

Reply by the authors to the Referee #1's comments on

“Revising global ozone dry deposition estimates based on a new mechanistic parameterisation for air-sea exchange and the multi-year MACC composition reanalysis” (#acp-2017-768)

Anonymous Referee #1 (RC1)

We are grateful to the Referee for his/her comments. In the following, we provide our responses to these comments.

(1) Comment: This paper proposes some updates to the paper the authors published earlier this year (10.5194/acp-17-3749-2017) describing the deposition of ozone to the ocean. Some changes are made to the parameterization and the resulting deposition velocities are used to explore the impacts on the global budget of ozone on the ACCESS-UK model. They have concerns about the veracity of their atmospheric chemistry model so explore the impact of the new deposition velocities with the MACC reanalysis. They conclude that their new parameterization has some skill in representing the rather sparse observational dataset and that with this new parameterization for deposition velocities, the mass of ozone deposited to the ocean is significantly reduced with implications for both the budget and distribution of ozone.

I have concerns that this paper represents a small incremental advance over the previously published paper. For example, Figure 5 only shows small difference between the new and old schemes which was published only a few months ago. Ideally this paper would have been coupled into the paper published only a few months ago. However, this is a decision to be made by the editor.

Response: The work conducted about a year ago by the authors that the Referee is referring to and that was published in November 2016 in ACPD and then in March 2017 in ACP (<https://doi.org/10.5194/acp-17-3749-2017>), provided the subsequent impetus and ideas to extend that work, resulting in the present work. The present work is novel in two important ways: First, it derives a new formula for the waterside ozone deposition velocity (Eq. 16) which corrects a basic flaw in the two-layer scheme reported in the previous paper by including chemical reactivity throughout the oceanic mixing layer (as is observed for dissolved iodide) rather than just within the reaction-diffusion sublayer a few microns thick. The new model will also apply to any other chemical compounds that are taken up by the oceanic mixing layer. Second, our work makes use of the European MACC ozone reanalyses for ten years to constraint the ozone dry deposition fluxes better and to provide a measure of interannual variability.

One could indeed say that the present paper represents an incremental advance (as is the case with much of the scientific research, if not most), and in our opinion this advance is significant.

We emphasise in the paper at a few places (e.g. see the 1st para on Page 16 and Figure 5) and the Referee also notes, that there is only a small difference between the new and old two-layer schemes in terms of performance in simulating oceanic deposition velocity data. However, the difference between the two, if you like, is that unlike the old scheme the new scheme performs well for the right reasons (the old scheme artificially limits chemical reactivity to the reaction-diffusion sublayer to compensate for the overestimation of the impact of waterside turbulence). The present work also demonstrates the importance of chemistry-turbulence interactions and how they differ in the new and old deposition schemes.

Changes in manuscript: We clarify the differences between the old and new two-layer schemes along the lines of the response given above.

(2) Comment: *Fundamentally this paper provides a description of an improved O₃ deposition parameterization for the oceans, shows that there is some fit between the observations reasonably well and fundamentally changes the tropospheric budget for ozone especially over oceanic regions. These are important conclusions.*

I have a few questions and queries to suggest for the improvement and shortening of the paper which I make below. Assuming that these can be made I would recommend publication.

Response: Thanks for the comment.

Changes in manuscript: None.

(3) Comment: *Major comments.*

Ocean O₃ lifetime.

The premise of the paper is that reaction between O₃ and I⁻ is the only sink for O₃ in the ocean. There is no discussion of the validity of this assumption. There is significant evidence that dissolved organic matter (DOM) may play a significant role in deposition of ozone to the surface (see for example 10.1029/2008GB003301). Yet this isn't discussed in the text. There should be some justification given for ignoring the role of DOM in their calculations.

Response: The open-ocean ozone deposition velocity data of Helmig et al. (2012) we have used for model testing are limited in sample size and contain substantial fluctuations. However, they are the best available and only ones that have used a surface based eddy-covariance approach which provides a direct way of measuring deposition velocity. The present work demonstrates that the chemical reaction of O₃ with dissolved iodide is able to adequately describe these deposition velocity data within the observed scatter and uncertainty in the input parameterisations (e.g. the second-order reaction rate constant k). We have done additional work on dissolved organic matter (DOM) and it is reported below.

