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

"A revised global ozone dry deposition estimate based on a new two-layer 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. The locations of the changes made refer to those in the non-tracked version of the revised manuscript submitted.

(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 more than a year ago by the authors that the Referee is mentioning was published in November 2016 in ACPD and then in March 2017 in ACP (https://doi.org/10.5194/acp-17-3749-2017). This 2017 ACP 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 two-layer 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) 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 gridded global MACC ozone reanalyses given at 3 hourly frequency for ten years to better constrain the oceanic ozone dry deposition fluxes.

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 (see last para on Page 21), 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 resulting from the particular form of eddy diffusivity used). The present work also demonstrates the importance of chemistry-turbulence interaction. To explain the difference further, if the deposition of another gas that is taken up by reaction in the ocean surface layer was modelled with the old scheme, the results in nearly every case would be inconsistent whereas with the new scheme they would, prima facie, be correct.

Changes in manuscript: We clarify the differences between the old and new two-layer schemes better (see Page 4, Lines 16–30; Page 5, Lines 9–15; last para on Page 22; addition of new Figure 2 and its description).

(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 most comprehensive 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 O_3 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). However, in response to the Referee's comment we have done additional work on the impact of dissolved organic matter (DOM) and this is included in the revised version.

Changes in manuscript: The additional work on DOM (or DOC, dissolved organic carbon) is included as a new Section 2.3 "Impact of ozone reaction with dissolved organic carbon (DOC)." The new Table 1 gives model performance statistics when DOC is included.

(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-O$_3$ reaction rate constant, and the deposition velocity data.

As suggested by the Referee, we have included an x-y plot of the modelled vs. observed deposition velocities as Figure 8. Additional work conducted on DOM is included as Section 2.3. The differences between the old and new two-layer schemes are now elucidated better (see Changes in manuscript under Response 1 above).

(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 work on DOM, we agree with the Referee that our current understanding of DOM is poor.

In Figure 5, we have added an additional curve as Option 6 which is the same as Option 4 (the latter option is used in our deposition flux calculations and involves a constant $\delta_m = 3$ microns with k given

by Eq. (21) using only the data of Magi et al. (1997)) but using the iodide concentration parameterisation of Chance et al. (2014). This parameterisation gives larger iodide concentrations than that by MacDonald et al. (2014).

Our results suggest that the deposition velocity data can also be described by the Chance et al. (2014) iodide parameterisation coupled but with smaller values of k (because it is the reactivity a, which is the product of the iodide concentration and second-order rate constant k, that goes into the deposition velocity calculation) within the uncertainty of the deposition velocity 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 reasoning and with the selected parameters provides a satisfactory comparison with the data. However, as the discussion of Figure 5 suggests, 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 ozone 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 (see new Section 5.3).

Changes in manuscript: Sensitivity to Chance et al.'s (2014) iodide parameterisation is included in Figure 5 as option 6 and the behaviour discussed in the text (Page 14, last paragraph). The new Table 1 includes performance measures for various deposition schemes and configurations including the Chance et al. iodide parameterisation. Additional work on uncertainty in ozone deposition flux, which also addresses Comment #5 made by Referee #2, is included as a new Section 5.3 "Uncertainty in annual ozone dry deposition."

(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, gridded, 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.

Considering only the lowest layer of the atmosphere, the ozone deposition flux equals the ozone deposition velocity times the ozone concentration. We argue that the MACC analyses provide the best available gridded estimate of the ozone concentration and our oceanic deposition velocity parameterisation the best estimate of the ozone deposition velocity, and, therefore, combined the best estimate of the ozone deposition rate.

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 sea ice), the respective figures are 566.7, 689.9 and 722.8 Tg yr^{-1} (see the top paragraph on Page 18 and Table 1 of the original manuscript). Thus the underestimation of ozone by ACCESS is reflected more prominently in the deposition to the 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 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 reactivity), flow properties and turbulent mixing, and surface characteristics) and prescribed parameters (e.g., ozone molecular diffusivity and solubility).

Changes in manuscript: In light of the above response, we do not agree with the Referee to remove the MACC data analysis and it is retained. However, we have included some of the above points as clarification (see Page 19, Lines 22–31). We do not use the ACCESS derived ozone flux. We use the ACCESS derived deposition velocity (which is unaffected by any shortcomings in the atmospheric chemistry scheme) coupled with the MACC ozone for the ozone flux calculation; therefore, we have shortened the description of the chemical component of ACCESS, and deleted the ACCESS-only (i.e. without MACC) 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 vn8.4). 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, cited)).

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

We use the MACC ozone reanalyses for the deposition flux calculations combined with the modelled deposition velocities. As mentioned earlier, the latter do not depend on the ozone chemistry in the model so ACCESS-UKCA's performance for ozone 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 (Page 33, Lines 6–9) and that the main difference lies in the oceanic deposition flux component.

Changes in manuscript: Following the above response, we have revised and expanded Section 3 on ACCESS-UKCA. The references of Bi et al. (2013) and Walters et al. (2014) are also included.

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

Response: Done.

Reply by the authors to the Referee #2's comments on

"A revised global ozone dry deposition estimate based on a new two-layer parameterisation for air-sea exchange and the multi-year MACC composition reanalysis" (#acp-2017-768)

Anonymous Referee #2 (RC2)

We are grateful to the Referee for a long set of comments. In the following, we provide a response to these comments. The locations of the changes made refer to those in the non-tracked version of the revised manuscript submitted.

(1) **Comment:** *A modified version of a recently presented ozone ocean dry deposition scheme [Luhar et al., 2017] is presented. The model performance is evaluated by comparing modelled ozone deposition velocities with previously published data from oceanic cruises. Further, the global ozone ocean flux is modeled based on this new model configuration, yielding a lower oceanic ozone sink than prior estimates. The ozone ocean flux is then compared with the ozone land sink, and a new total global ozone flux estimate is derived.*

Response: Thanks for the comment.

Changes in manuscript: None.

(2) **Comment:** *Major Comments:*

While the authors repeatedly highlight their work as being a new 'scheme', as far as I understand this modeling in essence differs only in one aspect (the ocean layer is described in two, rather than a single layer) from their prior ACP publication [Luhar et al., 2017] that was submitted only ten months prior to this current paper. The article claims this ozone flux parameterization and modeling to be a novel development. However, from reading the earlier publication [Luhar et al., 2017] again, and the works by Ganzeveld et al. [2009] and Fairall et al. [2007], it appears that the the physical and ocean biochemical dependency description were mostly adaptations of principles presented in these earlier publications.

Response: All the references mentioned above by the referee are included in our paper. We clearly elucidate what the shortcomings are of the previous model formulations, including the old two-layer formulation used by Luhar et al. (2017, https://doi.org/10.5194/acp-17-3749-2017). We agree that our new two-layer scheme (Eq. 16) includes the same overall physical and ocean biochemical processes as in the studies by these authors, but it improves the mathematical formulation by correcting a major flaw of the old two-layer scheme in that it includes chemical reactivity throughout the oceanic mixing layer (as is observed) rather than just within the top few microns of the water surface. The new model will also apply to any other chemical compounds that are taken up by the oceanic mixing layer. We accept

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that this represents an incremental advance in model development, but we believe it is a significant advance. Additionally, our work also makes use of the global, high resolution ozone reanalyses developed under the European MACC program to better constrain the ozone dry deposition budgets. These reanalyses have not previously been used for the ozone deposition problem and thus provide scope for novel application.

Changes in manuscript: To consider the Referee's point, we have qualified the title a little better to read "A revised global ozone dry deposition estimate based on a new two-layer parameterisation for air-sea exchange and the multi-year MACC composition reanalysis." We also clarify the differences between the various schemes better in Introduction (Page 4, Lines 6–30).

(3) **Comment:** *In this model the ozone ocean flux description builds exclusively on chemical removal of ozone by reaction with iodide (I-). Consideration of this reaction is not that novel, having been proposed quite some time ago. Other previous work has suggested that, while the I- reaction has high significance, other secondary reactions, such as those with dissolved organic matter (DOM) in the ocean surface microlayer, may play a role in the ozone reaction as well [Ganzeveld et al., 2009; Coleman et al., 2010]. Ganzeveld et al. [2009] showed, for example, that evaluation of the simulated O3 dry deposition velocities with a 1-layer version of the [Fairall et al., 2007] model, including only I- in the calculation of total reactivity, underestimated the measured coastal deposition velocities. The role of dissolved organic matter (DOM)-O3 chemistry was proposed to explain these discrepancies. [Coleman et al., 2010] specifically addressed the role of DOM-O3 chemistry in deposition to the Atlantic Ocean. These authors conclude: "… iodide reactions alone cannot account for observed deposition velocities. Consequently, we suggest a missing chemical sink due to reactions of ozone with organic matter at the air-sea interface." It does not appear that this Luhar et al. article takes this into consideration. The question if and how much uncertainty potentially results from this neglect is not addressed by their publication.*

Response: Part of this comment, particularly about DOM, is similar to Comment #3 made by Referee #1. We thus refer to our Response #3 to Referee #1 where we describe additional deposition calculations done with dissolved organic carbon (DOC, equivalent of DOM) included.

