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**Potential impact of iodinated replacement  
compounds  $\text{CF}_3\text{I}$  and  $\text{CH}_3\text{I}$  on atmospheric ozone:  
a three-dimensional modeling study” by  
Daeok Youn et al.**

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Anonymous Referee 1

Received and published: 12 August 2010 This paper presents two key results. (1) Calculation of the background atmospheric concentration of  $\text{CH}_3\text{I}$  using a 3-D model from known natural source distribution and comparison of the calculated concentra-

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tions with observations from PEM TB. (2) Calculations of the ODP values for CH<sub>3</sub>I and CF<sub>3</sub>I using both 3-D model and 2-D model with the somewhat surprising conclusion that the 2-D model gives very similar results.

#### Comments:

1) The authors claimed that the good comparison between model simulated and observed CH<sub>3</sub>I distributions is an indication that the 3-D model chemistry is reliable for evaluating ODP of iodine species. I do not think the statement is a justified. The good comparison, at best, provides some validation for convective transport of short-lived species and how much reaches the stratosphere. It does not speak to how iodine affects ozone.

→ We agree that we made too simplified a statement. The good comparisons between measured and modeled CH<sub>3</sub>I concentrations do not fully justify the set of iodine chemistry used in our model simulations. However, those comparisons do denote valid simulation of convective transport, vertical mixing and degradation chemistry of CH<sub>3</sub>I itself. After emission to the atmosphere, CH<sub>3</sub>I can be photolyzed or oxidized by the HO radical, to produce iodine radicals. Iodine produced from CH<sub>3</sub>I and other short-lived iodocarbons plays many important roles in marine boundary layer chemistry, influencing ozone destruction, the oxidizing capacity of the troposphere, denoxification, and particle formation [Vogt et al., 1999; Carpenter, 2003; O'Dowd et al., 2002]. The ultimate fate of gas phase iodine is abstraction to aerosol particles as iodide (I<sup>-</sup>) and iodate (IO<sub>3</sub><sup>-</sup>) in the troposphere. The aerosol chemistry was not included in our current study. Therefore, our derived ODPs of iodine species are the upper limit.

Accordingly, we changed the last paragraph in the abstract as below:

"Valid simulations of convective transport, vertical mixing and degradation chemistry of CH<sub>3</sub>I is shown with. . ."

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In the first paragraph of section 4, we added sentences to better describe CH<sub>3</sub>I chemistry as below:

"After the emissions to the atmosphere, CH<sub>3</sub>I can be photolyzed or oxidized by the HO radical, to produce iodine radicals. Photolysis of CH<sub>3</sub>I is a main pathway of its removal from the troposphere, so as to produce iodine atoms even under visible light conditions (Chameides and Davis, 1980; Davis et al., 1996). Iodine produced from CH<sub>3</sub>I plays many important roles in marine boundary layer chemistry, influencing ozone destruction, the oxidizing capacity of the troposphere, denoxification, and particle formation [Vogt et al., 1999; Carpenter, 2003; O'Dowd et al., 2002]. The ultimate fate of gas phase iodine is abstraction to aerosol particles as iodide (I<sup>-</sup>) and iodate (IO<sub>3</sub><sup>-</sup>) in the troposphere. Unfortunately, most of the existing measurements of iodine in marine aerosols are based on bulk measurement of total iodine, so the individual chemical iodine species contributing to particulate iodine have rarely been measured (O'Dowd and Hoffmann, 2005). Although recent modeling work tried to include aerosol phase reactions with organic substances (Pechtl et al., 2007), any aerosol chemistry was not included in our current study. Therefore, our derived ODPs of iodine species are the upper limit. In this section 4, a simulation of background CH<sub>3</sub>I concentrations in the atmosphere is evaluated to determine the capabilities of 3-D models towards accounting for CH<sub>3</sub>I chemistry."

In the last paragraph of section 4, we added two sentences discussing the comparisons between simulated and observed CH<sub>3</sub>I concentrations as below:

"The good comparisons between measured and modeled CH<sub>3</sub>I concentrations do not fully justify the set of iodine chemistry used in our model simulations. However, those comparisons do denote valid simulation of convective transport, vertical mixing and degradation chemistry of CH<sub>3</sub>I."

2) In figure 6a, is the difference between 10-1.5 ppt and 10-2.5 ppt significant, or it is more appropriate to consider them as the same small number so that the change in

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Cly has uniform mixing ratio in the stratosphere. Note that the expected result is that the change in Cly mixing ratio should be uniform because there is no sources and sink in the upper stratosphere.

→ CH3I and CF3I, the VSLs in this article, generate Iy instead of Cly. The values on contour lines in Fig. 6 are the base 10 logarithm of 'Iy mixing ratio in ppt' and thus contour values of about -1.5 to -2.5 in the stratosphere amount to about 0.03 to 0.003 ppt which is not significant. Despite the very small concentrations, total inorganic iodine from mid-latitude emission scenarios of iodine species in the stratosphere in Figs. 6a and 8b is notable because the distributions shows asymmetry about equator, differently from that from tropical emission scenario in Fig. 6b. We think that it would partly indicate dependency of short-lived ODS's ODP on emission location and support extratropical isentropic transport of Iy and the existence of Northern Hemisphere (NH) transport pathway (the NH summer monsoons as regions for transport) to the lower stratosphere as shown with satellite data and MOZART output by Park et al. (2004).

Accordingly, we added sentences at the text in the 5th paragraph of section 5 as follow: "However, since the values on contour lines in Fig. 6 are the base 10 logarithm of 'Iy mixing ratio in ppt', contour values of about -1.5 to -2.5 in the stratosphere amount to about 0.03 to 0.003 ppt which is not significant. Despite the very small concentrations, total inorganic iodine from mid-latitude emission scenarios of iodine species in the stratosphere in Fig. 6a (also in Fig. 8b) is noted because the distributions shows asymmetry about equator, differently from that from tropical emission scenario in Fig. 6b. It would partly indicate dependency of short-lived ODS's ODP on emission location and support the existence of Northern Hemisphere (NH) transport pathway (the NH summer monsoons as regions for transport) to the lower stratosphere as shown with satellite data and MOZART-3 output by Park et al. (2004)."

3) From figure 7, it is clear that the ODP values are mainly from ozone depletion in the troposphere. Does the similarity between the 3-D and 2-D results tell us any more that that the tropospheric ozone response is about the same?

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→ For CF3I emissions over mid-latitudes, in Fig. 7a, total ozone change simulated by the 3-D (2-D) model is -0.381 (-0.228) in Dobson units (DU) and the ozone change throughout the troposphere is -0.333 (-0.197) DU. Despite different values in magnitude, the 2-D and 3-D model-simulated results show clear similarity in that about 87

To clarify this, we added sentences in the 7th paragraph of section 5 as follow:

"The agreement between the two different model simulations is again shown with calculations of total ozone. For CF3I emissions over mid-latitudes, total ozone change simulated by the 3-D (2-D) model is -0.381 (-0.228) in Dobson units (DU) and the ozone change throughout the troposphere is -0.333 (-0.197) DU. Despite different values in magnitude, the 2-D and 3-D model-simulated results show clear similarity in that about 87

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