Changes in manuscript: With regards to DOM (or DOC, dissolved organic carbon), we include the following in the paper. This also addresses a comment made by Referee #2.

Reaction with dissolved organic carbon (DOC)

Some studies have considered the impact on ozone dry deposition of ozone reaction with dissolved compounds other than iodide. Chang et al. (2004) included reactions of ozone with iodide, dimethyl sulfide (DMS), ethene and propene and showed that the reaction with iodide was by far the fastest in most cases. In their global modelling, Ganzeveld et al. (2009) included ozone reaction with chlorophyll-a as a first order approximation to examine the possible role of dissolved organic matter (DOM), and found that this reaction significantly increased dry deposition velocities at coastal sites (with mixed results compared to observations) and yielded only small changes to deposition velocity for open ocean sites. Sarwar et al. (2016) included ozone reactions with iodide, dissolved organic carbon (DOC) (equivalent of DOM), DMS and bromide in their ozone modelling for summer months in the Northern Hemisphere, and found that the impact of DOC on the simulated deposition velocity was comparable to that of iodide, with the other reactions contributing much less. Coleman et al. (2010) showed that in addition to iodide the inclusion of DOC in their empirical scheme described daytime deposition observations better in coastal waters of North Atlantic. We are not aware of any previous study that has compared modelled deposition velocities involving the impact of the O₃-DOC reaction with the Helmig et al. (2012) data and their sea surface temperature (SST) dependence.

The work presented in our paper shows that the inclusion of only the iodide-O₃ reaction yields a satisfactory agreement of the modelled deposition velocities with the open-ocean observations of Helmig et al. (2012) within the uncertainty of the data and input parameterisations. Inclusion of additional reactions in the model would enhance the ozone loss to the ocean and thus increase deposition velocities. It is instructive, however, to carry out a simple sensitivity analysis involving ozone reaction with dissolved DOC.

For open ocean surface waters, Hansell et al. (2009) report DOC concentration values of 70–80 μM (M = molar or mole per litre) in tropical and subtropical regions (40°N to 40°S), ~ 40–50 μM in subpolar seas and in the circumpolar Southern Ocean (> 50°S), and about 70 μM in the Arctic Ocean (> 70°N). Based on Hansell et al. (2009), Sarwar et al. (2016) used a mean DOC concentration of 67 μM over the Northern Hemisphere. A recent analysis by Massicotte et al. (2017) gives an average DOC value of 52 μM for oceans.

There are no definitive, directly measured values available for the second-order rate coefficient (k) for the aqueous DOC-O₃ reaction. Coleman et al. (2010) empirically derived $k = 3.44 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ based on data fitting, whereas Sarwar et al. (2016) used $k = 4.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ noting that this value together with their selected DOC concentration yields a first order rate constant of ~ 268 s⁻¹ that lies between the two values 100 s⁻¹ (open-ocean) and 500 s⁻¹ (coastal waters) used by Carpenter et al. (2013) based on the modelling by Ganzeveld et al. (2009).

Clearly there is considerable uncertainty in the oceanic DOC concentration and its spatial and temporal variability, and in the corresponding second-order rate coefficient and its dependencies. For our purposes, we use a mean $k = 3.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (which lies in the middle of the above two values) and a DOC concentration of 52 μM (Massicotte et al., 2017) in our two-layer scheme, together with an integrated chemical loss rate $a = \sum_i k_i C_i$, where the summation is over the iodide and DOC reactions with ozone ($i = 1, 2$).

The attached Figure 1 shows the variation of αv_{dw} ($=1/r_c$) (where α is ozone solubility, v_{dw} is the waterside dry deposition velocity and r_c is the surface resistance) as a function of SST determined using our two-layer deposition scheme incorporating the ozone reaction with: only iodide (this curve is the same as Option 4 in Figure 3 of our paper, with the reaction-diffusion layer thickness $\delta_m = 3 \text{ μm}$), only DOC, and the two reactions together for three values of δ_m . Compared to the iodide-only curve, the inclusion of DOC leads to a progressive increase in αv_{dw} as SST decreases for all values of δ_m . As δ_m increases αv_{dw} decreases, but increasing δ_m beyond 6 μm has virtually no impact on αv_{dw} (not shown). When only DOC is considered, αv_{dw} decreases with SST.

