

Interactive comment on “ Ozone variability and halogen oxidation within the Arctic and sub-Arctic springtime boundary layer” by J. B. Gilman et al.

Anonymous Referee #1

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Review of the manuscript acp 2010-339

The manuscript reports on mostly ship-based measurements of O₃, VOC's and some related species in the North Atlantic and Arctic Oceans. Particular VOC ratios are interpreted in terms of Br and Cl-atom abundances. These observations significantly expand our existing database of these species in the Arctic and sub-Arctic springtime marine boundary layer. The data provide further insights into the influence of halogen catalysed destruction of surface O₃ in the northern high latitudes and the transport of O₃-poor air masses from the Arctic Basin to lower latitudes. In this reviewer's opinion this is a valuable data set that is certainly worth publishing, however major revisions (see below) are required to make the manuscript acceptable for publication in ACP. The

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paper describes the techniques, observations and results in sufficient detail, although clarifications are necessary in throughout the manuscript (a number of examples are given below). Although the authors made some efforts to provide a discussion of their data several opportunities to draw interesting conclusions have been missed.

These include:

- 1) The authors make no attempt to derive absolute concentrations of Br and Cl atoms. At least the time-integrated concentration should be relatively easy to calculate from the changes in the VOC ratios (see e.g. Ramacher et al. 1999). Together with the exposure time (see below) average concentrations along the trajectory can be inferred.
- 2) ICE "Exposures" are derived from FLEXPART model runs (see e.g. ordinate axis of Fig. 5), which can be interpreted – at best – as relative values, however exposure times would be what would be interesting.
- 3) Apparently the correlation in disturbances in O₃ and VOC-ratios persists for a rather long times (see Fig. 6). This is an interesting finding by itself and also would allow to calculate vertical mixing, which was not done.

There are a large number of unclear points in the manuscript which need to be corrected in a final version:

- 1) Page 15887, lines 4,5: Mixing with surrounding airmasses: Is this not rather vertical mixing?
- 2) Page 15887, lines 8,9: " ... linked to the presence of ... (Br) radicals... ": Here the authors jump right into the middle of the topic without giving appropriate explanations: O₃-destruction obviously must be a catalytic process (there are 4-5 orders of magnitude more O₃ than Br); the rate of O₃ destruction likely second order in Br; Br is thought to be liberated from sea ice; the role of Cl is unclear and likely insignificant (in particular if Br/Cl exceeds 1000 as stated later in the manuscript.); etc.
- 3) Page 15888, line 20: " .. data from two mid-latitude studies ...": State which studies

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(THD and NEAQS ?).

4) Page 15888, Para starting in line 23: This text belongs into the Methods section (2.).

5) Page 15889, line 3: ICELOT was not mentioned in the Introduction section, explain relationship to POLARCAT.

6) Page 15889, line 14: Much more interesting than the outer (!) diameter of the tube would be the residence time of the air in the tube.

7) Page 15889, lines 21ff: The explanation of the instrument is cryptic. Was the instrument originally equipped with FID and ECD detectors and then changed to use a MS-detector or were all detectors used? What is the point in describing the history of the instrument? Furthermore, the description of the interleaving procedure of the two columns is cryptic and should be improved.

8) Page 15890, para. starting in line 10: Who should be interested in an "old" system?

9) Page 15890, line 27: Explain ARPAC and its relation to POLARCAT.

10) Page 15891, lines 6-10: This uncertainty in acetylene measurements propagates into the acetylene/benzene ratios and thus derived Br atom levels, this should be stated clearly here and in the discussion section.

11) Page 15891, line 28ff: "Flasks are collected in stainless steel canisters ..." What is the meaning of this statement?

12) Page 15893, para's starting in lines 2 and 11: the explanation of the term "exposure" is cryptic, what is the significance of $1.0 \text{ kgs}^{-1} \text{m}^{-2}$? Probably it would be better to use "arbitrary units". As far as this reviewer understands "exposure" means a combination of residence time and vertical mixing of something (i.e. Br or Cl) exhaled from the surface into the air mass. Probably this could be said more clearly. Also calculating the exposure time would be most interesting (and perhaps just as good as "exposure").

13) Pages 15894 and 15895: The para starting in line 27 of page 15894 explains

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general features of the VOC ratio-technique, it therefore belongs into subsection 2.1.

14) Page 15895, line 7: "At this longitude the sub-Arctic is defined ..."

15) Page 15895: The April 4-6 depletion event is not mentioned.

16) Page 15896, line 8: What is the meaning of "... previously depleted in O₃ ..." Here is another place where it shows that the underlying concept of the interpretation was omitted. Apparently it is assumed that the O₃ is depleted "instantly" and is only subject to mixing in the following? How long ago did the depletion occur?

17) Page 15896, lines 13-15: The important question is here whether this Br/Cl ratio is consistent with the observed depletion of the VOC ratios?

18) Page 15897, lines 22ff: "the relative importance of Br and Cl radical chemistry was similar throughout the Arctic ..." It is unclear how this conclusion follows from the data presented. In particular nothing can be said about Cl, since Cl-atoms probably do not significantly contribute to O₃ depletion.

19) Page 15897, lines 25ff: Here general comments about the applicability of the VOC ratio technique are made these belong into section 2.1.

20) bottom of page 15897, Top of page 15898: There are underlying model concepts, which are not explained to the reader (see point 16). 21) Page 15898, lines 24ff: The question of different source emission ratios is central to the VOC-ratio technique, it should have been discussed much earlier.

21) Page 15901, line 2: The residence time is a central issue. the relationship between "exposure" and residence time should be explained.

22) Page 15902, first para.: It would be very interesting to separate the influence of FYI vs. MYI on O₃ depletion.

23) Page 15903, line 7: The DMS-anticorrelation is only discussed in terms of DMS sources, however DMS is also strongly depleted by reaction with BrO, which is usually

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always present when elevated levels of Br prevail.

24) Page 15903, last para.: The possible formation of CHBr₃ during bromine explosion events is an interesting observation (although difficult to explain) and should be repeated in the conclusions.

25) Page 15904, line 21: This conclusion can not be drawn, see point 18, above.

26) Page 15905, line 8ff: This sentence should be deleted or results (e.g. regarding CHBr₃) should be given.

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