

The authors would like to thank the reviewer for the constructive suggestions and comments. We have included point-by-point responses of how we have addressed each of the reviewer's questions and comments.

### **General Comments:**

- A) *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 Ramacher et al. 1999). Together with the exposure time average concentrations along the trajectory can be inferred.*

A detailed analysis, including time-integrated halogen mixing ratios, of the ozone depletion event observed during the Arctic leg of the ICEALOT cruise is discussed in the forthcoming Lerner et al. manuscript [in preparation, 2010], so it is not included in this study. We have modified the text in Sect. 3.2 in order to strengthen the connection between the two companion papers.

We readily acknowledge that time-integrated halogen mixing ratios are an important metric for the discussion of halogen oxidation chemistry within the Arctic; however, the application of this metric to the present study of the influence of halogen oxidation on determining the variability of ozone and VOCs throughout the Arctic and sub-Arctic is problematic. Time-dependent halogen concentrations, which are determined from changes in a particular VOC from a user-defined "background" value (e.g., Jobson, et al. [1994], Ramacher et al. [1999]), requires several assumptions and estimates leading to a significantly large uncertainty in the calculation of the halogen concentrations over the broad geographic area studied in this work. For example, the background value of many of the VOCs, acetylene in particular, changed over the course of the campaign as the ship headed northward. While a variable background value of acetylene as a function of latitude could theoretically be determined, it introduces a fundamental uncertainty in the time integrated halogen concentrations. If we were able to report an absolute exposure time (see next response), we would have to make the additional assumption that the reaction time and exposure time to the sea ice are equivalent (i.e., halogen oxidation chemistry was occurring the whole time that the air mass was over the ice). The validity of this assumption is not entirely clear.

- B) *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.*

We agree that exposure times would be very useful; however, constraints to the FLEXPART model do not currently allow for the calculation of an absolute exposure time. Regardless, the FLEXPART model output is a robust and highly quantitative measure of an "inert ice tracer" (in units of ppbv), which is directly proportional to the time an air mass was in contact with FYI or MYI (i.e., exposure time). While the reviewer is correct in pointing out that ICE exposure is

discussed in relative values, this has no bearing on the interpretation of the correlations between the modeled ICE exposure and the measured trace gases presented in this study.

- C) *Apparently the correlation in disturbances in O<sub>3</sub> 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.*

In reference to Fig. 6, the reviewer was correct in noting that the correlations between O<sub>3</sub> and sea ice exposure persists throughout the air masses modeled 20-day history. In response, we have added a short discussion on the fraction of air masses that remain in the footprint layer, exposed to sea ice, for the majority of their modeled histories.

### **Clarifications:**

- 1) *Page 15887, lines 4,5: Mixing with surrounding air masses: Is this not rather vertical mixing?*  
Mixing can occur in both the horizontal and vertical; therefore, we have kept the more general description of 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.*  
We have modified the second paragraph of Sect. 1 to include a brief explanation of the catalytic destruction of O<sub>3</sub> by Br and the role of Cl oxidation as it pertains to VOCs.
- 3) *Page 15888, line 20: "... data from two mid-latitude studies ...": State which studies (THD and NEAQS).*  
Correction made.
- 4) *Page 15888, Para starting in line 23: This text belongs into the Methods section.*  
Correction made.
- 5) *Page 15889, line 3: ICEALOT was not mentioned in the Introduction section, explain relationship to POLARCAT.*  
Correction made.
- 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.*  
Correction made.
- 7) *Page 15889, lines 21ff: The explanation of the instrument is cryptic.*  
The instrument description of the GC-MS has been reworked and further clarified per both reviewers' apt suggestions.

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

All references to the original instrument configuration have been removed.

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

Correction made.

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.

The measured differences in the acetylene standards used by NOAA GMD (ARCPAC, BRW, THD datasets) and NOAA CSD (ICEALOT dataset) affects the magnitude of the [Acetylene]/[Benzene] ratio; however, it does not affect the correlation between this ratio and O<sub>3</sub> which is the primary focus of this study. The derived [Br]/[Cl] ratio that is presented in a companion paper by Lerner, et al. (in preparation) was determined from relative changes in VOC concentrations during the ICEALOT ODE compared to measured background values (e.g., Jobson, et al. [1994], Ramancher et al. [1999]), so any uncertainty in the acetylene calibration factor will not propagate to the derived halogen atom concentrations. Sources of uncertainty to the derived Br atom levels include how well Cl oxidation of acetylene can be accounted for and how accurately the "background" value of acetylene is known.

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

Correction made.

12) Page 15893, para's starting in lines 2 and 11: The explanation of the term "exposure" is cryptic, what is the significance of  $1.0 \text{ kg s}^{-1} \text{ m}^{-2}$ ? 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. Also, calculating the exposure time would be most interesting.