Given that the r_c term dominates in the determination of v_d , the behaviour of αv_{dw} represents that of v_d (as is evident from Figures 3 and 4 in the paper). This suggests that the inclusion of DOC in the deposition scheme would worsen the model-data agreement shown in Figure 4, particularly for cooler water temperatures. Lowering the DOC concentration in the model to the lowest levels (~ 40 μM) reported by Hansell et al. (2009) does not improve the agreement either. A second-order rate coefficient for the DOC-O₃ reaction that decreases with SST (like that for the iodide-O₃ reaction) could explain the deposition velocity data better but any such observations are lacking at present. Clearly, more comprehensive observations of deposition velocity, its dependencies, and relevant input parameters for deposition calculations are needed to further constrain the waterside processes of ozone deposition.

In summary, there are considerable uncertainties concerning the oceanic DOC concentration and no directly measured values of the second-order rate coefficient (k) for the aqueous DOC-O₃ reaction.

Given the agreement of the existing soundly based iodide mechanism with the available uptake measurements for the open ocean, the inclusion of DOC in the open ocean ozone deposition is not undertaken. We note that for coastal waters, not investigated here, the case is probably different. The way coastal grid cells are treated in our global modelling is detailed in our Response #7 to Referee #2.

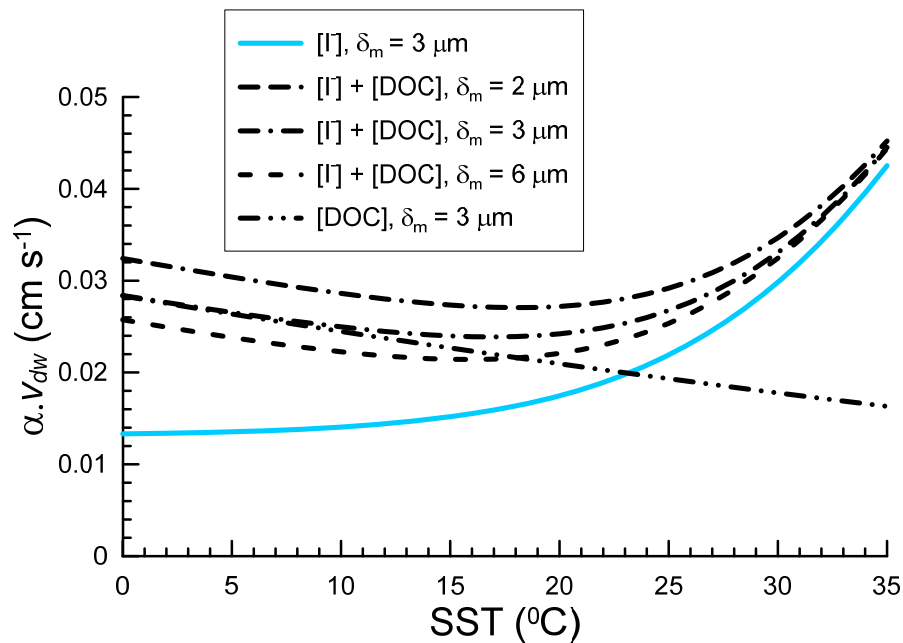


Figure 1: Variation of the oceanic component of ozone dry deposition velocity multiplied by ozone solubility, αv_{dw} ($= 1/r_c$), as a function of sea surface temperature. Curves determined using the present two-layer deposition scheme incorporating the ozone reaction with iodide [I], dissolved organic carbon [DOC], and the two reactions together ([I] + [DOC]). The waterside friction velocity (u_{*w}) used was 0.01 m s^{-1} .