One novelty of our work is to provide a better mathematical formulation for the inclusion of waterside chemical reactivity. The work of Luhar et al. (2017) demonstrated clearly the limitation of the one-layer scheme of Fairall et al. (2007) in describing the deposition velocity data of Helmig et al. (2012) (as a result of overestimation of waterside turbulence-chemistry interaction in this scheme). The two-layer scheme used by Luhar et al. (2017) was successful in simulating the deposition velocity data but it employed an arbitrary constraint on chemical reactivity (as stated in Response #1 above). The two-layer model presented here removes this arbitrary constraint and thereby is a more realistic model of ozone interaction with ocean water.

The focus of modelling in our paper is on ozone deposition to open-ocean regions. Using the one-layer Fairall et al. (2007) scheme, Ganzeveld et al. (2009) showed that the inclusion of the O_3-DOM reaction (with DOM represented by chlorophyll-a) significantly increased deposition velocity at coastal sites but

gave mixed results compared to observations. For open ocean sites there were only small changes to deposition velocity due to the inclusion of DOM. The work of Coleman et al. (2010) also relates to coastal waters. None of the papers by Fairall et al. (2007), Ganzeveld et al. (2009) and Coleman et al. (2010) has used the more recent open-ocean deposition velocity data of Helmig et al. (2012) (because these data had not been available at the time) that Luhar et al. (2017) and the present work use.

Our work suggests that the ozone-iodide reaction is able to describe the available open-ocean deposition velocity data within the uncertainty of model parameters and the scatter in the data. Clearly more observations are needed to establish the relative role of additional ozone reactions for different ocean regions.

There is some evidence (e.g. Coleman et al., 2010) that ozone deposition velocities over coastal waters are larger than those over open oceans. The deposition approach used for coastal grid cells in our model is qualitatively consistent with that behaviour and is described in our Response #7 below.

We have calculated a measure of uncertainty in the global oceanic and total ozone deposition fluxes and those details are given in our Response #5 below.

Changes in manuscript: Additional calculations on DOC are included as a new Section 2.3 "Impact of ozone reaction with dissolved organic carbon (DOC)." The new Table 1 includes performance measures for various deposition schemes and configurations, including when DOC is added. Introduction is revised and new Figure 2 is included to clarify the differences between the various deposition schemes.

(4) **Comment:** *Further, building exclusively on O3 + I- chemistry, the proper description and consideration of I- in the ocean must be of high importance. The article does not provide any detail on what data the I- oceanic description builds on. Are these new observations? Or is the I- modeled based on other relationships? In [Ganzeveld et al., 2009], I- was estimated based on its correlation with nitrate. While this seemed to be a reasonable, and possibly the best possible approach at that time, does this paper take advantage of the much improved I- description presented by Chance et al. [2014]? Despite this progress, there certainly remains large uncertainty in the spatial and temporal representation of I-, e.g. its concentrations in high-latitude waters, which is hampered by a lack of in-situ observations. This is actually the region where, according to this study by Luhar, the largest differences in the O3 dry deposition velocities compared to the older/other deposition approaches are observed (Figure 9 in [Luhar et al., 2017]). As far as I understand, these uncertainties are likely many times larger than the rather narrow uncertainty windows in the ozone deposition budgets that are presented in this new Luhar et al. publication. Unfortunately, the authors do not elaborate on this question, which I consider a severe neglect.*

Response: It is clearly stated in our paper that the ocean iodide concentration used is based on Eq. (20), which is from MacDonald et al. (2014). Chance et al. (2014) examined statistical relationships between iodide and parameters such as sea surface temperature (SST), nitrate, salinity, chlorophyll-a, and mixed layer depth and found that SST was the strongest predictor of iodide. MacDonald et al. (2014, with Chance as a co-author) used data from several cruises in the Atlantic and Pacific oceans covering the latitudes 50°S–50°N to derive their parameterisation for iodide concentration, which we have used. A

sensitivity analysis involving the iodide parameterisation of Chance et al. (2014) was reported by Luhar et al. (2017) (see their Figure 5) and it was compared with the behaviour obtained using the MacDonald et al. (2014) iodide parameterisation. We have included some discussion on the use of the Chance et al. parameterisation and included a deposition velocity curve as Option 6 in Figure 5 based on this parameterisation in our Response #5 to Referee #1.

We agree that there is considerable uncertainty in the representation of ocean iodide concentration, particularly in high-latitude waters, due to the lack of in-situ observations. The rather narrow uncertainty windows in our annual ozone deposition fluxes are solely due to the interannual variability inherent in the modelled meteorology and the MACC ozone concentration fields. We have now done additional calculations to determine the uncertainty range better, and this is given as a response to Comment #5 below.

Changes in manuscript: The sensitivity to the Chance et al. (2014) iodide parameterisation conducted in our Response #5 to Referee #1 is included in Section 2.2 (see option 6 in Figure, and last paragraph on Page 14). The new Table 1 includes performance measures for various deposition schemes and configurations including the Chance et al. iodide parameterisation. Additional work on uncertainty reported below under Response #5 is also included.

(5) **Comment:** *Developed flux estimates are presented with error windows (see abstract line 23) that are on the order of 5%, but those windows are simply the standard deviation of the year to year variability in the modeled flux based on changing meteorology. They are not the uncertainty in the estimates of the ozone flux. Those, likely, would be much larger, making the way this is presented quite misleading.*

Response: The Referee is correct—the reported uncertainty in our annual ozone deposition fluxes is solely due to the interannual variability in the modelled meteorology (with nudging) and the MACC ozone concentration fields. We have done additional calculations to estimate uncertainty in deposition flux to the ocean better and this is described in Section 5.3.

Changes in manuscript: A new Section 5.3 "Uncertainty in annual ozone dry deposition." is included. With the revised uncertainty estimation, the global oceanic and total deposition fluxes of ozone are 98.4 ± 30.0 Tg yr^{-1} and 722.8 ± 87.0 Tg yr^{-1}, respectively.

(6) **Comment:** *Secondary analyses, such as comparison of modeled boundary layer ozone, global ocean flux budgets, and attribution of the oceanic flux to the total global flux that build on this modeling, are consequently highly uncertain as well. I therefore question the value of these secondary analyses. For instance, differences between the two schemes shown in Figures 9 and 10 are on the order of 0-25%. Of how much value are these results when the uncertainty in the reactivity is maybe on the order of 100-200%? To me, what I think needs to be addressed most urgently are these questions:*

- How much of the total oceanic ozone flux can be attributed to I-, versus other reactants?

Response: Please see our Response #3 to Referee #1 on DOM which demonstrates that the ozone-iodide chemistry is sufficient to describe the available open-ocean v_d measurements and their dependency on SST, and that the inclusion of DOM would deteriorate model performance.

As mentioned above, we used the iodide parameterisation of MacDonald et al. (2014) which is based on data from several cruises in the Atlantic and Pacific oceans covering the latitudes 50°S–50°N. This parameterisation is a function of SST, so depends on location and time. We have done additional uncertainty calculations as mentioned above. See Response #5 to Referee #1 on the Chance et al. (2014) iodide parameterisation.

Changes in manuscript: Additional calculations on DOM included in Section 2.3. Details of the iodide parameterisation used are provided on Page 10, Lines 12–15. Sensitivity to Chance et al.'s (2014) iodide parameterisation is included as option 6 in Figure 5, the behaviour discussed, and the performance of this parameterisation reported in the new Table 1.

(7) **Comment:** *Other Comments:*

The Bariteau et al. [2010] article makes a point that ozone fluxes are higher near the coasts compared to the open ocean. Was that considered in this modeling? And if not, how much uncertainty is potentially due to this neglect?

Response: In our global modelling, the coastal grid cells that include terrestrial surface fractions are handled as follows.

A grid-box mean deposition velocity is calculated using the individual modelled deposition velocities weighted by the fractions of the surface types present in the grid box. Our two-layer deposition scheme for the ocean is only used when the fraction of water surface in a grid box is greater than 60%. In all other cases Wesely's (1989) scheme for v_d is used, including the use of r_c = 2200 s m^{-1} for water surface. Thus for coastal water grid cells that include fractions of other surface types, the modelled deposition velocities are greater than those for the grid cells fully covered by water (as evident in revised Figure 9) because terrestrial surfaces have higher deposition velocities than water and also because of the use of r_c = 2200 s m^{-1} for the water surface tile when its fraction is less than 60%.

