"**The contribution of oceanic methyl iodide to stratospheric iodine**" by S. Tegtmeier et al.

Response to Anonymous Referee #2

We thank the reviewer for the positive feedback and helpful comments. We have addressed all reviewer comments in a revised manuscript. Our detailed answers to the comments can be found below in italics.

The paper describes a two way approach to constrain stratospheric Iy by (1) estimating the vertical profile of CH3I based on ship-observations from various recent campaigns, and (2) comparing these estimates with recent aircraft observations. The manuscript is well within the scope of ACP, and warrants publication after the following issues have been addressed.

Comments:

1) The title 'The contribution of oceanic methyl iodide to stratospheric iodine' is somewhat misleading, as no estimate for the contribution of CH3I to total iodine in the stratosphere is actually presented. The manuscript would benefit from discussion about what is known about the different reservoirs of iodine in the stratosphere, and existing constraints on stratospheric Iy, as well as discussion on what measurements (species, altitude ranges) are most likely to provide a meaningful constraint on stratospheric Iy.

Since CH_3I must release I_y once it is in the stratosphere, we are able to give the 'contribution of oceanic methyl iodide to stratospheric iodine' in form of the estimates of CH_3I entrained into the stratosphere. As explained in Chapter 3 the entrainment is derived as the mixing ratio of CH_3I at the cold point which we have chosen as upper estimate of the ''no-wash-out level''. For the contribution of oceanic methyl iodide to stratospheric iodine we give three numbers in the Summary and Discussion: ''In the East Pacific region, … the observations and the model indicate that around 0.01 to 0.02 ppt of CH_3I enter the stratosphere. However, other tropical regions, which are subject to stronger convective activity are suggested to have larger CH_3I entrainment, e.g., 0.08 ppt in the West Pacific. … While our current understanding of the CH_3I contribution to stratospheric iodine … our model results suggest an overall tropical contribution of 0.04 ppt.''

In order to make this more clear we have added some text at the end of the introduction ''We present the contribution of oceanic CH_3I to stratospheric iodine in form of the model estimated CH_3I mixing ratios at the cold point.'' Additionally we have added the sentence ''Overall our model results suggest a tropical contribution of 0.04 ppt CH_3I to stratospheric iodine.'' to the abstract.

As suggested by the reviewer we have added information on stratospheric iodine and existing measurements ''Stratospheric iodine exist mostly in the form of free radicals (iodine atoms and iodine monoxide), so that the partitioning of free radicals to total halogen content is much higher for iodine than for chlorine or bromine (Brasseur and Solomon, 2005). Investigations of inorganic iodine species, in the form of iodine monoxide (IO) or iodine dioxide (OIO), in the lower stratosphere reveal only undetectably low amounts give an upper limit of IO of 0.3 ppt based on ground-based measurements (Wennberg et al., 1997) and 0.2 ppt based on solar-occultation balloon-borne measurements (Pundt et al., 1998). Further balloon campaigns, however, detected no IO or OIO in the upper TTL above the detection limit at 0.1 ppt (Bösch et al., 2003; Butz et al., 2009).''

2) It is not correct that 'Investigations of inorganic iodine species, in the form of iodine monoxide (IO) or iodine dioxide (OIO), in the lower stratosphere reveal only undetectably low amounts.' The data by Wennberg et al. (1997) claim detection of IO in the stratosphere. Recent field observations of free tropospheric IO further indicate that these concentrations may actually be lower limits (Dix et al., 2013).

We agree with the reviewer that the study from Wennberg et al. (1997) needs to be cited in the context of stratospheric IO observations. We have changed the text to ''Investigations of inorganic iodine species, in the form of iodine monoxide (IO) or iodine dioxide (OIO), in the lower stratosphere give an upper limit of IO of 0.3 ppt based on ground-based measurements (Wennberg et al., 1997) and 0.2 ppt based on solar-occultation balloon-borne measurements (Pundt et al., 1998). Further balloon campaigns, however, detected no IO or OIO in the upper TTL above the detection limit at 0.1 ppt (Bösch et al., 2003; Butz et al., 2009). As a result the total amount of stratospheric I_y is currently estimated to be below 0.15 ppt (Montzka and Reimann et al., 2011) arising from the detection limit of inorganic iodine (0.1 ppt) given by the latter studies and the iodine supply in form of CH_3I (0.05 ppt).''

3) The authors say 'In order to quantify the contribution of CH3I to the stratospheric Iy budget observations of CH3I and IO with a good global coverage would be necessary. Such observational evidence of global upper air iodine abundances does not exist so far.' There is certainly a need for more observations. In addition to references in comment #2, a missing reference is Puentedura et al. (2012). The increasing experimental evidence suggests consistently that a hemispheric IO background is likely present, and on the order of 0.1-0.4 ppt IO may reside in the global free troposphere. Inorganic iodine is thus likely of similar order of magnitude as the estimates of organic iodine in Fig. 5.

We agree with the reviewer that observations of tropospheric IO have not been discussed sufficiently in the manuscript. Therefore we have added ''In order to quantify the contribution of CH_3I to the stratospheric Iy budget observations of CH_3I and IO with a good global coverage would be necessary. While in the UTLS, such observational evidence of global upper air iodine abundances does not exist so far, recent measurements in the free troposphere over the Canary Islands (Puentedura et al., 2012) and the Pacific Ocean (Dix et al., 2013) report significant amounts of IO of up to 0.4 ppt and suggest that IO occurs in the lower troposphere on a global scale.'' to paragraph 5 of the Introduction.

Later in the manuscript we have added to the discussion of Figure 5 ''Note that in the free troposphere, the CH_3I estimates are of similar order of magnitude as recent observations of inorganic iodine (Puentedura et al., 2012; Dix et al., 2013).''.

4) It is currently unclear whether the primary source of iodine from the ocean to the atmosphere is in organic or inorganic form. Further, heterogeneous recycling on aerosol surfaces may extend the atmospheric lifetime of inorganic iodine beyond that of organic iodine precursors. There is increasing evidence for a source of I2 and HOI from heterogeneous reactions at the ocean surface (Carpenter et al., 2013) and on aerosols (Dix et al., 2013). This information is currently missing in the manuscript.

We have added the text '' If CH_3I is photolyzed before reaching the stratosphere, the generated inorganic iodine can be removed from the atmosphere by wash-out. It has been suggested recently that heterogeneous recycling of inorganic iodine on aerosol surfaces can occur (Dix et al., 2013) which could enable a longer atmospheric lifetime and possibly the direct entrainment of inorganic iodine into the stratosphere.'' to the fourth paragraph of the Introduction.

Additionally, we have added the text ''Note that current studies suggest that organic sources of iodine cannot explain iodine oxide concentrations in the lower troposphere over the tropical oceans (Jones et al., 2010; Mahajan et al., 2010) and that emissions of inorganic iodine following heterogeneous reactions at the ocean surface can account for a primary source of oceanic iodine emissions (Carpenter et al., 2013).'' at the end of the second paragraph of the Introduction.

5) Uncertainties about the lifetime of inorganic iodine, together with the variability of CH3I in upper air pose a major uncertainty in estimating stratospheric Iy. This should be clearly stated.

We agree with the reviewer that this should be stated clearly and have added the sentence ''In addition to the unknown variability of CH_3I in the TTL, uncertainties in the knowledge of the atmospheric lifetime of inorganic iodine (e.g., Dix et al., 2013) possess a major challenge for the quantification of the stratospheric iodine budget.'' at the beginning of the introduction. Furthermore we have added a similar sentence to the Summary and Discussion.

References:

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