The model description has been modified in order to address the reviewer's suggestions and comments where appropriate. The units of  $\text{kg s}^{-1} \text{ m}^{-2}$  are standard units for emission fluxes used as input to the FLEXPART model and are analogous to those used for more common tracers such as CO. We have considered the use of arbitrary units, but have decided that it is more appropriate and accurate to maintain the units of the model output. We have modified the text in order to clearly state the assumption that the ice tracer is instantaneously mixed within the gridded footprint volume upon emission. We agree that exposure times

would be very useful; however, constraints to the FLEXPART model do not currently allow for the calculation of an absolute exposure time.

- 13) *Pages 15894 and 15895: The paragraph starting in line 27 of page 15894 explains general features of the VOC ratio-technique; it therefore belongs into subsection 2.1.*

Portions of the specified paragraph have been moved to section 3.1, which includes the discussion of the use of VOC ratios. We keep Sect. 2 for the description of the physical measurements and FLEXPART model.

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

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

We have added a short discussion of the observed decrease in O<sub>3</sub> on 6 April 2008 to Sect. 3.2 and highlighted this time period in Fig. 2.

- 16) *Page 15896, line 8: What is the meaning of "... previously depleted in O<sub>3</sub> ..."*  
*Apparently it is assumed that the O<sub>3</sub> is depleted "instantly" and is only subject to mixing in the following? How long ago did the depletion occur?*

We agree that the above statement warrants further explanation, but we have chosen to simplify the text by removing the specified statement since it was ancillary to the discussion at hand. However, we address the reviewer's comments below.

It is important to note that we do not assume that ozone is depleted "instantly." The fluctuations in O<sub>3</sub> that we observed are either due to 1) active halogen destruction of O<sub>3</sub> occurring at the measurement site or 2) the transport of an air mass to the measurement site that was "previously depleted in O<sub>3</sub>" (i.e., the chemistry occurred elsewhere at an unspecified time). While it can be difficult to distinguish between these two scenarios, Lerner, et al. (in preparation) was able to determine that the ODE encountered on 15-20 April 2008 was the result of O<sub>3</sub>-poor air being transported to the measurement site and the rapid fluctuations from sample to sample reflect varying degrees of air mass mixing. While it is not possible to determine how long ago the observed O<sub>3</sub> depletion occurred, it was possible to rule out the present time (i.e., active chemistry occurring at the measurement site).

- 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?*

The VOC ratios were used to determine the [Br]/[Cl] ratio. This has been clarified in the text.

- 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 O<sub>3</sub> depletion.*

We agree that the statement regarding the “relative importance of Br and Cl radical chemistry” throughout the Arctic may have been unclear, so we have modified the text in Sect. 3.3 in an effort to further clarify our statements and the basis of our conclusions. Specifically, we have expanded the text in order to better explain the contribution of Cl oxidation on the observed slope between [Acetylene]/[Benzene] and O<sub>3</sub> for the arctic datasets.

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

These comments have been removed for brevity.

20) *bottom of page 15897, Top of page 15898: There are underlying model concepts, which are not explained to the reader (see point 16).*

Correction made. See response to reviewer comments #16 and #18.

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.*

Discussion of the affect of different source emission ratios is now mentioned in earlier in Sect. 3.1 rather than 3.2.

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

We have replaced the mention of “residence time” here with the term “exposure” in order to maintain consistency in the language throughout the text. The relationship between the modeled ice exposure and residence time of an air mass over sea ice has been further clarified in the model description.

23) *Page 15902, first para.: It would be very interesting to separate the influence of FYI vs. MYI on O<sub>3</sub> depletion.*

We agree that it would be very interesting to separate the influences of the different types of sea ice, in fact, it was the key question which motivated the FLEXPART modeling effort discussed here. Unfortunately, the relative importance of exposure to FYI or MYI in determining O<sub>3</sub> variability remains inconclusive for the ICEALOT data set as mentioned in the text.

24) *Page 15903, line 7: The DMS anti-correlation is only discussed in terms of DMS sources; however, DMS is also strongly depleted by reaction with BrO, which is usually always present when elevated levels of Br prevail.*

The text has been appropriately corrected to include the possibility of DMS oxidation via BrO and how this would further enhance the observed negative correlation with ICE exposure.

25) Page 15903, last para.: *The possible formation of  $\text{CHBr}_3$  during bromine explosion events is an interesting observation (although difficult to explain) and should be repeated in the conclusions.*

We have included the results of the  $\text{CHBr}_3$  correlation with ICE exposure in the conclusions.

26) Page 15904, line 21: *This conclusion cannot be drawn, see point 18, above.*

The text has been revised in accordance with the manuscript modifications of Sect 3.3 as outlined in our response to comment #18.

27) Page 15905, line 8ff: *This sentence should be deleted or results (e.g. regarding  $\text{CHBr}_3$ ) should be given.*

The results regarding the correlations between the other trace gases and ICE exposure has been added to the conclusions.