There is some evidence that the ozone deposition velocities over coastal waters are larger than those over open oceans (e.g. Coleman et al., 2010; Bariteau et al., 2010), which could be due to factors such as advection from land if the distance between the monitor and coastline (i.e. fetch) is limited, stronger chemical reactivity and turbulence etc. Our approach for treating coastal grid cells is qualitatively consistent with ozone deposition velocities over coastal waters being larger than over the open sea. But we do not include any additional/special processes for coastal waters.

Changes in manuscript: The above details are included in the paper (see Page 19, Lines 14–21; revised Figure 9 and its description on Page 26, Lines 8–18). The revised Figure 9 now includes coastal grid boxes with deposition velocities.

(8) Comment: *The performance of the deposition model leans heavily on data from the six open ocean cruises shown in Figures 4 and 5. Did the authors attempt other comparisons, for instance using any of the other data sets that were summarized in [Helmig et al., 2012]? Given that, as currently done, it appears that the validation relies exclusively on the data from a single group, it should be shown that those cruises are representative for the entirety of available data. Furthermore, these data do not appear to be publicly available, or hosted by any data center? In our research center (and I think this is becoming more common within the community) it is customary to cite the doi of the data set, invite the providers of the data for co-authorship, or at least acknowledge the data providers, whenever those data make a significant contribution to a publication, including comparisons in modeling studies.*

Response: It is correct that our model performance testing is based on published data from Helmig et al. (2012) which cover the latitudinal range 45°N–50°S. Surface based ozone flux stations employing the eddy-covariance technique enables a direct measurement of ozone dry deposition velocity. The data of Helmig et al. (2012) are the only such measurements available over the ocean.

We looked up the very sparse datasets by other researchers summarised by the above authors. None of these studies involved surface-based eddy-covariance technique over the ocean. The ones that used such a technique were coastal measurements (i.e. Gallagher et al., 2001; Whitehead et al., 2010). The measurements by Lenschow et al. (1982) and Kawa and Perason (1989) used aircraft-based eddy-covariance over the ocean.

The considerably larger sample size and the (perceived) use of improved instrumentation and analysis techniques in the cruise measurements of Helmig et al. (2012) compared to those reported by earlier studies provide an incentive to use these data.

In the original manuscript, on lines 23–26 on Page 14 we say "As in Luhar et al. (2017), the v_d versus SST cruise data used for comparison with the model are those with the wind speed dependence retained (Ludovic Bariteau, personal communication, 2016) and not the data originally reported by Helmig et al. (2012) in which the wind-speed dependence was removed. While this approach is logically correct, there is not a large difference between the data with and without the wind-speed dependence." The same is stated in the revised paper.

Changes in manuscript: The above response is summarised on Page 20, Lines 5–11. Dr. L. Bariteau is now included in the acknowledgements (as was done in Luhar et al. (2017)).

(9) Comment: *Page 1/Line 11: I don't see what the term 'consistent' qualifies in this context (consistent with what?)? So, I recommend deleting this.*

Response: Done.

(10) Comment: *1/17: As detailed above, I think the term 'new' is a bit of an overstatement. Yes, this paper does present some advancements in the ozone ocean uptake modeling, but most of the mechanisms, considered reactants, and dependencies were presented in prior publications.*

Changes in manuscript: At this location, we now use 'two-layer' in place of 'new'. Also, as we mentioned earlier, we have changed the paper title slightly to read "A revised global ozone dry deposition estimate based on a new two-layer parameterisation for air-sea exchange and the multi-year MACC composition reanalysis."

(11) Comment: *1/25: Atmospheric models appear to mostly overestimate surface ozone [Parrish et al., 2014]. The results presented in this Luhar et al. manuscript show an increase of modeled ozone, thereby further increasing the discrepancy between models and observations. So, from that perspective, don't these changes go in the wrong direction?*

Response: The ACCMIP multi-model study by Young et al. (2013) shows an overall overestimation of ozone in the lower troposphere in northern mid-latitudes and underestimation in southern tropics and mid-latitudes. Parrish et al. (2014) also show that models overestimate ozone in northern mid-latitudes. Our version of UKCA in ACCESS generally underestimates observed tropospheric ozone, particularly in mid to high latitudes.

Our aim is to improve the process modelling of ozone deposition to the ocean. If a model performs worse when a particular process is improved then this points to issues with some other component(s) of the model.

To constrain the deposition fluxes better, we have used the MACC ozone reanalyses and in that case the deposition fluxes do not depend on ACCESS-UKCA's ozone chemistry because the modelled deposition velocity field used in the deposition flux calculation is solely a function of the physical component of the model and input parameterisations (e.g., SST, flow properties and turbulent mixing, reactivity, ozone molecular diffusivity and solubility in water, and surface characteristics).

Changes in manuscript: We note that because we have used the MACC ozone reanalyses the deposition fluxes do not depend on ACCESS-UKCA's ozone chemistry (Page 19, Lines 22–25).

(12) Comment: *3/1: Is this ('commonly') indeed still the case, given that Ganzeveld et al. [2009] published a process-based parameterization and model implementation some 8 years ago?*

Response: To our knowledge, all common global chemistry models reported in the literature continue to use the Wesely (1989) approach for deposition to the ocean (involving a constant value of r_c of around 2000 s m^{-1} for the surface resistance). Luhar et al. (2017) showed that the Wesely approach overestimates the deposition velocity data of Helmig et al. (2012). Ganzeveld et al. (2009) included the Fairall et al. (2007) one-layer scheme for ozone deposition velocity to the ocean in a global model, and found that compared to the Wesely approach it leads to only a small (6%) reduction in the total oceanic

deposition of ozone. Luhar et al. (2017) showed that Fairall et al.'s one-layer scheme overestimates the deposition velocity data due to flaws with its turbulence diffusivity assumption. Using better assumptions, the two-layer approach as presented in our paper describes these data much better.

Changes in manuscript: A summary of the above response is included in Introduction (Page 4, Lines 6–30).

(13) **Comment:** *3/9: Ganzeveld et al. [2009] should also be cited here?*

Response: We do not think the Ganzeveld et al. (2009) reference is appropriate here because they used a one-layer scheme (of Fairall et al., 2007) and not a two-layer scheme.

Changes in manuscript: None.

(14) **Comment:** *3/28: How is the oceanic layer between the surface and 10 m depth represented?*

Response: The assumption regarding how the top oceanic layer is represented goes in the derivation of the expression for the waterside component of deposition velocity (or conversely surface resistance). This expression is implemented in the dry deposition module of our atmosphere-only global model. The global model itself does not include any explicit oceanic layer since there is no ocean model coupled. The prescribed SSTs are used in some of the input parameterisations for the waterside deposition velocity (Eq. 16) obtained using the two-layer scheme. Our scheme assumes that: chemical reactivity (or reactant) is present throughout the oceanic mixing layer; in the top few micros of the oceanic layer ozone loss is dominated by chemical reaction (with no turbulent transfer); and in the oceanic layer below, both chemical reaction and turbulent transfer act together. We now provide a diagram (as suggested by Referee #3) to make this clearer (see our Response #2 to Referee #3).

Changes in manuscript: A new diagram (Figure 2) is provided to make this clearer (also see our Response #2 to Referee #3).

(15) **Comment:** *3/24: As mentioned earlier already, a section is needed here explaining how oceanic I-concentrations were derived and included in the modeling.*

Response: The following paragraph is added:

Changes in manuscript: On page 10, Lines 12–17, we add "This parameterisation is based on iodide data from cruises in the Atlantic and Pacific oceans covering the latitudes 50°S to 50°N, and is a function of SST (Ts (K)) which varies with location and time. Eq. (20) yields highest iodide concentrations in warm tropical waters and lowest in cool waters at higher latitudes. Chance et al. (2014) examined statistical relationships between iodide and parameters such as SST, nitrate, salinity, chlorophyll-a and mixed layer depth, and found that SST was the strongest predictor of iodide in surface waters. Ganzeveld et al. (2009) used oceanic surface nitrate as a proxy for iodide." Sensitivity to

Chance et al.'s (2014) iodide parameterisation is included as option 6 in Figure 5 and the behaviour discussed. The performance of this parameterisation reported in the new Table 1.

(16) **Comment:** *4/14: …considered, but a ….*

Response: Done.

(17) **Comment:** *5/1: Why 'consistent' ?*

Response: The word has been deleted.

(18) **Comment:** *5/21: …. included, and a ….*

Response: Done.

(19) **Comment:** *16/1: ….that the new ….*

Response: Done.

(20) **Comment:** *16/2: …..(2017), but unlike the latter, the new ….*

Response: Done.

(21) **Comment:** *Figure 5: As mentioned earlier, this figure nicely shows that improvements made through this work are merely nuances, while very large uncertainties and deficiencies in other areas are overlooked.*

Response: As we said in our Response #1 to a comment by Referee #1 and in the paper, there is only a small difference between the new and old two-layer schemes in terms of their performance compared to the data. However, it can be said that unlike the old two-layer scheme, the new scheme leads to right results for right reasons. The present work also emphasises the importance of the impact of chemistry-turbulence interactions on deposition.

