

***Interactive comment on* “Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere” by A. Saiz-Lopez et al.**

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Anonymous Referee #3

RC: Referee comments – AR: Author Replies

RC: Saiz-Lopez et al. present an interesting paper regarding an issue currently gaining attention in the literature, namely halogen-related tropospheric ozone loss. Whilst other global modelling studies, notably von Glasow et al. (2004) and Yang et al. (2005), have included effects of bromine chemistry on the tropospheric ozone column, the main advances of this manuscript are that it includes calculations of the radiative impact of halogen-induced changes in O₃ and also includes iodine chemistry. The paper is well

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structured and generally well-written and offers as far as I'm aware the first estimates of the radiative impact of such chemistry. I think the main weakness of the paper is that the halogen emission schemes used are premature. Further, the manuscript would benefit from uncertainty estimates of some of the calculations, and better comparisons with similar work from other researchers. These points are expanded below.

AR: The referee claims that the main weakness of the manuscript is that the halogen emission schemes used in the model are rather premature. Such sources include very short-lived (VSL) bromocarbons, VSL iodocarbons, molecular iodine (I₂) and halogen release from heterogeneous recycling on sea-salt aerosols. They have been described in the companion paper by Ordoñez et al. (2012) and in the present manuscript.

Since this manuscript illustrates that the largest effect of VSL halogenated sources on the Earth's radiative balance (through their impact on tropospheric ozone) takes place in the free troposphere, the most relevant VSL sources for this analysis are those that can be transported higher up in the troposphere. That is the case of bromoform (CHBr₃), dibromomethane (CH₂Br₂), and methyl iodide (CH₃I). The combined mass emission flux of CHBr₃ and CH₂Br₂ contributes more than 90% to the total VSL bromocarbon flux (Ordóñez et al., 2012). CH₃I is the only iodocarbon considered in the model with a long enough lifetime to be transported to the upper troposphere within deep convection cells (WMO, 2011). Unlike them, the halogen release from sea-salt particles, which are rapidly deposited or scavenged, and the emissions of the very photolabile I₂ are only relevant within the marine boundary layer (MBL). Ordóñez et al. (2012) presents a detailed evaluation of vertical profiles for CHBr₃, CH₂Br₂, and CH₃I; overall the simulated mixing ratios of these species are within the range of variability of aircraft observations throughout most of the tropospheric profile. That paper also assesses the model's performance for other less abundant VSL bromocarbons (CH₂BrCl, CHBr₂Cl, CHBrCl₂) and three shorter lived iodocarbons (CH₂IX, with X = Cl, Br, I). In the new version of the manuscript we indicate that Ordóñez et al. (2012) discusses the limitations of our emission approach. It is worthwhile to mention that

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CAM-Chem does not overestimate the observations of IO and BrO (see comparison with observations from a variety of platforms, Figure 2). This gives some confidence that the effect of halogen chemistry on tropospheric ozone will not be overrated in the model.

As indicated below, we have included comparisons with similar work made by von Glasow et al. (2004) and Yang et al. (2005), who estimated the effect of bromine sources on tropospheric ozone at the global scale. The reviewer also suggests including uncertainty estimates in the calculation of halogen-driven ozone loss as well as comparing the individual effects of the different VSL halogenated sources. Some of those issues have already been addressed by the mentioned analyses (von Glasow et al., 2004; Yang et al., 2005), which used offline Chemistry Transport Models (CTMs) at a coarser horizontal resolution and somewhat simpler mechanisms than those used here. At present time we are conducting model simulations to quantify the relative contribution of the different halogenated sources (bromocarbons, iodocarbons and heterogeneous recycling of halogens) on tropospheric ozone loss and estimate the associated uncertainties within our model. 1-dimensional modelling studies will also be very beneficial for some of those analyses. However those issues are out of the scope of this manuscript and will be the object of future publications. The main objective of this manuscript is to evaluate the overall effect halogens on tropical tropospheric ozone, including iodine sources for the first time, and to estimate the resulting impact on the Earth's radiation balance.

Detailed replies to the referee's comments are shown below.

