of this manuscript and for his/her comments and suggestions. We have addressed all of his/her comments in the revised manuscript and below, in the order in which they were raised. All page numbers and line numbers are in reference to those in the revised version of the manuscript, except where indicated otherwise.

1) The ODE definition (section 2.2) could be presented in a much more compact way by saying that ODEs and MODEs are defined by O₃ falling below thresholds of <15 ppb and 10 ppb, respectively, for > 1 hour. Starting times are defined by O₃ levels falling below 90% . . . (ODE) or below the threshold level, respectively while stop times . . . All remaining information (including the review of ODE definitions by other authors) could be transferred to the supplementary material.

-Section 2.2 (beginning p. 12, line 260) has been rewritten more concisely according to the referee's suggestion. The remaining material has been moved to the Supplement.

2) Section 2.4 could also be shortened by saying that there are basically two (extreme) explanations for ODEs: (1) Advection of already depleted air (dynamic hypothesis, DH), (2) in-situ chemical destruction (chemical hypothesis CH), of course also combinations are possible (and in fact likely). Throughout the manuscript these two hypotheses are frequently mixed, which is rather confusing. For instance all arguments made about the size of ODEs rest on the DH, while the discussion about measured BrO-levels being too low assumes the CH being correct. The DH and the CH in their pure form are mutually

exclusive (unless one assumes some combination, but this is not attempted in the manuscript) and this should be clearly said. Since it may be impossible from the data to decide which hypothesis is correct it is of course warranted to study both under the headlines “assuming the DH being correct we can conclude . . .” (e.g. conclusions about the spatial extent of ODEs can be drawn) and “assuming the CH being correct we can conclude . . .” (e.g. about the level of BrO and other halogen species), respectively.

We did note in the original manuscript that observed O₃ depletion can be some combination of local, in-situ chemistry, and the advection of air already depleted in O₃, but the extent to which each mechanism dominates is unknown based on this data set (e.g., p. 30235, line 10-11; p. 30247, line 11-13 of the original manuscript). But, we like the referee’s suggestion, and so we have incorporated two abbreviations throughout the main text in order to make our assumptions clearer for the analyses performed (introduced in the revised manuscript in Sect. 1, p. 5, paragraph beginning on line 91): CM (chemical mechanism(s)) and the TM (transport mechanism(s)) (analogous to the referee’s suggested “chemical hypothesis (CH)” and “dynamic hypothesis (DH)”). It is now noted more clearly when one scenario dominates the other, e.g.:

i) p. 17, line 384-386: we state that the we explore the observed O₃ decrease timescales for the limit of a dominant CM and minimal TM for this section.

ii) p. 23, sentence starting on line 508-512: we state that the spatial scale and Monte Carlo analyses in this section are performed for the limit of a dominant TM and minimal CM.

3) Section 2.4, Monte Carlo “Experiment”: The justification and usefulness of the Monte Carlo study (or numerical experiment) does not become clear, in particular, why do the Monte Carlo numerical experiments “provide statistical support” (page 30246, line 6) to

the DH? The description of the Monte Carlo numerical experiments could be deleted altogether or moved to the supplementary material. Likewise Fig. 9 does not appear to provide much information and could be deleted or moved to the supplementary material.

The Monte Carlo experiment is presented as a simplified thought experiment. That is, if we have large O₃-depleted air masses (per the estimated size distribution), this presupposes that large portions of the Arctic are at least partially depleted of O₃, and thus large areas could be conducive to O₃ depleting chemistry. For example, (as now stated on pp. 14-15, lines 316-318 of the revision) in the limit of an ODE the size of the Arctic Ocean, it is impossible for this ODE to be observed primarily due to TM. The question is then raised whether, given our distribution of ODE sizes, it is statistically reasonable that we observe such large events and are not in the presence of significant amounts of in-situ chemistry (i.e. is it a possible scenario that all observed events result from a TM mechanism, and the local CM is minimal?). The results of the Monte Carlo simulation do not provide evidence on whether TM mechanisms dominated over CM mechanisms in our observations, merely that this scenario is not implausible (given our size distribution). We have made these points clearer in Sect. 2.4 (beginning p. 14, line 313) of the revision, and maintain that this analysis is useful to the discussion that the TM is not inconsistent with the observed depletion spatial scales (as discussed in Sect. 3.2, p. 25, paragraph starting on line 563).