Changes in manuscript: Some changes made in the relevant text to better clarify the differences between the schemes (Page 4, Lines 16–30; Page 5, Lines 9–15; last para on Page 21). Figure 5 in the original manuscript is deleted as it does not add much to what is stated in words, i.e. the model-data agreement using the new two-layer scheme is very similar to that obtained by the old two-layer reactivity scheme (Page 21, Lines 24–27). A new Table 1 is added to report model-data comparison

statistics for various deposition schemes/configurations considered. The questions about uncertainties are considered in Responses #3–6.

(22) **Comment:** *Figure 6: Ganzeveld et al. [2009], in their Figure 3a and 3b provide similar analyses for January and July. Unfortunately, they do not show annual mean analyses. However, comparing their data with this Figure 6 reveals some very large differences. While Ganzeveld et al. [2009] report the high latitude oceans exhibiting the highest ozone deposition velocities, this Figure 6 shows that the ocean deposition velocity is highest over the tropical oceans. Isn't that a rather large disagreement that should trigger an in depth analysis and discussion?*

Response: The work by Ganzeveld et al. (2009) has been adequately commented upon by Luhar et al. (2017), including their Figure 3a and 3b (see in the latter paper the last para on Page 3761, and also in the first para of Section 7.3 on Page 3762). We do not think it is necessary to repeat that exercise here.

Changes in manuscript: None.

(23) **Comment:** *18/9-10: ACCESS-UKCA then seems to differ from other models that seem to overestimate surface ozone [Parrish et al., 2014]?*

Response: As shown by Woodhouse et al. (2015) and Luhar et al. (2017) our version of UKCA in ACCESS generally underestimates observed tropospheric ozone, particularly in mid to high latitudes. The potential reasons for the model underestimation of tropospheric ozone include inaccuracies in the emission fields of precursor species, and shortcomings in chemical or physical processes simulated in the model. However, as mentioned earlier, we determine the ozone deposition flux using the MACC ozone reanalyses and the modelled deposition velocities which do not depend on ACCESS-UKCA's ozone chemistry. Thus this model's performance for ozone is not relevant in our paper.

Changes in manuscript: A clarification is given in the last two paragraphs of Section 3.

(24) **Comment:** *20/6: As mentioned earlier, this seems to disagree with the results from [Ganzeveld et al., 2009]?*

Response: That is true, and as mentioned earlier the differences with the Ganzeveld et al. (2009) have been adequately commented upon by Luhar et al. (2017).

Changes in manuscript: None.

(25) **Comment:** *20/10: Replace 'concentration' with 'mixing ratio'.*

Response: Done.

(26) Comment: *21/5: This really should not be called 'uncertainty' then. Maybe use the term 'error bar'.*

Response: We now say error bounds.

(27) Comment: *26/15-21: In this discussion about the differences between this and the previous studies, changes are attributed to a better representation of the commonly applied constant rc of Wesely's scheme, as already demonstrated by Ganzeveld et al. [2009]. Their process-based approach arrived at a global O3 oceanic deposition budget that was not that different from models using Wesely's constant rc. This, in my opinion, calls for a discussion of how these large differences between these two process-based approaches, one being extended to two layers, only considering I-, and the other one using a single layer but including more reactants including DOM, can be reconciled.*

Response: The Referee's is correct in saying that the one-layer, process-based scheme (of Fairall et al. (2007)) implemented by Ganzeveld et al. (2009) gives a global O_3 oceanic deposition budget that is not too different from models using Wesely's constant surface resistance (r_c) approach. We have clarified the reason for this earlier, and it is discussed at length by Luhar et al. (2017). The main reason for that is that the one-layer scheme overestimates the turbulence-chemistry interaction in the waterside viscous sublayer by assuming a turbulent diffusivity that increases linearly with depth. This assumption is not consistent with existing knowledge about turbulence in the viscous sublayer (Fairall et al., 2000). The two-layer approach eliminates this problem. What this also implies is that getting the waterside turbulence-chemistry interaction correct in the model formulation can be more important than including additional reactants (e.g. DOM).

The topic of DOM is discussed in detail in our reply to Referee #3.

Changes in manuscript: As mentioned earlier, a discussion on DOM based on our Response #3 to Referee #1 is included as a new Section 2.3. The Introduction is revised to clarify the differences between the various schemes better. New Table 1 and new Figure 2 are also added.

(28) Comment: *26/29: …., whereas that ….*

Response: Done.

(29) Comment: *27/26: Given my reservations detailed above in my opinion this is a rather subjective and invalid evaluation.*

Response: In our work, we developed a new two-layer parameterisation for deposition velocity that builds upon, and corrects a flaw of, the previous process-based schemes, tested it within the limitations of the available data and input information required, and used it with the 10-year MACC global ozone reanalyses for calculating deposition budgets, with a comparison of these budgets with those from other studies.

While we do not agree with Referee's comment, we have clarified various points (e.g. uncertainty, DOM, iodide, and coastal grids) raised by the referee in our replies above, which we think address this particular comment.

Changes in manuscript: None.

(30) **Comment:** *28/8: ….deposition, an increase ….burden, and an ….*

Response: Done.

Reply by the authors to the Referee #3's comments on

"A revised global ozone dry deposition estimate based on a new two-layer parameterisation for air-sea exchange and the multi-year MACC composition reanalysis" (#acp-2017-768)

Anonymous Referee #3 (RC3)

We are grateful to the Referee for his/her comments. In the following, we provide our responses to these comments. The locations of the changes made refer to those in the non-tracked version of the revised manuscript.

(1) **Comment:** *1 Overview*

The work described in this manuscript builds on the previous work of Luhar et al., 2017 in which the authors developed a more detailed, process based, two layer parametrization for dry deposition of ozone to oceans. In this study the two layer parametrization is refined and then implemented in the UKCA model. The model output is combined with MACC reanalysis data to calculate new estimates for global ozone deposition to water/oceans and total global ozone deposition. These new estimates are considerably less than current estimates of global ozone deposition. The model output combined with MACC reanalysis data is also used to analyse inter-annual trends in ozone dry deposition.

Response: Thank you for your comment.

Changes in manuscript: None.

(2) **Comment:** *2 General comments*

Overall this manuscript is well written and describes an improved parametrization for ozone dry deposition to water. The improved parametrization addresses uncertainty in deposition of ozone to water, which is the main driver of uncertainty in global ozone dry deposition. The manuscript is generally well laid out and the figures are clear. My main comments refer to Section 2. This section is quite important as it describes the new deposition parametrization, but it is a bit hard to follow.

(i) It would helpful if the authors could include a diagram of the different layers that form within the sea surface micro layer (e.g. reaction-diffusion sub-layer, bottom layer) that shows a summary of the processes (e.g. chemistry, chemistry/turbulence and reaction with iodide) that occur for in each layer and the main equations that are used to parameterize these processes.

(ii) I think it would also be helpful in Section 2 if the authors could more clearly describe how their improved scheme differs from that described in Luhar et al., 2017.

Response and changes in manuscript: (i) We agree with the referee. We include two new diagrams to illustrate the different ocean layers (see Figures 1 and 2).

(ii) The old two-layer scheme assumes that chemical reactivity is present only in the reaction-diffusion sublayer a few microns thick even though chemical reactivity is observed to be present throughout the ocean mixing layer. The new two-layer scheme eliminates this arbitrary assumption. However, as mentioned in the paper in the last paragraphs on Pages 4 and 21, the results obtained by the two schemes are similar. This is because in the old scheme assuming chemical reactivity only in the reaction-diffusion sublayer was necessary to compensate for the overestimation of the impact of turbulence that results from the use of a waterside turbulent diffusivity parameterisation that is not valid very close to the water surface. The new scheme overcomes that limitation by assuming that only molecular diffusion occurs in the reaction-diffusion sublayer and from then on both molecular diffusion and turbulence are present. Chemical reaction takes place in both layers. This is an approximation to the nature of mixing near surfaces.

We clarify the differences between the two schemes better in Introduction (Page 4, Lines 16–30; Page 5, Lines 1–15) and through the addition of new Figure 2.

(3) Comment: *3 Specific comments*

3.1 Section 1

P4, L13-14: Consider rephrasing to "A more appropriate parametrisation for Kt which varies with zm in the viscous sublayer..." to improve the readability and meaning of the sentence.

Response: Done.

(4) Comment: *P4, L20-22: Could the authors provide a brief description of the "asymptotic behaviour" (also mentioned in the abstract). Or refer the reader to section 2.1.*

Response: Done.

(5) Comment: *3.2 Section 2*

P5, L20-22: Consider rephrasing to "The second layer, which is deeper than the reaction-diffusion sublayer,..." to improve the readability and meaning of the sentence.

Response: Done.

(6) Comment: *P6, L12-13: Consider rephrasing to "The first two, namely the flux at the water surface (z = 0) obtained using Eq. (4) should be equal to F0 and the concentration at the interface..." to improve the readability and meaning of the sentence.*

Response: Done.