RC1: Where is the evidence that sea-air emission of all VSL halocarbons depends on the actinic flux? Emissions of the most important VSL iodocarbons are likely to follow the opposite diurnal variation to that assumed since they will be photolysed within the surface water column. In the case of bromine species, model results indicate that bromoform emissions exhibit a minimum in summer and a maximum in early winter due to changes in the depth of the ocean mixed layer (Hense and Quack, 2008).

AR1: There are no clear evidences of a direct or an inverse proportionality of VSL halocarbon emissions to the actinic flux. While the hypothesis of the reviewer (i.e. decrease of bromoform surface water concentration at daytime as a consequence of photochemical loss) is very plausible, other studies (e.g. Reeser et al., 2009) suggest that at least some organohalides could arise from photochemical processes in salt-water solutions containing chlorophyll. Some discussion on this is included now in the corresponding part of Section 2.

The shape of the diurnal emission profiles used here was adopted as a part of the top-down approach used in Ordóñez et al. (2012) to estimate sea-to-air fluxes of VSL halocarbons. This was done to reproduce diurnal cycles reported in the literature for near-surface IO and BrO (e.g. Read et al., 2008). Note that the diurnal profile of emissions is not very important for the VSL bromocarbons due to their relatively long atmospheric lifetimes (ranging from weeks for CHBr₃ to months for other bromocarbons). That shape is much more relevant for the shorter lived iodocarbons such as CH₂I₂, as seen from the sensitivity simulation on the diurnal cycle of emissions presented in Ordóñez et al. (2012). As indicated above, we now refer to that paper for a detailed discussion of the limitations of the emission approach used here.

As pointed out by the reviewer, simulations with a coupled physical-biogeochemical water column model for the tropical Eastern Pacific Ocean reveal a pronounced seasonal cycle of bromoform outgassing to the atmosphere with a minimum in summer and a maximum in early winter (Hense and Quack, 2009). Although CHBr₃ will be photolysed within the surface water column, the seasonal behaviour found by them is mainly controlled by seasonal changes in wind speed and mixed layer depth. Note that the atmospheric concentration of CHBr₃ is set constant in that study whereas the authors recognise that the use of a seasonally varying field would probably lead to a seasonal emission cycle of smaller amplitude. The CHBr₃ emission field used in our simulations was derived with a top-down approach that used a climatology of satellite-derived chlorophyll-a (chl-a) over the tropical oceans and atmospheric observations of

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bromoform (Ordóñez et al., 2012). The geographical distribution of our bromocarbon fluxes follows that of chl-a over the tropical oceans, while their magnitudes have been determined to match observations of these species from airborne campaigns. Our CHBr₃ emission field follows a similar seasonal cycle for the same location of Hense and Quack (2009), although with a smaller amplitude that resembles more closely the surface concentration rather than the air-sea-flux of bromoform estimated by that study. We do not add these comments to the main text, because the discussion on the seasonality of VSL halocarbon emissions is out of the scope of this manuscript.

RC2: The paper states that the majority of iodine emissions are assumed to be in the form of I₂ (since previous studies shows that VSL iodocarbons are not sufficient to produce measured IO levels), yet the authors apparently have no information on the magnitude, spatial and temporal distribution of such emissions – the number used is simply an inferred flux of I₂ at one location (Cape Verde). In addition, if the main carrier of iodine was not I₂ (and with no field information on this than at present it does not appear possible to conclude either way), then the results/vertical variation of IO could be quite different.

AR2: We agree with the reviewer that there is very little information on the magnitude as well as on the spatial and temporal distribution of I₂ emissions. As we mention in the corresponding paragraph of Section 2, there are even indications of non-biological sources of I₂ from the oceans that we are not considering. For simplicity, we have adopted a parameterisation of I₂ emissions equivalent to that of iodocarbons, with a time and space varying flux that on average over the tropical oceans matches that estimated by Mahajan et al. (2010) for the location of Cape Verde. This simple parameterisation together with the top-down approach used for VSL halocarbons and the release of halogens from sea-salt aerosols yield atmospheric mixing ratios of the two main reactive iodine and bromine species (i.e. IO and BrO) that are in reasonably good agreement with observations from a variety of platforms (see our Figure 2). As mentioned in our reply to the previous comment, the diurnal evolution of these two species

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also looks reasonable in the model.

