

Interactive comment on “Interactions of bromine, chlorine, and iodine photochemistry during ozone depletions in Barrow, Alaska” by C. R. Thompson et al.

Anonymous Referee #2

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Thompson et al. investigate interactions of bromine, chlorine, and iodine photochemistry during ozone depletions in Barrow, Alaska. The topic of the study is very interesting, and initially I rated it as “excellent”. However, looking deeper into the details, I found several weaknesses in the modeling approach that require major revisions as described below.

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General comments

- Cl₂ is constrained to measurements but bromine is not. This makes it difficult to interpret the model results. I would prefer to either constrain all halogens or none.
- The authors say they could not reproduce the day-to-day variability in Br₂ from only the heterogeneous chemistry. An additional prescribed bromine flux was necessary to estimate Br₂ and BrO observations. Why then is heterogeneous chemistry included in the model at all? Wouldn't it be more straightforward to prescribe gas-phase bromine concentrations directly? What additional value has the heterogeneous chemistry in the model?
- It is mentioned that the variability seen in the ambient NO_x data is not represented or tested. I wonder if the model results are still useful then. NO_x has a large impact on halogen chemistry.
- To increase iodine, the model switches from 1 ppt IO to 0.5 ppt I₂. Why is a different molecule chosen now? I think simply increasing IO by a certain factor would be more useful.

Specific comments

- Page 28687: “We simulated a 7 day period during late March that included a full ozone depletion event lasting 3 days and subsequent ozone recovery”.
The recovery of ozone is mentioned here in the abstract but I cannot find any information in the text how it was modeled.

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- Page 28691: “Most recently, I_2 at levels ≤ 0.5 pptv have been observed by our research group at Barrow, Alaska”.

Can you please add a reference to this statement?

- Page 28691: “Halogen atoms can react with formaldehyde”

This statement is certainly true for Cl and Br but is the reaction of iodine atoms with formaldehyde significant?

- Page 28692: “Halogen chemistry also generally increases the Leighton ratio ($[NO_2]/[NO]$)”.

It should also be discussed here that XO reacts with NO_2 and forms XNO_3 . This decreases the Leighton ratio.

- Page 28695: What is the difference between J coefficients and J values? If they are identical, why are two different names used?

- Page 28698/99: “Because the I_2 flux is constant during the ODE, while Br_2 , and especially Cl_2 are decreased, iodine becomes more dominant for reaction with O_3 and IO increases.”

I understand that the relative importance of iodine increases under these conditions but why should the absolute values of IO increase when ozone is depleted?

- Page 28702: “it is generally accepted that bromine is the dominant reactant leading to ozone destruction. However, this has not been quantified, nor has this been investigated for varying chemical conditions.”

I find this statement too bold. There are many studies which look at this question. I agree, though, that there are still many open questions left.

- Page 28716: “From our analyses it is clear that the interactions between bromine, chlorine, and iodine are very complex”

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I think this was already clear before this study started.

- Page 28717: “While chlorine is clearly not necessary to cause ozone depletion, it can significantly impact the rate of ozone depletion.”

According to Table 8, chlorine increases the ozone depletion rate from 5.2 to 5.3 ppb/h. I would not call this significant.

- Page 287: “In light of these new data, it is crucial that future Arctic modeling studies take into account the activity of chlorine.”

Indeed, it is crucial to include chlorine chemistry in the models. However, it is important for hydrocarbons, not for ozone.

- Page 28731: The reference Vogt 1999 is incomplete.
- Page 28740: Why are the heterogeneous reactions of XNO_3 not considered here?
- Page 28750: In Fig. 4, it seems that the values for Br, Cl, and I add up to 100 %. This is different from the data in Table 7 which is calculated based on equation (4). Why is equation (4) not used for Fig. 4?
- Page 28750: Another question I have are about the nighttime values in Fig. 4. What is their meaning? At night, the concentrations of ozone-destroying Cl and Br atoms are close to zero.

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