20

(7) Comment: *Figure 1 caption: Consider rephrasing to "Figure 1: Variation of the oceanic component of ozone dry deposition velocity multiplied by ozone solubility as a function of sea surface temperature (SST, °C), (a, c); and reactivity a (s-1), (b, d). Curves determined using the two-layer deposition scheme (Eq. (16)) for several c0 values used in $\delta m = c0\ l\ m$, (a, b) and several δm values, (c, d). The variations obtained using the one-layer deposition scheme with (Eq. (18)) and without (Eq. (19)) waterside turbulent transfer (i.e. reaction-diffusion only) are also shown. The waterside friction velocity (u*w) used was 0.01 m s-1." to improve the readability.*

Response: Done

(8) Comment: *3.3 Section 5.2*

P21, L5-10: Can the authors suggest why there are larger ozone dry deposition velocities in the Northern Hemisphere?

Response and changes in manuscript: We state in the paper that "Oceanic deposition in the Northern Hemisphere (49.0 ± 3.4 Tg yr^{-1}) is somewhat larger than that in the Southern Hemisphere (44.9 ± 4.5 Tg yr^{-1}) due to the higher O_3 concentrations and slightly larger oceanic deposition velocities in the former, although the Earth's area covered by the ocean is larger by approximately 30% in the Southern Hemisphere."

The average oceanic deposition velocity (weighted by the grid-cell area) for the Northern Hemisphere is slightly larger than that for the Southern Hemisphere (i.e. 0.020 vs. 0.017 cm s^{-1} for the year 2005). The main reason for this difference is that the average sea surface temperature (SST) (weighted by the grid-cell area) for the Northern Hemisphere is larger than that for the Southern Hemisphere (i.e. 295.3 K vs. 291.2 K for the same year). As mentioned in the paper, in our formulation of deposition velocity to the ocean is dominated by the surface-resistance term (r_c) which in turn depends on SST. Overall the higher the SST the higher the oceanic deposition velocity.

We include the above clarification on Page 29, Lines 14–18.

Reply by the authors to L. J. Carpenter's comment on

"A revised global ozone dry deposition estimate based on a new two-layer parameterisation for air-sea exchange and the multi-year MACC composition reanalysis" (#acp-2017-768)

Comment: *I enjoyed reading this paper which carefully lays out improvements to the authors' previous oceanic O3 dry deposition formulation by including chemical reactivity below the reaction-diffusion sublayer. I have a question which I don't think any of the reviewers raise, on the reaction-diffusion sublayer thickness: how were the values of the constant c0 chosen?*

Response and changes in manuscript: We thank Prof. Lucy Carpenter for her views on our work.

In the reaction-diffusion sublayer, $l_m = (D/a)^{1/2}$ is an appropriate length scale. Thus, using scaling argument, it is reasonable to assume that the thickness of the reaction-diffusion sublayer (δ_m) is proportional to l_m with the coefficient of proportionality (c_0) being a constant of the order unity. In Figures 1a and 1b of our paper, we plot $1/r_c$ curves for three values of c_0, viz. 0.2, 0.4 and 0.7, which fall within the two asymptotic limits (equivalent to $c_0 \to 0$ and $c_0 \to \infty$). The value $c_0 = 0.4$ was selected for further sensitivity analysis reported in Figure 3 because it leads to a $1/r_c$ variation that roughly lies in the middle of the two asymptotic limits as shown in Figures 1a and 1b. As mentioned on Page 12 Line 13, in all our subsequent deposition calculations we used Option 4 with $\delta_m = 3$ microns (see the 1st para on Page 13) which obviously does not need a specification of c_0 (but of course there will be an implied variation of c_0 via the relation $c_0 = \delta_m / l_m$).

We include the above clarification in the revised version of the paper (Page 14, Lines 5–9).

A r~~Revis~~ed~~ing~~ global ozone dry deposition estimate~~s~~ based on a new two-layer~~mechanistic~~ parameterisation for air-sea exchange and the multi-year MACC composition reanalysis

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Abstract. Dry deposition at the Earth's surface is an important sink of atmospheric ozone. Currently, dry deposition of ozone to the ocean surface in atmospheric chemistry models has the largest uncertainty compared to deposition to other surface types, with implications for global tropospheric ozone budget and associated radiative forcing. Most global models assume that the dominant term of surface resistance in the parameterisation of ozone dry deposition velocity at the oceanic surface is constant. There have been recent mechanistic parameterisations for air-sea exchange that account for the simultaneous waterside processes of ozone solubility, molecular diffusion, turbulent transfer, and first-order chemical reaction of ozone with dissolved iodide and other compounds, but there are questions about their performance and consistency. We present a new two-layer parameterisation scheme for the oceanic surface resistance by making the following realistic assumptions: (a) the thickness of the top water layer is of the order of a reaction-diffusion length scale (a few micrometres) within which ozone loss is dominated by chemical reaction and the influence of waterside turbulent transfer is negligible; (b) in the water layer below, both chemical reaction and waterside turbulent transfer act together and are accounted for; and (c) chemical reactivity is present through the depth of the oceanic mixing layer. The new parameterisation has been ~~incorporated into the ACCESS UKCA global chemistry climate model and the results are~~ evaluated against dry deposition velocities from recent open-ocean measurements. It is found that the inclusion of only the aqueous iodide-ozone reaction satisfactorily describes the measurements. In order to better quantify the global dry deposition loss and its interannual variability, ~~the~~ modelled 3-h ozone deposition velocities are combined with the 3-h MACC (Monitoring Atmospheric Composition and Climate) reanalysis ozone for the years 2003–2012. The resulting ozone dry deposition is found to be 98.4 ± 30.0 Tg O_3 yr^{-1} for the ocean and 722.8 ± 87.3 Tg O_3 yr^{-1} globally. The new estimate of the ocean component is approximately a third of the current model estimates. This reduction corresponds to an approximately 20% decrease in the total global ozone dry deposition, which (with all other components being unchanged) is equivalent to an increase of approximately 5% in the modelled tropospheric ozone burden and a similar increase in tropospheric ozone lifetime.

1 Introduction

~~Ozone (O₃) in the atmosphere acts as a greenhouse gas, and adversely impacts human health and plant productivity (e.g., Young et al., 2013; Monks et al., 2015).~~ In the troposphere, the budget of ozone (O_3) is determined by its transport from the stratosphere, dry deposition at the Earth's surface, and chemical production and loss. Dry deposition is a significant sink of ozone (Galbally and Roy, 1980), influencing ozone concentration, its lifetime and long range transport. The average dry deposition velocity of O_3 to the ocean is less than that to terrestrial surfaces, but because of the larger coverage of the Earth's surface by the oceans there is substantial dry deposition to water. A current estimate of ~~The 'present day' (~2000)~~ total global dry deposition of O_3 ~~estimated by climate-chemistry models~~ is ~~reported to be~~ 1094 ± 264 Tg yr^{-1} (IPCC, 2013; Young et al., 2013), of which about 35% is to the ocean (Ganzeveld et al., 2009; Hardacre et al., 2015). Hardacre et al. (2015) observed that ozone dry deposition to the water surface in models has the largest uncertainty compared to other surface types. A proper treatment of dry deposition to the ocean in atmospheric chemistry models is thus necessary for more realistic ozone estimates and better representation of feedback cycles, e.g. that involving iodine chemistry (Carpenter et al., 2013). Although dry deposition of ozone to the ocean is the focus of the present paper, we also place ocean dry deposition in the context of total global dry deposition ~~and examine its interannual variability~~. In this paper the word deposition means dry deposition.

The dry deposition flux, F_{O_3}, of ozone to the surface is normally calculated as the product of its concentration, $[O_3]$, in the air near the surface and a (downward) dry deposition velocity, v_d :

$$F_{O_3} = v_d \, . [O_3] . \tag{1}$$

A common approach to parameterising v_d is to express it as a linear sum of three resistances (e.g., Wesely, 1989):

$$v_d = \frac{1}{r_a + r_b + r_c} , \tag{2}$$

where the aerodynamic resistance r_a is the resistance to transfer by turbulent mixing in the atmospheric surface layer, the atmospheric viscous, or quasi laminar, sublayer resistance r_b is the resistance to movement across a thin layer (0.1 – 1 mm) of air that is in direct contact with the surface, and the surface resistance r_c is the resistance to uptake by the surface itself that can be controlled by physical, chemical, biological or other processes depending on the surface type and species of interest.