References

- Carpenter, L.J., MacDonald, S.M., Shaw, M.D., Kumar, R., Saunders, R.W., Parthipan, R., Wilson, J., Plane, J.M.C.: Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine. *Nat. Geosci.* 6, 108–111. <http://dx.doi.org/10.1038/ngeo1687>, 2013.
- Coleman, L., Varghese, S., Tripathi, O. P., Jennings, S. G., O'Dowd, C. D.: Regional-scale ozone deposition to North-East Atlantic waters. *Advances in Meteorology*, 2010, 16 pages, <http://dx.doi.org/10.1155/2010/243701>, 2010.
- Ganzeveld et al. (2009). As referred to in the paper.
- Hansell, D.A., Carlson, C.A., Repeta, D.J., Schlitzer, R.: Dissolved organic matter in the ocean. *Oceanography* 22, 202–211, 2009.
- Massicotte, P., Asmala, E., Stedmon, C., Markager, S.: Global distribution of dissolved organic matter along the aquatic continuum: Across rivers, lakes and oceans, *Science of the Total Environment* 609, 180–191, <http://dx.doi.org/10.1016/j.scitotenv.2017.07.076>, 2017.
- Sarwar, G., Kang, D., Foley, K., Schwede, D., Gantt, B., Mathur, R.: Technical note: Examining ozone deposition over seawater. *Atmos. Environ.* 141, 255–262, <http://dx.doi.org/10.1016/j.atmosenv.2016.06.072>, 2016.

(4) Comment: *The parameterization appears to do a reasonable job of simulating the deposition observation (Figure 4) without the need for an additional ocean side O₃ sink. However there has been a tuning of the model (top half of page 12) so it isn't obvious that a missing O₃ sink process (such as that offered by DOM) would be 'diagnosed' though a model to measurement comparison. Figure 4 looks very similar to a figure shown in the author's previous paper. It would be useful to show this data in an x-y plot and give some indication of the error associated with the parameterization against the observations.*

Response and changes in manuscript: As mentioned in our response on DOM above, the data available and used for model testing are not detailed enough to clearly discern or diagnose the potential impact of other reactions, let alone provide guidance on parameter values (e.g. reaction rate constant). Obviously, given such limitation there is some parameter value fitting, but this is informed by parameter bounds, for example the reaction-diffusion length scale, the asymptotes and the scatter in the iodide-O₃ reaction rate constant, and the deposition velocity data.

As suggested by the Referee, we will include the attached Figure 2 showing an x-y plot of the modelled vs. observed deposition velocities. It presents the observed deposition velocities averaged over the data from each of the five cruise experiments versus the corresponding average values obtained from the model (with the error bars representing one standard deviation variation).

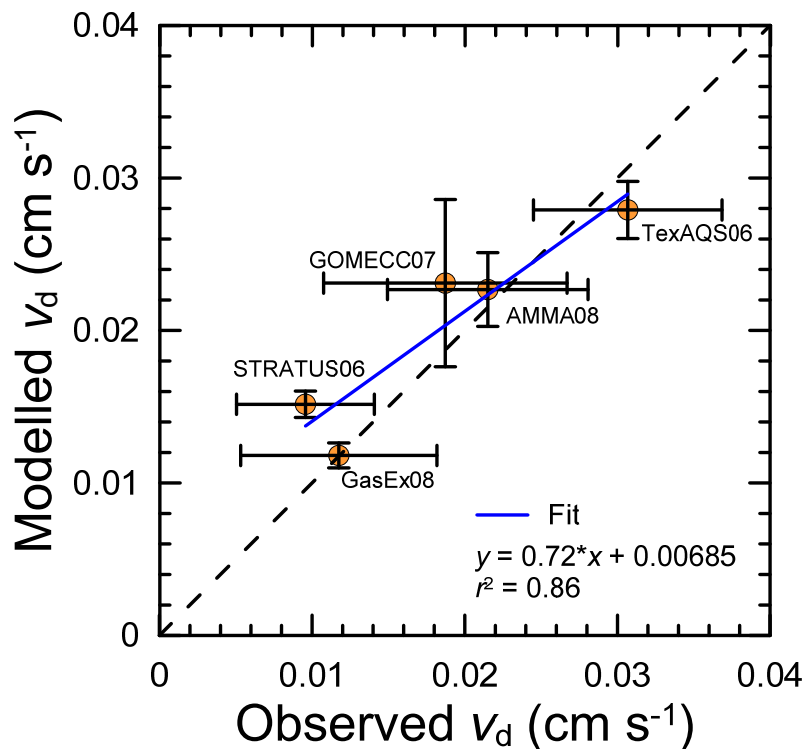


Figure 2: Scatter plot of the ozone dry deposition velocities (v_d) obtained from the five cruise experiments versus the corresponding values obtained from the ACCESS-UKCA model using the new two-layer scheme (Eq. 16). Each point corresponds to the average over all values from one experiment. The error bars represent one standard deviation variation. Horizontal error bars are for the observed values and the vertical ones are for the modelled values.