4) Section 3.1, On page 30249 the authors state that the measured BrO levels lead to an underprediction of the rate of O₃ loss by a factor of 3.6 (on average). Is this finding not a clear indication that the CH is wrong and the DH correct? This point should be discussed

-We believe this is a misunderstanding and have clarified this discussion in the text (paragraph beginning Sect. 3.1, p. 17, line 384 of the revision). The factor of 3.6 (recently updated to 4.1 based on model revision) is obtained from a regression between two different calculations of $d[\text{O}_3] dt^{-1}$ from Stephens et al. (2013) (now Thompson et al. (2014)): the net O_3 chemical destruction rate (Eq. 4 in the revised manuscript), and Eq. 3 of the revision (based on Le Bras and Platt (1995) and Platt and Janssen (1995)). It was found that if we used only Eq. 3 to estimate the O_3 depletion rate, we could be underestimating $d[\text{O}_3] dt^{-1}$ by a factor of 4.1 as a result of neglecting other chemical mechanisms accounted for by Eq. 4. In other words, this is a comparison of two different calculations of the magnitude of $-d[\text{O}_3] dt^{-1}$, assuming CM dominates. That Eq. 3 underestimates the net $d[\text{O}_3] dt^{-1}$ is also consistent with Liao et al. (2012) and Liao et al. (2014) (both now cited in the revised manuscript: pp. 40-41, lines 887-897) who report that the O_3 loss rate due to the BrO self reaction amounts for only 35% of the loss rate due to $\text{BrO} + \text{HO}_2$. Liao et al. (2012) report significant Br_2 concentrations, which produce Br atoms via photolysis, a process that competes very favorably with that represented by Eq. 3. Note that Fig. 6 (p. 56) was updated to reflect the altered required BrO numbers based on the updated factor from Thompson et al. (2014), though the updated BrO values were not significantly different from before.

5) Page 30252 and 1st para of page 30253: The attempt to “potentially test for missing chemistry” should be deleted in view of the fact that the CH is probably not correct (see point 4, above).

-Given that point #4 resulted from a misunderstanding, we have left this paragraph (pp. 21-22, paragraph starting on line 474) within the revised text.

6) Section 3.3 describes interesting conclusion, it is convincingly written and should be retained, but shortened. For instance the text on page 30258, lines 14 to 24 could be replaced by saying that the same analysis as for the T-dependence was performed for wind speed.

-This section was rewritten in a more concise way, at the suggestion of the referee (starting on p. 27, line 613 of the revised manuscript).

Minor comments

1) Abstract: The changes in the main body of the manuscript (e.g. DH vs. CH discussion) must be reflected in the abstract

-We have updated the abstract to be more consistent with the changes made throughout the manuscript. This includes references to the assumptions made for each analysis (i.e., p. 2, lines 33–39, BrO estimations were made assuming the CM dominates, while the spatial scales were estimated assuming the TM dominates).

2) Page 30236, lines 9ff: “the prominent regional tropospheric oxidation pathways . . . other than OH radicals, notably . . .” What is the evidence for this statement?

-This statement has been clarified on p. 3, lines 54-56. We now specify that the regional tropospheric oxidation pathways shift for hydrocarbons in low ozone / OH conditions, and have included an additional reference (Cavender et al., 2008).

3) Page 30236, line 21: R4 is not destroying O3 (the O3 consumed by Br+O3 is re-generated by the photolysis of OCIO making R4 part of a null-cycle. However the other two product channels of the BrO + ClO reaction lead to O3 destruction

-The correct reactions are now listed in Sect. 1, p. 3, lines 66-67. A note was also included (p. 4, lines 69-70) to explain why we did not include the formation of OCIO in our reaction listings. Additionally, the BrO + ClO rate constant used in Sect. 3.1 to calculate expected BrO was for the OCIO pathway (i.e., $k_{\text{BrO}+\text{ClO}\rightarrow\text{OCIO}+\text{Br}} = 8.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) in the ACPD version of the manuscript. This rate constant has been updated (p. 19, line 420) to ($k_{\text{BrO}+\text{ClO}\rightarrow\text{BrCl}+\text{O}_2} + k_{\text{BrO}+\text{ClO}\rightarrow\text{Br}+\text{Cl}+\text{O}_2} = k_{\text{BrO}+\text{ClO}} = 8.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2007)) to reflect the O₃ destroying pathways, and all relevant calculations were redone. However, the calculated expected BrO in each case was only altered by ~0.2-0.3 pmol mol⁻¹, and therefore no changes were made to the figure (p. 56) or the discussion within Sect. 3.1, beginning on p. 17, line 384.