Finally, the lifetime of I2 is too short to be transported to the mid-upper troposphere. As a consequence, the model results in the region for which we find the largest effect of VSL halogenated sources on the Earth's radiative balance are not very sensitive to the magnitude or distribution of the I2 flux. This was already indicated in the ACPD version of the manuscript.

RC 3: Does the model include sea spray sources of BrO? There appears to be no description of this. Since sea spray is the dominant source of BrO in the MBL, it is surprising that the authors can reproduce O3 loss at Cape Verde without including a proper treatment. This in turn brings into question the results in the upper troposphere.

AR3: Please see our reply to the main scientific question addressed by referee #1.

RC4: The authors should make clear whether the modeled ozone loss includes the indirect effect of decreased NOx levels (which should be more pronounced near coastlines downwind of major NOx sources).

AR4: As mentioned in Section 2 of the manuscript, the version of CAM-Chem we use includes a detailed representation of Ox-NOx-HOx-VOC tropospheric chemistry that has been previously evaluated by Emmons et al. (2010). Ordóñez et al (2012) documents the extension of that chemistry scheme to incorporate VSL halogenated sources from the ocean, their photochemical breakdown and reactive halogen chemistry.

In Section 2 of the manuscript we also indicate that we show results from two simulations with and with no VSL halogen sources, while the rest of the tropospheric chemistry scheme is based on that of Emmons et al. (2010) for both of them. The surface ozone loss and the ozone column loss represented in Figures 5 and 7, respectively, have been calculated from the difference between these CAM-Chem simulations. As a consequence, the ozone loss represented in Figure 7, on which the main message of the paper builds, is only due to the inclusion of VSL halogen sources in the model

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although their effect is not decoupled from HO_x and NO_x cycles. In the last section of the manuscript (Concluding remarks) we already highlight that since bromine and iodine chemistry is coupled with HO_x and NO_x chemistry, halogens may alter ozone concentrations in a different way under changing NO_x regimes.

RC5: Pg 32012. It would be worthwhile to compare the individual effects of (a) the VSL bromocarbons, (b) the VSL iodocarbons and (c) the sea spray bromine sources (if included) on column O₃, since each of these sources may change in different ways with environmental change.

AR5: Performing such an analysis would require running long model simulations with different configurations where only some sources are active while others are switched off. At present time we have started to perform CAM-Chem simulations with only bromine or iodine sources to separately quantify the impact of bromine and iodine on tropospheric ozone as well as to evaluate the single effect of halogen catalytic release from sea-salt. However, as indicated at the end of our reply to the general comments by the reviewer, we consider that this is out of the scope of the manuscript.

RC6: Pg 32012. If VSL bromocarbons dominate the column O₃ loss then the results of this study should presumably be similar to those of von Glasow et al. (2004) and Yang et al. (2005). There is little discussion of these papers other than in the introduction, but direct comparisons of the results regarding bromine-induced ozone change should be made.

AR6: We agree with the reviewer that such comparisons were missing in the original manuscript. The overall impact of halogen chemistry on tropical tropospheric ozone as simulated by CAM-Chem has now been compared to results from global modelling analyses by von Glasow et al. (2004) and Yang et al. (2005). They respectively used the CTMs MATCH-MPIC and p-TOMPCAT, with horizontal grids considerably coarser than that of CAM-Chem.

Given the limited knowledge of the sources for tropospheric inorganic bromine at that

time, von Glasow et al. (2004) tested different hypothetical source scenarios to reflect various source types/regions. For their scenario “tropics” they used a generic organic bromine compound (with fixed mixing ratio of 30 ppt Br) that was broken down into Br by reaction with OH. In that scenario they also considered heterogeneous recycling of bromine on aerosols but did not explicitly treat the release of bromine from sea-salt aerosol. They computed a zonally and annually averaged tropical tropospheric ozone loss due to bromine chemistry of 12–18%.

Yang et al. (2005) considered the effect of bromine gas phase chemistry and heterogeneous recycling of bromine on sea-salt aerosols. That analysis included VSL bromocarbon sources from Warwick et al. (2006), which should be much closer to ours than the generic organic bromine source used by von Glasow et al. (2004), and two different sea-salt formulations. They found an ozone reduction due to bromine chemistry of 4–6% throughout most of the tropical troposphere. A maximum loss of around 8% was found for the southern tropics.