(5) Comment: *Our current understanding of DOM, its reactivity to O₃ and distribution is poor. However, the authors should discuss the implications of them ignoring the potential DOM sink. Whilst they are doing that they should also discuss the implication of their choice of iodide distribution. They are using the distribution based on the parameterization of McDonald, but the literature also includes the Chance parameterization which gives higher I⁻ concentrations and I think gives a slightly different spread. What are the implications of this?*

There should be more of a discussion of the uncertainties of the O₃ lifetime in the ocean, and how the parameterization tuning to the observations provides some solid ground to base the subsequent budget analysis. What impact do these uncertainties have on the budget?

Response: As demonstrated in our response above on DOM, we agree with the Referee that our current understanding of DOM is poor.

A sensitivity analysis involving the iodide parameterisation by Chance et al. (2014) was reported by Luhar et al. (2017, <https://doi.org/10.5194/acp-17-3749-2017>) (see their Figure 5) and it was compared with the behaviour obtained by the MacDonald et al. (2014) iodide parameterisation. The Chance et al. (2014) iodide parameterisation gives larger iodide concentrations than the latter.

The attached Figure 3 is the same as Figure 3 in our present paper except that we have included an additional curve as Option 6 which is the same as Option 4 (the latter option is used in our deposition flux calculations) but using the iodide concentration parameterisation of Chance et al. (2014) $[I^-](nM) = 0.225(SST - 273.16)^2 + 19$. Compared to Option 4, Option 6 results in larger αv_{dw} ($=1/r_c$) values and the relative difference between the two increases with SST; for example, for SSTs 5, 20 and 30°C, the Option 6 value is larger by 13, 29, 33%, respectively. Consequently, Option 6 overestimates the observed ozone deposition velocity data of Helmig et al. (2012) presented in Figure 4 of the paper, almost passing along the upper limits of the observed fluctuations in v_d . However, if Option 6 is used along with the second-order rate constant (k) without considering the data point of Hu et al. (1995) as in Option 3 (which gives lower k values), then the values of deposition velocity obtained by Option 6 with the Chance et al. (2014) parameterisation are comparable to those by Option 4 that we have used.

What the above analysis suggests is that the deposition velocity data can also be described by the Chance et al. (2014) iodide parameterisation coupled with smaller values of k (because it is the reactivity a , which is the product of the iodide concentration and second-order rate constant, that goes into the deposition velocity calculation) within the uncertainty of the deposition velocity data and second-order rate constant data.

Here we are guided and limited by the scant amount of deposition velocity observations that we have. Our deposition velocity scheme is developed based on sound arguments and with the selected parameters provides a good comparison with the data. However, as we have seen above, there is uncertainty in parameter values which would eventually be reflected in the deposition flux estimates. We have done additional work to estimate uncertainty in deposition flux taking into account the scatter in the ocean deposition velocity data, and this is described in our response to Comment #5 made by Referee #2.