4) Page 30243, line 7: Detection limits for BrO between 2-4 E13 molec./cm2 are quoted, this does not seem to fit with a stated noise level of the measured BrO-column density of 4 E13 molec./cm2. The detection limit is usually taken as twice or three times the noise level.

This has been clarified in the main text within Sect. 2.1. The stated noise level on p. 30242, line 24 of the ACPD manuscript is an upper bound, while the detection limit quoted on p. 30243, line 7, is based on a distribution of dSCD errors. However, because each individual measurement is the product of multiple differential slant column density (dSCD) measurements, our sensitivity to BrO is higher than what the dSCD errors would indicate. To make this point clearer, we have modified the manuscript (pp. 11-12, lines 237–250 of the revision) to discuss our detection limit in terms of a vertical column density (VCD) rather than a dSCD, which is more comparable to

satellite BrO measurements. We also added additional details on our determination of the detection limit within the same paragraph.

5) Page 30246, line 9: Why are the depletion regions assumed to be circular? The satellite observations clearly show that they are not.

While a lot of recent work has gone into more accurately dissecting satellite measurements of BrO (Choi et al., 2012; Salawitch et al., 2010; Theys et al., 2011), we believe there are still questions as to whether current methods can accurately probe the BrO profile in the surface layer, where the O-Buoy measurements are conducted. Thus, it is not clear to us what component of the satellite-retrieved shapes is actually in the boundary layer vs. the free troposphere, and the effect of tropopause variability. Since we do not have accurate information on the shapes of ODEs, we make a default assumption of a circular shape. Sect. 3.2 (p. 24-25, lines 543-546 of the revision) has been modified to include language about the assumptions of circular depletion regions; that is, the assumption that ODEs are circles could underestimate the area if only a secant passes over the buoy, or that the areas could be overestimated if the shapes are more irregular, as discussed below.

6) Page 30253, section 3.2: Could one not just simply say that the diameter $D_{ode} = v_{wind} \times t_{ode}$ (with v_{wind} = average wind speed, t_{ode} = ODE-duration)? However, this assumes that the (circular) ODE is blown across the measurement site in such a way that the centre of the ODE crosses the buoy. If just a secant crosses, then the above D_{ode} is just a lower limit to the true diameter of the ODE! Likewise, if the ODE is not circular, its area

might be overestimated by calculating it as $0.25 \times D2 \times \text{Pi}$. These points should be discussed.

Such an analysis is mentioned in the original manuscript in Sect. 3.2 (p. 30254, lines 5-7 of the submitted ACPD version) when comparing the means of the size distributions between methods. However, the method used was not explicitly stated, though it was performed as the referee described. We have now included this method and discussed the associated assumptions in Sect. 2.3 (p. 14, lines 295-301) and Sect. 3.2 (p. 24-25, lines 543-546 of the revised manuscript), respectively.

7) Section 3.1: When the DH is correct (which is likely, see above) then not only the O₃ depletion times are interesting but also the O₃ recovery time scales should be analysed.

-We agree that O₃ recovery is an important topic, as discussed by the very recent Moore et al. (2014) (now cited on p. 41, lines 911-913), and we believe there is merit in performing such an analysis using O-Buoy data. However, we feel that such an analysis is outside of the scope of this manuscript, which focuses primarily on the timescales of O₃ depletion and the ODE spatial scales. Recovery is likely a result of synoptic scale events, the observational data for which is problematic for the Arctic Ocean, and a large effort will be required to produce a paper on that subject.

8) Page 30248, line 13: did Morin et al 2005 really observe O₃ depletion within 3min?

-Morin et al. (2005) did report O₃ depletion occurring within 3 minutes on the sea ice (5 km off the coast of Alert) at the conclusion of a meteorological event, as discussed on p. 17, lines 378-380.

9) Page 30249, Eq. (3): this calculation and the assertion that BrO + HO₂ dominates over BrO + BrO only rests on Stephens et al. 2013b “in prep.” The arguments used by these authors can not be verified by the reader, therefore this part (including Eq. (3) should either be explained or removed.

- As discussed above, Liao et al. (2012) and Liao et al. (2014) also report that the O₃ loss rate due to BrO self reaction is only 35% of the loss rate due to BrO + HO₂ during OASIS. These citations have been added to Sect. 3.1, p. 18, lines 390-391. That Br₂ is an important source of Br atoms in the Arctic boundary layer is now verified and certain.

10) Page 30256, Sentence starting in line 24 is redundant and should be deleted.

-We have removed this sentence as suggested.

We would like to thank again Anonymous Referee #1 for his/her comments and suggestions, and feel sincerely the manuscript has benefitted from them.