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Interactive comment on “Potential impacts of CF_3I on ozone as a replacement for CF_3Br in aircraft applications” *by* Y. Li et al.

Y. Li et al.

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Response to comments on “Potential impacts of CF3I on ozone as a replacement for CF3Br in aircraft applications” by Y. Li, K. Patten, D. Youn, and D. Wuebbles

“Discussing the ODP of CF3I used in aircraft fire fighting and fuel inerting is a timely subject. In think the paper should be published. I have two general issues. The first one is the presentation of the material. Judging from the title, the focus should be on the ODP calculations. Yet, this occupies only about 1/4 of the text. The discussion on iodine chemistry provided a good summary but is not well focused, and lacks the details to be scientifically useful. Second, if I understand the results correctly, much of the ozone depletion that contributes to the ODP value occurs in the troposphere. The authors failed to make this clear in the paper.”

Your advice is highly appreciated. We attempted to give a complete description of iodine chemistry in the paper, because there are not many discussions on this topic available and this is definitely important as a foundation for our later discussion on CF3I. For ozone depletion by CF3I emissions, as emphasized in the manuscript, it is highly related to the location (latitudes, altitudes, etc.). For example, large ozone depletion often occurred in the troposphere for the Van Horn and the NIST emission profiles because most of CF3I emissions were released near the surface or quite below the tropopause. However, the majority of the ozone depletion for the Rupnik profile, which has much of CF3I emission in the upper troposphere, was in the stratosphere as shown in Figure 8.

“The authors need to clarify many of the results presented. For example, I assume figure 3 is from the present day atmosphere. The amount of Iy should be stated. There should be an explanation to explain how the ozone efficiency in figure 4 is defined. Is it based on local photochemical ozone loss per unit iodine and chlorine added, or is it the actual ozone change per unit iodine and chlorine added? I suspect it is the former. In the latter case, the authors should also specify whether the added iodine or chlorine is uniform or not. Finally, have the ozone concentration changes in Figure 6 been normalized to the same CF3I input, or are they just changes from the different model run with different amount of CF3I put in to get a 1% ozone depletion? The figure suggest to me that depositing CF3I in the tropics give a larger ODP, not because of more Iy ends up in the stratosphere, but because there is larger ozone depletion in the troposphere in the southern hemisphere.”

The figure 3 is based on the current model atmosphere, annually averaged. This has now been made clear in the model description. The ozone depletion efficiency (ODE) has been defined and explained in section 3.4. To account for all the ozone loss procedures (efficiency) involving a chemical species, the formula is given as total local chemical reaction rates of iodine-related catalytic cycles divided by those of chlorine-related catalytic cycles on the per unit mass basis. The species are added as uniformly distributed perturbations. For ODP calculations, as mentioned in the manuscript, “all the model runs were scaled to deplete 1% global total ozone from the background atmosphere.” Please refer to Wuebbles et al. (2001) for more details. The largest ozone depletion occurred in the polar regions in the upper troposphere and lower stratosphere (UT/LS). This is because the iodine species generated by the CF3I emissions were transported to the polar regions from lower latitudes and the UT/LS in the polar regions has favorable conditions for iodine catalytic cycles as discussed in Section 2.3.3.

“I would like the authors to explain the following results. I expect the difference in ozone depletion between the Rupnik and the Van Horn profile is governed by where the odd iodine radicals are produced. Those produce at lower altitudes are just more prone to washout. However, I have a difficult time explaining why the emission profile makes such a big difference in the CF3I lifetime (from 0.7 days to 0.1 days). With a lifetime of a few days, the atmospheric lifetime is just the reciprocal of the local photolysis rate. I will like to see a plot of the photolysis rate as a function of latitude and altitude. I also find it surprising that the depletion from the NIST profile is larger compared to the Van Horn profile despite releasing at lower altitudes.”

The CF3I lifetime is governed by its photolysis reaction. For the tropical scenario, much of CF3I emission in the Rupnik profile is at the level where cloud can negatively affect photochemical reaction rates, which leads to the longer CF3I lifetime. A contour plot of the photolysis rate in the latitude/altitude crossection is available at http://www.atmos.uiuc.edu/~yueli2/phot.jpg. The ozone depletion is caused by the iodine species generated by the CF3I photolysis through iodine catalytic cycles. If more CF3I can reach the stratosphere, more ozone will be depleted. The Van Horn estimate has much lower emission profile than the Rupnik estimate, which means CF3I emissions for the Van Horn profile has less exposure to the ultraviolet light which is essential for the photolysis. The NIST profile has about 15% emissions in the upper troposphere and lower stratosphere, while the Van Horn profile only has about 7%. The iodine species generated from CF3I emissions at higher altitudes have a better chance to survive the rainout processes and therefore stay longer in the atmosphere to deplete ozone.