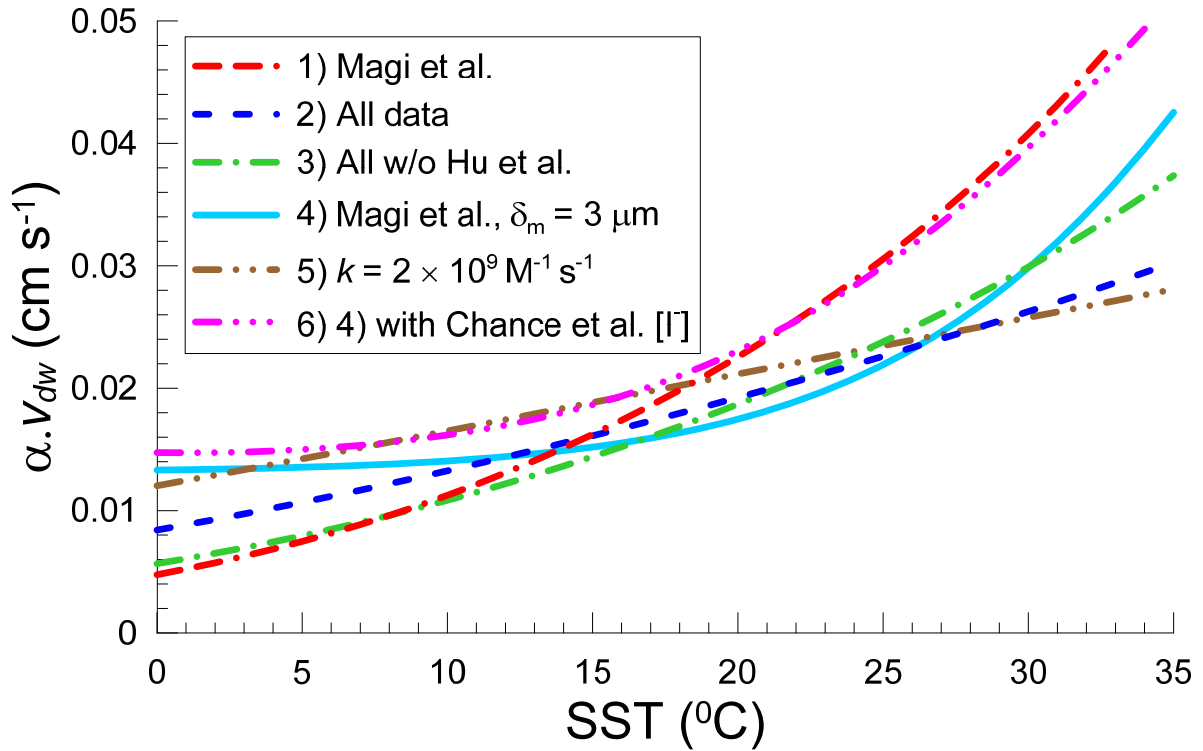


Figure 3: Variation of the oceanic component of ozone dry deposition velocity multiplied by ozone solubility, αV_{dw} ($= 1/r_c$), as a function of sea surface temperature (SST, $^\circ\text{C}$). Curves determined using the two-layer deposition scheme (Eq. 16) for various options for parameterising the second-order rate coefficient (k) (see text). The waterside friction velocity (u_{*w}) used was 0.01 m s^{-1} .

Changes in manuscript: We will include the bulk of the above discussion in the paper. The additional work on uncertainty in deposition flux which is described in our response to Comment #5 made by Referee #2 will also be included.

(6) Comment: Diagnosing the ozone deposition flux

The new parameterization is put into the ACCESS-UKCA model and this gives a global flux of O₃ deposition to the ocean of ~ 86 Tg yr⁻¹. The model is known to have a low bias for O₃ and so a significant body of work is done to calculate the flux from the MACC analysis fields of O₃ and then a bias corrected MACC analysis fields. This lengthens the paper significantly for almost no gain. The canonical value for ocean deposition of O₃ is around the 340 Tg yr⁻¹ from the Hardacre study. The new parameterization gives the ACCESS model a deposition of 86 Tg yr⁻¹, the MACC Analysis 93 Tg yr⁻¹ and the bias corrected MACC Analysis 98.4 Tg yr⁻¹. Compared to the Hardacre values these numbers are essentially the same (25%, 27% and 28%) respectively especially when the uncertainty in the parameterization are considered. There are pages of text describing the MACC data but I don't think it substantially changes the conclusions especially as the authors are forced to bias correct the MACC data. Would it not make more sense to bias correct the ACCESS data?

My suggestion is to remove this section or to perform the bias correction on the ACCESS data. It doesn't add anything to the story but it makes the document substantially longer.

Response: The multi-year global MACC reanalyses are high-resolution, quality controlled data on atmospheric composition that are a valuable tool in developing and evaluating modelling schemes. They have not previously been used for deposition purposes. Their application in the second half of the paper together with the modelled deposition velocity distribution is an important component of

our work and is aimed at further reducing the uncertainty by constraining the ozone dry deposition budgets better.