2

At this point it is useful to define the waterside layers near the sea surface that are relevant here (Figure 1). The top few millimetres of the sea surface is often termed the sea surface microlayer which may be composed of various sublayers or scales depending on the physical, chemical or biological properties being considered (Soloviev and Lukas, 2014; Carpenter et al., 2015). Very close to the water surface is a viscous sublayer (~ 1 mm) within which viscous processes dissipate the

5 turbulent kinetic energy associated with the smallest of the eddies (of the size of Kolmogorov microscale) into heat. Thus the viscous sublayer thickness is of the order of the level at which the turbulent eddy diffusivity falls below the kinematic viscosity. A level exists within the viscous sublayer at which the diminishing eddy diffusivity falls below the molecular diffusivity, and this level is approximately the thickness of the diffusive sublayer (~ 50 μm for ozone). Embedded within the diffusive sublayer can be another sublayer (which we call reaction-diffusion sublayer) characterised by chemical reactivity

10 and molecular diffusivity, whose thickness is scaled by a reaction-diffusion length scale (typically 3 μm for the ozone-iodide reaction in water). In the surface turbulent layer (or mixing layer) (~ 10–50 m) below the surface microlayer, turbulent processes dominate.
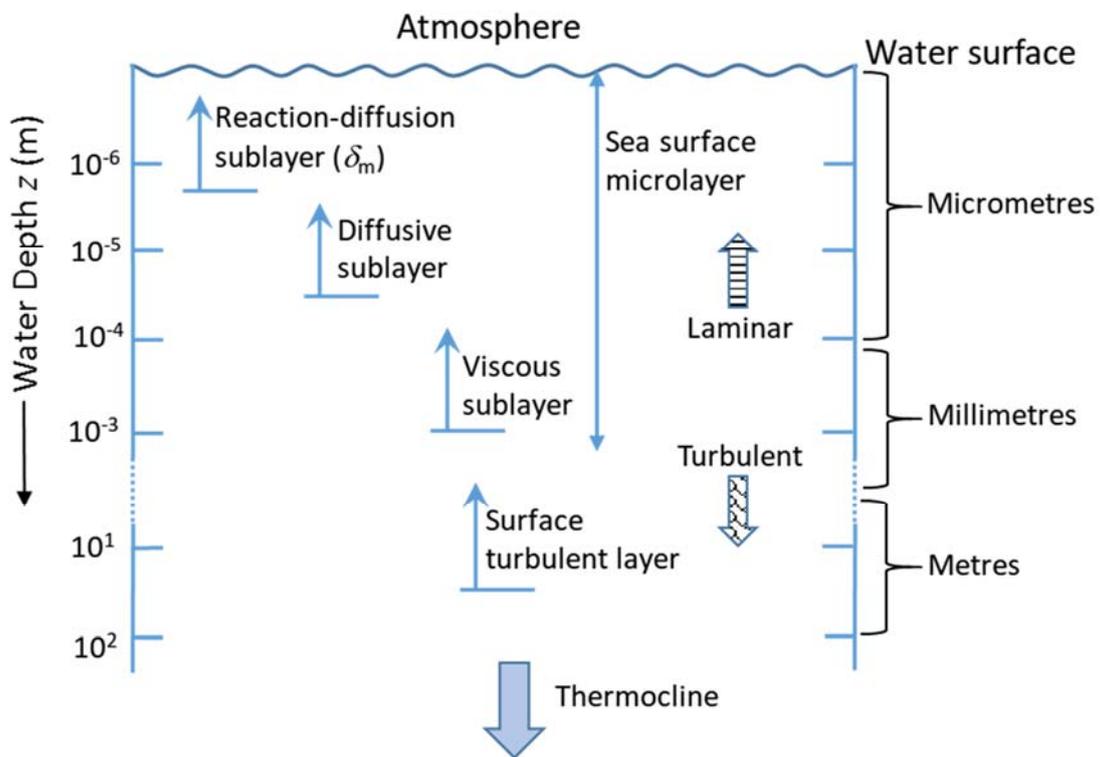
15 **Figure 1: Idealised representation of the vertical structure of the top few metres of sea water. The depth of the reaction-diffusion sublayer (δ_m) will vary according to the chemical reactivity of the ocean water to ozone**

For ozone dry deposition to water surfaces, r_c is the dominant term in Eq. (2). It is commonly assumed that r_c for water is constant (≈ 2000 s m^{-1}) based on Wesely's (1989) deposition parameterisation, and to our knowledge this approach is used by default in most global chemical transport models, e.g. MATCH-MPIC (von Kuhlmann et al., 2003), MESSy (Kerkweg et

5 al., 2006), MOZART-4 (Emmons et al., 2010), CAM-chem (Lamarque et al., 2012), GEOS-Chem (Mao et al., 2013) and UKCA (Abraham et al., 2012).

Recently, Luhar et al. (2017) demonstrated that the use of a constant r_c for water results in a ~~an unrealistic,~~ near-constant behaviour of v_d with sea surface temperature (SST) which ~~progressively~~ overestimates the ~~best available,~~ open-ocean deposition velocity measurements of ~~(~~Helmig et al.~~,~~ (2012) by as much as a factor of 2 to 4 for cooler SSTs ~~as sea surface~~

10 ~~temperatures (SSTs) decrease~~. Luhar et al. (2017) also tested a mechanistic, one-layer reactivity scheme for r_c proposed by Fairall et al. (2007) which includes the influence of waterside processes acting on ozone, namely solubility, molecular diffusion, turbulent transfer and a first-order chemical reaction of ozone with dissolved iodide, and found that the one-layer scheme also overestimates the deposition velocity measurements (albeit to a slightly lesser degree than the constant r_c approach) due to an overestimation of turbulent diffusivity within the waterside viscous sublayer. Ganzeveld et al. (2009)

15 included the one-layer scheme in a global model, and found that compared to the Wesely constant r_c approach the one-layer scheme leads to only a slight reduction in the total oceanic deposition of ozone, which is consistent with the findings from the one-layer scheme by Luhar et al (2017).

Following Fairall et al. (2007), Luhar et al. (2017) formulated a two-layer reactivity scheme for r_c ~~based on the approach of Fairall et al. (2007) which derives r_c by solving a simplified form of the mass conservation equation for ozone and includes~~

20 ~~the influence of waterside processes acting on ozone, namely solubility, molecular diffusion, turbulent transfer and a first-order chemical reaction of ozone with dissolved iodide (deposition velocity increases as the magnitude of each of these processes increases).~~ in which ~~In the Luhar et al. (2017) formulation,~~ the chemical reactivity of ozone with dissolved iodide was assumed to be present only within the reaction-diffusion sublayer ($\delta_m \sim 3$ µm) ~~was determined as the product of the pertinent second order rate coefficient and iodide concentration,~~ with ~~but in~~ the water region below δ_m ~~it was assumed that~~

25 ~~there is~~having a near-zero background chemical reactivity (through the assumption that ~~, meaning that~~ the iodide concentration below δ_m was~~is~~ virtually zero). Th~~is~~ two-layer reactivity~~e Luhar et al. (2017)~~ scheme when used in a global chemistry-climate model, namely ACCESS-UKCA (Australian Community Climate and Earth System Simulator – United Kingdom Chemistry and Aerosol), was able to describe well the absolute magnitude and the sea surface temperature dependence of the deposition velocity measurements of Helmig et al. (2012) over the ocean.

Although the two-layer reactivity scheme of Luhar et al. (2017) was successful in describing the observations, its assumption that~~limiting the~~ chemical reactivity (and hence ~~the~~ iodide~~) concentration~~ is only present ~~in this scheme to~~ within a depth of water that is of the order of only a few micrometres is ~~not a realistic~~arbitrary ~~assumption~~ given that~~because~~ in reality iodide is present through the depth of the oceanic surface turbulent layer (~ 10–50 m) and even deeper (Chance et al., 2014). The primary reason the two-layer reactivity scheme worked well was that limiting the ~~dissolved~~ iodide concentration to the reaction-diffusion sublayer artificially compensated for the effects of the overestimation of turbulent (or eddy) diffusivity (K_t) (see below) in this layer, thereby effectively restricting the vertical extent of the ozone-iodide reaction and its interaction with turbulence to the scale δ_m~~the thickness of the reaction-diffusion sublayer~~ and thereby circumventing an overestimation of v_d .

The overestimation of K_t alluded to above in both one- and two-layer formulations results from the use of the linear parameterisation $K_t = \kappa u_{*_w} z$ ~~(assuming neutral stratification)~~, where u_{*_w} is the waterside friction velocity, κ is the von Karman constant (= 0.4) and z is depth from the surface. This parameterisation is valid for a fully turbulent surface layer that lies beyond the viscous sublayer. For depths within the viscous sublayer, the viscous dissipation of turbulence causes the eddy diffusivity to diminish much more rapidly with decreasing z than provided by the above linear relationship. A more appropriate parameterisation for K_t which varies as z^m in the viscous sublayer where $m = 2$–3 (Fairall et al., 2000) can be considered but a corresponding analytical solution for r_c that includes chemical reaction, molecular diffusion and turbulent transfer has not so far been found.