“Specific comments: impacts THAN CF3Br” and delete the last half of the sentence.”

We have changed it..

“I suggest changing the subtitle for section 4 and 5. I would like to see the two section combined and labeled as ODP for CF3I in different applications.”

We have changed it.

“Is the clean-air act value of 0.2 that important? How is it related to EPA ‘s value of concern of 0.05? I would suggest staying away from those discussions.”

It is important from the viewpoint of determining ht epoint at which policy kicks in and ODPs have high relevance to policy considerations. The Clean Air Act describes one of a number of pieces of legislation relating to the reduction of smog and atmospheric pollution in general. The United States Congress passed the Clean Air Act in 1963, the Clean Air Act Amendment in 1966, the Clean Air Act Extension in 1970, and Clean Air Act Amendments in 1977 and 1990. Any chemical that has ODPs larger than the control values in the Clean Air Act will be banned for usage, while the EPA’s value provides suggestion on the limited use of certain chemicals.

“p. 5166, line 9 Delete first part of the sentence. Use of word “objectively” is awkward.”

We have changed it.

“Section 2. I am surprised to find no description of the troposphere. Again, if the ODP values are due to depletion in the troposphere, it is important to talk about dispersion of Iy in the troposphere and the ozone chemistry in the troposphere. If the ODP values are dominated by depletion in the stratosphere, it is important to talk about convection in the model.”

More description on model treatment of the tropospheric processes has been added to the manuscript. As we mentioned in the manuscript, “we recognize the limitations of two-dimensional models, particular in representing tropospheric processes. The next stage for further analysis of CF3I impacts on ozone would be to perform similar studies with a three-dimensional chemistry-transport model of the troposphere and stratosphere”. However, our model includes most of atmospheric physical processes in the troposphere, such as convection, eddy diffusion and eddy transport.

“Section 3.2 and 3.3 It would be better to move the last portion in 3.3 (assumed rates for ClO + IO and BrO + IO in Solomon et al. to the beginning of section 3.2. It is a bit tiresome to keep reading that there is incomplete understanding in iodine chemistry.”

The discussion by Solomon et al. (1994) was in Section 3.3 because it was focused on catalytic cycles. Section 3.2 describes the general iodine-related chemical processes.

“p. 5172, line 24. How tiny a fraction gets to the stratosphere? I would very much like to see a number. Again has to do with whether the ODP values are driven by depletion in the troposphere, or difference in Iy loading in the stratosphere.”

In the case of uniform surface emission in the Northern Hemisphere, about 0.1% CF3I gets to the stratosphere. The fraction values can be quite different for various emission profiles. It is found through our various tests that at most 1% of CF3I can reach the stratosphere finally. CF3I does not lead to ozone destruction directly. Its photolysis products (Iy) do. ODP values are governed by the total ozone depletion, which is highly dependent on the emission scenarios in this study.

“Table 2. Identify rate-limiting steps by asterisks in the Table.”

We have identified it accordingly.

“Figure 3: The numbers indicate that the local lifetime of ozone to iodine chemistry is a few years in the troposphere and 100 years in the lower stratosphere. I worry that in the ODP calculations, so much CF3I has to be put in to get 1% depletion that the non-linear Iodine self-reacting catalytic cycle is over emphasized. This may be an overestimate of the ODP because it is not linear.”

As you mentioned, 1 % global total ozone was depleted due to the CF3I perturbation. The 1% change is not strong enough to change the atmospheric composition significantly and the catalytic cycles reaction rates tend to be proportional to concentrations of the chemicals involved in it. We have done calculations with smaller perturbations with no difference in the resulting ODPs. Therefore, the non-linearity is not likely to be a big issue here.

“Figure 4. What season is it?”

“Annually averaged” was mentioned in the figure caption and it has been added to manuscript.

References

Davis, D, Crawford, J., Liu, S., McKeen, S., Bandy, A., Thornton, D., Rowland, F., and Blake, D.: Potential impact of iodine on tropospheric levels of ozone and other critical oxidants, J. Geophys. Res., 101 (D1), 2135-2147, 1996.

Seinfeld, J. H. and Pandis, S. N., Atmospheric Chemistry and Physics, Chapter 4: Chemistry of the Stratosphere, John Wiley & Sons, Inc., 1998.

Wuebbles, D. J., Patten, K. O., Johnson, M. T., and Kotamarthi, R.: The new methodology for Ozone Depletion Potentials of short-lived compounds: n-propyl bromide as an example, J. Geophys. Res., 106, 14551-14571, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5163, 2006.