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Comment on acp-2021-680

Anonymous Referee #1

Referee comment on "Full latitudinal marine atmospheric measurements of iodine monoxide" by Hisahiro Takashima et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-680-RC1, 2021

Takashima and colleagues present IO and O_3 data from a number of ship cruises in the western Pacific spanning from the Arctic to Antarctic albeit with a gap in the southern tropics to subtropics. The work focuses on two empirical findings high IO observed in the western Pacific warm pool (WPWP) and a negative correlation between IO and O_3 observed at low O_3 mixing ratios. The authors demonstrate that a 0-D chemical box model using the dominant O_3-dependent iodine flux from the ocean surface cannot capture this anti-correlation then posit that O_3-independent pathways (missing global models) are necessary to reproduce the trend.

This latter point is well made, however, as it advocates for a rethinking of the representation of iodine fluxes from the ocean it demands a rather high level of scrutiny. The critical illustration is Fig. 3, in which three box-model cases: 1) only O_3-dependent iodine fluxes, 2) roughly half dependent half independent fluxes, 3) fully independent fluxes are compared with observations of O_3 and IO. While the overall correlation is negative, The Case-1 envelop guides the eye to see that the low O_3 observations appear to cluster as two populations which are displaced along the overall negative correlation but individually have positive correlation. All box model cases show consistent behavior for O_3 above ~13 ppbv, roughly parallel to the overall correlation, only those with an O_3-independent iodine source can reproduce the lowest O_3 mixing ratios. However, without offering specific evidence of the O_3-independent source other explanations bear consideration. I have the following suggestions for the authors to consider:

- Is there any specific evidence to support an O_3-independent source of iodine?
  - What measurements of organic iodine fluxes and concentrations are available in the study area, what are the modeled organic fluxes from e.g. Ordóñez et al., (2012)?
  - For the photooxidation of I^- (Watanabe et al., 2019) is there a difference in solar illumination or some other photo-activity proxy between the different observations?
- Since the points not captured by Case 1 are plausibly only vertically displaced from it, what is the effect of varying the initial O_3 mixing ratio? This could be caused by some upwind loss process or else reflect variable entrainment (Kanaya et al., 2019).
- The subcases already illustrate the effect of varying the magnitude of the iodine flux, and by extension sea-surface I^-, but what about the speciation of the iodine flux (i.e. I_2 vs HOI), would changing this change the correlation? There is likely a pH dependence

to speciation of the O_3-dependent fluxes (e.g. Macdonald et al., (2014); Moreno and Baeza-Romero, (2019)). In addition, since the photooxidation pathway emits I_2 (and not HOI) this could offer insight into that hypothesis also.
- It seems that the authors have not included heterogeneous reactions which recent studies have suggested have been previously underestimated (Tham et al., 2021), could these impact the trend?

Furthermore, it would be helpful if the authors could be more specific in where they expect the posited O_3-independent source to be relevant. Is this a feature of the WPWP or relevant across latitudes? Is it possible that there is a less direct influence O_3 might play? In particular, studies of ice cores and tree rings (Cuevas et al., 2018; Legrand et al., 2018; Zhao et al., 2019) indicate a roughly threefold increase in iodine since c. 1950 at least ~50% attributed to anthropogenic O_3. If half of the inorganic flux were O_3-independent as suggested by Case 2, then either some other cause should be searched for, or the change in O_3-dependent fluxes to produce the observed change is even more dramatic than previously thought.

I have the following specific comments through the manuscript:

Line 160-161: Chlorophyll alone is not enough to exclude an organic iodine source on two counts. Firstly, organic iodine fluxes are not necessarily biotic in origin but might have an abiotic source. Secondly, the mesotrophic conditions characterized by MODIS correspond to those conditions observed to have the largest fluxes of organic iodine in some previous studies e.g. Jones et al., (2010).

Line 167: The authors state that there are insufficient data to document diurnal IO variations accurately, however, Fig. 2 indicates good temporal coverage was achieved for some days and it seems evident that there is wealth of IO data more generally. Is there some particular set of data which are missing or something else limiting the retrieval of diurnal variation?

The authors describe an "iodine fountain" in the WPWP which does appear to exist in Fig. 4, however, as the authors acknowledge Fig. 6 shows no clear correlation between SST and IO. The evidence for attributing the fluxes to SST seems at best mixed. For both the WPWP and the Maritime Continent it is clear that there is a lot of variability. Examining the temperature contours it doesn't seem clear that SST would better explain the pattern than latitude. What distinguishes the "fountain" from being a tropical feature of unknown cause from specifically tying it to SST?

Relatedly, the authors have described a number of differences between the western Pacific and Atlantic, e.g. higher SST, lower O_3. Related to the point above about latitudes, the authors seem to suggest that the "iodine fountain" is a particularity of the WPWP and perhaps maritime continent but not of the Atlantic. But a clearer message on this point would be helpful.

I have the following technical comments through the manuscript:

Line 34: "006C" here is presumably "I"

Line 39: More recent papers on the O_3-dependent iodine source which should be mentioned for offering further consideration of physical and chemical drivers include Inamdar et al., (2020) and Carpenter et al., (2021).

Line 71: Inamdar et al., (2020) or else Mahajan et al., (2019) which includes the underlying measurements bear mentioning as more recent measurements of IO on the

open ocean.

Line 88: Is this exposure time the same for all ELs or is this for a specific EL? If the latter the angle should be specified.

Line 96-101: The version of MMF described in Friedrich et al., (2019) uses Tikhonov regularization rather than optimal estimation for the aerosol retrieval. Was a more recent version used? Could the author provide the version numbers for MMF and VLIDORT?

Line 103-104: These *a priori* values are presumably the column integrals, this is should be more explicit by e.g. specifying the IO VCD

Line 104: While Sa is well understood by an expert audience to be the *a priori* covariance this should be defined for a non-expert audience.

Line 123: "they" here is presumably the fluxes, this is not clear. Line 32: Another recent paper with field evidence for iodine-derived aerosol particles is He et al., (2021)

Line 125: Hayase et al., (2010) and Hayase et al., (2012) predate Shaw and Carpenter, (2013) and show similar effects.

Line 141: Some more information on the O_3 data filtering would be useful, e.g. is the hourly average a running average or discrete average? What is the typical magnitude or relative magnitude of σ?

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