The aims of the present paper are twofold. First, to formulate a~~n~~ ~~alternative~~ new two-layer ~~reaction-diffusion-turbulence~~ parameterisation for r_c that eliminates the assumption~~some of the inconsistencies~~ inherent in the (old) two-layer reactivity scheme ~~reported by Luhar et al. (2017)~~that chemical reactivity is only present within the top few microns of the water surface.~~.~~ ~~In particular, the new scheme does not unrealistically limit the iodide concentration to a very thin water layer.~~ ~~I~~instead the new scheme~~it~~ makes the valid assumption that reactivity~~iodide~~ is present through the depth of the oceanic mixing layer,~~which i~~as supported by observations. The new scheme employs a plausible assumption with regards to the extent of reaction-dominated deposition regime, and has an asymptotic behaviour that is consistent with the known limits when turbulent transfer dominates over chemical reaction and vice versa (see Section 2). ~~T~~his new scheme is incorporated into ACCESS-UKCA and the results on deposition velocity are compared with the data of Helmig et al. (2012) ~~and the two-layer reactivity scheme of Luhar et al. (2017)~~.

Second, there are significant biases in global modelling for ozone in the lower atmosphere and one alternative to constrain ozone dry deposition budgets better is to use ozone reanalyses involving data assimilation, which are taken as a more reliable source of near-surface ozone data than that obtained by models alone. By adopting this approach, ~~Second,~~ the oceanic and global dry deposition budgets of ozone are ~~better~~ estimated by combining the gridded global reanalyses for near-surface

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ozone from the European MACC (Monitoring Atmospheric Composition and Climate) program reanalysis for ozone concentration fields for ten years (2003–2012) and the ozone deposition velocities estimated from using the new oceanic deposition scheme in ACCESS-UKCA for ten years (2003–2012). The interannual variability and uncertainty inof these budgets areis investigated and the lattery are compared with those from other studies.

2 A consistent new two-layer scheme for surface resistance r_c

Assuming horizontal homogeneity and stationarity, the mass conservation equation for a chemical species in water is (Geernaert et al., 1998; Fairall et al., 2007):

$$\frac{\partial}{\partial z}\left[\{D + K_t(z)\}\frac{\partial C(z)}{\partial z}\right] - a\,C(z) = 0\,, \tag{3}$$

where z is the depth from water surface, $C(z)$ is the concentration of the species, D is the molecular diffusivity of the species in water, $K_t(z)$ is the turbulent diffusivity and a is a first-order reaction rate coefficient (s^{-1}) which for the ozone-iodide reaction ($O_3 + I^- \rightarrow$ products) is determined as the pertinent second-order rate coefficient (k) multiplied by the iodide concentration ($[I^-]$).

A flux variable F_0 (which we will just refer to as flux) that is invariant with water depth z can be defined by integrating Eq. (3) (Fairall et al., 2007):

$$-[D + K_t(z)]\frac{\partial C(z)}{\partial z} + a\int_0^z C(z)dz = F_0\,. \tag{4}$$

The first term on the left hand side of Eq. (4) is the mixing flux (molecular diffusion plus turbulent mixing) which decreases with depth as the reacting gas is absorbed. This component is balanced by the second term on the left hand side which is the integrated loss rate of ozone by chemical reaction between the ocean surface and depth z.

We now consider an alternative two-layer approach in which chemical reaction in the top water layer of depth δ_m (i.e. the reaction-diffusion sublayer that is embedded within the viscous sublayer) is fast enough such that it dominates over turbulent transfer, with the assumption $K_t = 0$, and transport is maintained by molecular diffusion (Figure 2). The thickness of this layer is thus of the order of the so-called reaction-diffusion length scale $l_m = (D/a)^{1/2}$ for the ozone-iodide reaction in seawater which is typically a few micrometres. This length scale for the said reaction is even smaller than the Kolmogorov

6

microscale (the latter is indicative of the smallest of the turbulent eddies present in the flow) so it is fair to assume that $K_t = 0$ within the reaction-diffusion sublayer. The second layer which is deeper than the reaction-diffusion sublayer (i.e. $z > \delta_m$) has both chemical reaction and turbulent mixing included, and a linear parameterisation for turbulent diffusivity $K_t = \kappa u_{*w} z$ is used (Figure 2). The second layer can thus include the viscous sublayer and extend to the surface turbulent layer. The chemical reaction of ozone predominantly occurs in the first layer. In the second layer, turbulence-chemistry interaction is weak compared to transfer by turbulent mixing. It is therefore reasonable to use a linearly varying K_t throughout the second layer. Both layers have the same reactivity a, i.e. the iodide concentration is uniform through the oceanic surface mixed layer. (In contrast to Figure 2, the two-layer scheme of Luhar et al. (2017) assumed $K_t = \kappa u_{*w} z$ in the first layer and $a \approx 0$ in the second layer. The one-layer scheme of Fairall et al. (2007) is equivalent to setting $K_t = \kappa u_{*w} z$ in the first layer too or $\delta_m \to 0$ in Figure 2.)
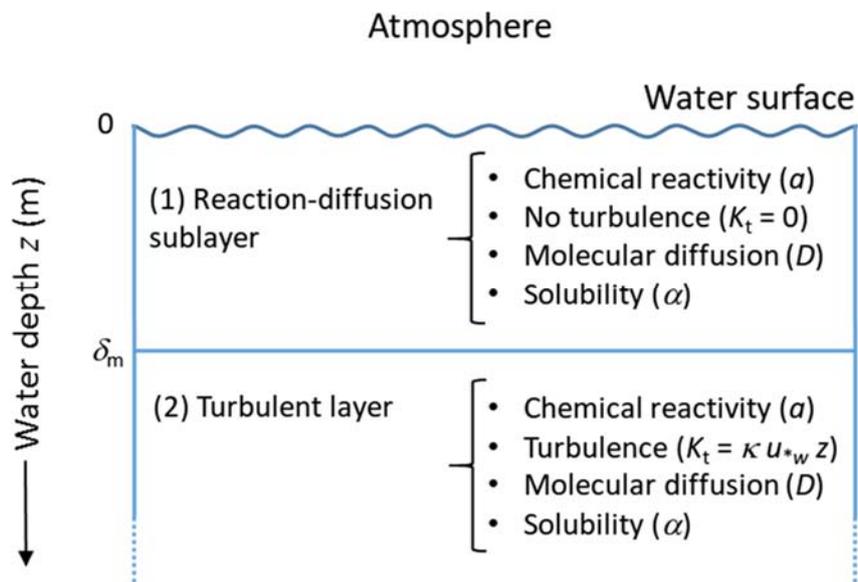
Figure 2: A simplified, two-layer structure used to represent the near-surface ocean in the model and the processes included in the calculation of ozone dry deposition to sea water.

With the above assumptions, Eq. (3) can be solved for concentration in the first (i.e. top) layer (C_1) and that in the second (i.e. bottom) layer (C_2) to yield:

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$$C_1(z) = A_1 \exp\left(z\sqrt{\frac{a}{D}}\right) + B_1 \exp\left(-z\sqrt{\frac{a}{D}}\right), \tag{5}$$

$$C_2(z) = B_2 \, K_0(\xi), \tag{6}$$

where $\xi = [2ab(z + (bD/2))]^{1/2}$, $b = 2/(\kappa u_{*w})$, $\kappa = 0.4$, and $K_0(\xi)$ is the modified Bessel function of the second kind of order 0.

The expressions for the mixing component (which includes both turbulent and molecular diffusion parts) of the flux F_0 in the first and second layers follow from the first part on the left hand side of Eq. (4) coupled with Eqs. (5) and (6):

$$F_{m1}(z) = -(aD)^{1/2}\left[A_1 \exp\left(z\sqrt{\frac{a}{D}}\right) - B_1 \exp\left(-z\sqrt{\frac{a}{D}}\right)\right], \tag{7}$$

$$F_{m2}(z) = \frac{B_2}{b}\xi K_1(\xi), \tag{8}$$

where and $K_1(\xi)$ is the modified Bessel function of the second kind of order 1.

The three unknown coefficients A_1, B_1 and B_2 are determined by imposing three boundary conditions. The first two, namely the flux at the water surface ($z = 0$) obtained using Eq. (4) should be equal to F_0 and the concentration at the interface of the two layers ($z = \delta_m$) should be continuous, lead to the following equations, respectively:

$$F_0 = F_{m1(z=0)} = (aD)^{1/2}(-A_1 + B_1), \tag{9}$$

$$A_1 \exp(\lambda) + B_1 \exp(-\lambda) - B_2 K_0(\xi_\delta) = 0, \tag{10}$$

where $\xi_\delta = [2ab(\delta_m + (bD/2))]^{1/2}$ and $\lambda = \delta_m(a/D)^{1/2}$.