Summarising, the tropical tropospheric ozone loss due to bromine chemistry calculated by von Glasow et al. (2004) and Yang et al. (2005) is of around 12–18 % and 4–8%, respectively. The tropical tropospheric ozone loss due to bromine and iodine chemistry in CAM-Chem is of around 6–20%, considerably larger than that calculated by Yang et al. (2005) and closer than the values given by von Glasow et al. (2004). This information, together with a detailed discussion on the differences in the ozone loss for these analyses, has been included in Section 3.3.

RC7: Finally – both the column ozone loss and the change in radiative flux need uncertainty estimates.

AR7: This reply is divided into two parts:

a) Column ozone loss.

To calculate uncertainties in the column ozone loss we would need to switch off some

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emission sources or processes, evaluate different formulations for some reaction rates, etc. This would be computationally very expensive for a global chemistry-climate-model like CAM-Chem. As indicated above, this is also out of the scope of this manuscript. We are planning some sensitivity simulations like those indicated in our reply AR5 as well other simulations where some processes involving reactive halogen species are improved or switched off. That will be the main object of another publication.

b) Change in the radiative flux.

For the determination of uncertainty estimates it would be necessary to perform a multi-model analysis. Results from previous comparisons for a number of models calculating the radiative forcing (RF) due to tropospheric ozone changes are reported here. The IPCC-TAR (Ramaswamy et al., 2001) reported annual average RFs per tropospheric ozone column changes (referred hereafter as normalised radiative forcing, NRF) since pre-industrial times. For clear sky conditions, their NRFs range from 0.041 to 0.057 W m⁻² DU⁻¹, with a mean value of 0.049 W m⁻² DU⁻¹. For total sky conditions, their NRFs are between 0.033 and 0.056 W m⁻² DU⁻¹, with a mean value of 0.042 W m⁻² DU⁻¹. In another multi-model analysis organised within ACCENT (Atmospheric Composition Change: the European NeTwork of excellence), a single radiative transfer model was applied to 11 sets of modelled tropospheric ozone changes in the 21st century (Gauss et al., 2003). The resulting annually and globally average net NRF was between 0.032 and 0.040 W m⁻² DU⁻¹, significantly narrower than the range reported in IPCC-TAR.

Note that CAM-Chem is the only climate-chemistry model with bromine and iodine sources. This is the first time that a global model has been used to compute the combined effect of bromine and iodine chemistry on tropospheric ozone and on the Earth's radiative balance (by only taking into account effects on tropospheric ozone over the tropics). As a consequence, at present time it does not look realistic to use a multi-model approach like those presented above for our analysis. What we did instead in the ACPD version of the manuscript is to verify that if the tropical tropospheric ozone

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change we calculate (-2.5 DU) is scaled by the NRF given by the IPCC-TAR for total sky conditions ($0.042 \text{ W m}^{-2} \text{ DU}^{-1}$) then the change in the radiation flux will be of around -0.105 W m^{-2} , very similar to that calculated in our study (-0.103 W m^{-2} , see net flux for all-sky in Table 1). This indicates that our radiative flux calculations do not deviate from those in previous analyses. A NRF estimated from our analysis would be very similar to the mean of the IPCC-TAR models but larger than the mean value given by the ACCENT models for total sky conditions. However, we are examining changes in the tropics, where the same models tend to show the highest sensitivities (Gauss et al., 2003). For simplicity, we do not include the reference Gauss et al. (2003) in the manuscript and only keep the comparison with the IPCC-TAR models.

RC: Minor issues/typos Pg 32010. The following sentence needs breaking up to make it clearer: “For two longer lived bromocarbons, CH_3Br and CH_2Br_2 – total lifetime (considering not only photochemical loss in the atmosphere but also uptake to oceans and soil) of $\hat{\text{a}}/\text{Lij}0.8 \text{ yr}$ and local lifetime of $\hat{\text{a}}/\text{Lij}123 \text{ days}$, respectively (WMO, 2011) –, that additionally contribute to the tropospheric halogen burden, the average modelled profiles throughout the tropical troposphere are also comparable to the observations (Fig. 1).”

AR: The referee is right. We have split that long sentence.

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