From the point of view of ozone deposition to the ocean, the Referee is correct in saying that the deposition figures obtained using ACCESS, and the MACC analysis with and without the bias correction, are very similar (i.e. 86.1, 93.9 and 98.4 Tg yr⁻¹, respectively). However, when the total global deposition loss is calculated (including ocean, land and ice), the respective figures are 566.7, 689.9 and 722.8 Tg yr⁻¹ (see the top para on Page 18 and Table 1). Thus the underestimation of ozone by ACCESS is reflected more prominently in the deposition to non-ocean surfaces. We have used the MACC data to derive both oceanic and global deposition estimates, and we do think that these data have been usefully employed in the paper to constrain the oceanic and non-oceanic deposition losses of ozone.

Note that our modelled deposition velocity distribution that is multiplied with the MACC ozone data to calculate deposition flux does not depend on the chemistry component of the model. Deposition velocity is solely a function of parameters of the physical component of the model (e.g., SST (for iodide concentration), flow properties and turbulent mixing, and surface characteristics) and prescribed parameters (e.g., ozone molecular diffusivity and solubility).

ACCESS is based on the global UM-UKCA modelling system developed by a UK consortium (including the Met Office and Cambridge University) and we are dependent on them with regards to major model changes and upgrades. The UM-UKCA (v8.4) that we have implemented on our computer system generally underestimates tropospheric ozone. We hope have a better version in the future that would have a less bias. However, as mentioned above the ozone deposition velocity as determined in the model does not depend on the chemistry component of the model so its performance for ozone is not relevant here.

We are not sure what the Referee means by bias correcting the ACCESS data. If it means having a model that is almost bias free, then we do not think such a model is available as yet. If it means using ozone observations to bias fix ACCESS, then wouldn't this, in principle, be akin to using the MACC reanalyses which are basically bias corrected (or data assimilated) model estimates?

Changes in manuscript: In light of the above response, we do not agree with the Referee to remove the MACC data analysis. However, we will include some of the above points as clarification. In addition, since we do not use the ACCESS derived ozone flux anyway, and instead use the ACCESS derived deposition velocity coupled with the MACC ozone for the ozone flux calculation, we will delete relevant parts detailing the chemical component of ACCESS and also delete the ACCESS derived deposition flux estimates.

(7) Comment: *Minor Comment.*

There should be more details on the performance of the ACCESS physical model. There are no details of performance, parameterization choices etc. There should be more details given. What aspects of the model impact the parameterization used?

Response: ACCESS-UKCA uses the same physical atmosphere component as the UK Met Office's Unified Model (UM) and includes the UK Chemistry and Aerosol (UKCA) model for atmospheric composition (at UM v8.4). In our simulations, ACCESS-UKCA is basically the same as UM-UKCA since the ACCESS specific ocean and land-surface components are not invoked. This is because we run the model in atmosphere-only mode with prescribed SSTs, and the UM's original land-surface scheme (JULES) is used.

For UKCA, we cite <http://www.ukca.ac.uk>, Morgenstern et al. (2009), Abraham et al. (2012), O'Connor (2014) and Woodhouse et al. (2015). The reference Abraham et al. (2012) is available at

http://www.ukca.ac.uk/images/b/b1/Umdp_084-umdp84.pdf which includes some detail of the dry deposition scheme (which is based on Wesely (1989)).

For ACCESS, a reference by Bi et al. (2013; <http://www.bom.gov.au/amm/docs/2013/bi1.pdf>) can be used. The assimilation of the ERA-Interim meteorological data into ACCESS is described by Uhe and Thatcher (2015; cited in the paper).

We use the MACC ozone reanalyses for the deposition flux calculations combined with the modelled deposition velocities. The latter do not depend on the chemistry component of the model so, as mentioned earlier, its performance is not relevant. Deposition velocity in the model is solely a function of parameters of the physical component of the model and prescribed inputs. Therefore, in effect we only use the physical atmosphere component of the model, and this component relevant to our model version is described by Walters et al. (2014, <https://www.geosci-model-dev.net/7/361/2014/gmd-7-361-2014.pdf>). A list of technical reports on UM given at <http://cms.ncas.ac.uk/wiki/Docs/MetOfficeDocs> (but accessing them requires username and password).

We show in the paper that our total deposition flux to non-water surfaces is similar to that calculated by other researchers (Lines 24-26, Page 25) and that the main difference lies in the oceanic deposition flux component.

Changes in manuscript: Based on the above response, we will revise the information and references provided in the paper.

(8) Comment: *Typo on page 10, line 14 “fullydescribe” missing a space*

Response: Done.