The third boundary condition can be imposed in a couple of ways, both of which lead to the same answer. First, the total flux at the interface is continuous, i.e.

$$F_{m1}(\delta_m) + a\int_0^{\delta_m} C_1(z)dz = F_{m2}(\delta_m) + a\int_0^{\delta_m} C_1(z)dz, \tag{11}$$

which leads to $F_{m1}(\delta_m) = F_{m2}(\delta_m)$. This after substituting the flux Equations (7) and (8) yields

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$$(aD)^{1/2}\{A_1\exp(\lambda)-B_1\exp(-\lambda)\}+\frac{B_2}{b}\xi_\delta K_1(\xi_\delta)=0 . \tag{12}$$

Another option as ~~used~~ suggested by Fairall et al. (2007) is that as $z\rightarrow\infty$ the mixing term in Eq. (4) becomes 0 so F_0 equals the total absorption of concentration by chemical reaction, i.e.

$$F_0=a\int_0^{\delta_m}C_1(z)dz+a\int_{\delta_m}^\infty C_2(z)dz . \tag{13}$$

This condition leads to exactly the same expression as Eq. (12) when F_0 is substituted from Eq. (9).

5   Solving Eqs. (9), (10) and (12) yields

$$B_1=\frac{F_0\exp(\lambda)}{2(aD)^{1/2}}\left[\frac{\psi K_1(\xi_\delta)+K_0(\xi_\delta)}{\psi K_1(\xi_\delta)\cosh(\lambda)+K_0(\xi_\delta)\sinh(\lambda)}\right]. \tag{14}$$

Now A_1 and B_2 can be determined using Eq. (9) and (10), respectively, after substituting B_1 from Eq. (14). Using Eqs. (5) and (9) we can obtain an expression for the waterside deposition velocity v_{dw} as the flux (F_0) divided by concentration (C_0) at $z=0$

$$v_{dw}=(aD)^{1/2}\left[\frac{-A_1+B_1}{A_1+B_1}\right], \tag{15}$$

10   which after substituting for A_1 and B_1 results in ~~yields~~

$$v_{dw}=(aD)^{1/2}\left[\frac{\psi K_1(\xi_\delta)\cosh(\lambda)+K_0(\xi_\delta)\sinh(\lambda)}{\psi K_1(\xi_\delta)\sinh(\lambda)+K_0(\xi_\delta)\cosh(\lambda)}\right], \tag{16}$$

where $\psi=\xi_\delta/(ab^2D)^{1/2}=[1+(\kappa u_{*w}\delta_m/D)]^{1/2}$. Eq. (16) is the final expression for v_{dw} and is used to determine r_c as

$$r_c=\frac{1}{\alpha v_{dw}}, \tag{17}$$

9

where α is the dimensionless solubility of ozone in water (which is the ratio of the aqueous-phase ozone concentration to its gas-phase concentration and is related to Henry's law coefficient). The modified Bessel functions that appear Eq. (16) are calculated using the algorithms given in Press et al. (1997).

2.1 Asymptotic limits

5   In the limit $\delta_m \to 0$, Eq. (16) reduces to

$$v_{dw} = (a\,D)^{1/2} \left[\frac{K_1(\xi_0)}{K_0(\xi_0)} \right], \tag{18}$$

where $\xi_0 = b(a\,D)^{1/2}$. This is equivalent to the one-layer model of Fairall et al. (2007) which employs a linearly varying K_t with z and which as mentioned in Introduction overestimates the oceanic deposition velocity measurements of Helmig et al. (2012) by as much as a factor of 2–3 for lower SSTs (Luhar et al., 2017).

In the limit $\delta_m \to \infty$, the waterside turbulent transfer is neglected and the formulation becomes equivalent to the diffusion-

10   reaction formulation considered by Garland et al. (1980):

$$v_{dw} = (a\,D)^{1/2}, \tag{19}$$

which underestimates the oceanic deposition velocity measurements for SSTs below 15°C (Luhar et al., 2017).

2.2 Behaviour of the new scheme and specification of δ_m

The above scheme for determining the oceanic ozone deposition velocity requires specification of the dissolved iodide concentration $[I^-]$ and, the second-order rate coefficient (k) for the ozone-iodide reaction used in the calculation of

15   chemical reactivity via $a = k.[I^-]$, the dimensionless solubility of ozone in water (α), and the molecular diffusivity of ozone in water (D) and the waterside friction velocity (u_{*w}). We useIn the first case the parameterisations employed by Luhar et al. (2017) are used.

$$[I^-] = 1.46 \times 10^6 \exp\left(\frac{-9134}{T_s}\right) \tag{20}$$

10

from MacDonald et al. (2014) where $[I^-]$ is in mole per litre (or molar, M) and T_s (K) is the water temperature. This parameterisation is based on iodide data from cruises in the Atlantic and Pacific oceans covering the latitudes 50°S to 50°N, and is a function of SST (T_s (K)) which varies with location and time. Eq. (20) yields highest iodide concentrations in warm tropical waters and lowest in cool waters at higher latitudes. Chance et al. (2014) examined statistical relationships between iodide and parameters such as SST, nitrate, salinity, chlorophyll-a and mixed layer depth, and found that SST was the strongest predictor of iodide in surface waters. Ganzeveld et al. (2009) used oceanic surface nitrate as a proxy for $[I^-]$.

The second-order rate coefficient quantity k (M^{-1} s^{-1}) based on the data from Magi et al. (1997) is

$$k = \exp\left(\frac{-p}{T_s} + q\right) , \tag{21}$$

where $p = 8772.2$ and $q = 51.5$.

The ozone solubility is (Morris, 1988)

$$\log_{10}(\alpha) = -0.25 - 0.013(T_s - 273.16). \tag{22}$$

The molecular diffusivity quantity D (m^2 s^{-1}) of ozone in water is given as (Johnson and Davis, 1996)

$$D = 1.1 \times 10^{-6} \exp\left(\frac{-1896}{T_s}\right). \tag{23}$$

The waterside friction velocity u_{*w} is calculated as $u_{*w} = (\rho_a / \rho_w)^{1/2} u_*$ where u_* is the airside friction velocity, ρ_a is the air density and ρ_w is the water density.

The depth of the reaction-diffusion sublayer (δ_m) needs to be specified. As mentioned earlier, it is of the order of the reaction-diffusion length scale $l_m [= (D/a)^{1/2}]$ so one option is to take $\delta_m = c_0 l_m$ (in that case $\lambda = c_0$), where c_0 is a constant. (With the above parameterisations for $[I^-]$, k and D, l_m varies between 24.0–1.2 µm for the SST range 2–33°C, and it is 3 µm at 23°C.) Figure 3 presents the variation of the oceanic component of dry deposition velocity multiplied by the ozone solubility, i.e. αv_{dw} ($= 1/r_c$), calculated from Eq. (16) as a function of SST (Figure 3a) and reactivity (a) (Figure 3b) for three c_0 values for a typical value of the waterside friction velocity (u_{*w}) of 0.01 m s^{-1} (which corresponds to an airside u_* of approximately 0.3 m s^{-1}). The plotted variations show that αv_{dw} increases with SST and with the logarithm of a.

both in a very similar manner. As c_0 decreases (hence δ_m decreases) the two-layer model behaviour approaches the behaviour of the one-layer scheme given by Eq. (18) in which turbulent diffusivity is a linear function of depth and chemical reaction is included. On the other hand, as c_0 gets larger (hence δ_m gets larger) the extent of the reaction-diffusion regime in the two-layer scheme gets larger and the model behaviour approaches the limiting behaviour $\alpha v_{dw} = \alpha(a\,D)^{1/2}$ (Eq.

5   (19)) as originally discussed by Garland et al. (1980). In the old two-layer reactivity scheme of Luhar et al. (2017), in some cases αv_{dw} can go below the variation implied by the diffusion-reaction limit (19) which is not realistic and which does not occur within the new scheme.

In Figure 3b, as a decreases δ_m increases (since $\delta_m = c_0 (D/a)^{1/2}$) the model approaches the diffusion-reaction limit Eq. (19) of Garland et al. (1980), and as a increases δ_m decreases and the model approaches the one-layer solution Eq. (18).

10 Figure 3a shows the same behaviour but in terms of SST.

It is found that the use of $\delta_m = c_0\,l_m$ (so $\lambda = c_0$) together with the parameterisations (20)–(23) does not fully describe the variation of the measured deposition velocities with SST (presented later) regardless of the value of c_0. For example, with $c_0 = 0.7$ there is an underestimation by the model of the measured deposition velocities for SSTs less than 18°C and an overestimation for higher SSTs. For $c_0 < 0.7$ the overestimation gets worse. For $c_0 > 0.7$ the underestimation gets worse

15 and the αv_{dw} variation approaches the diffusion-reaction behaviour.

Another method for specifying δ_m is to assume that it is constant. Figure 3 shows the variation of αv_{dw} calculated from Eq. (16) as a function of SST (Figure 3c) and a (Figure 3d) for several fixed values of δ_m between 0.5 and 10 μm. These variations look different compared to those in Figure 3a and Figure 3b but like the latter they all fall within the two limits. As δ_m decreases the αv_{dw} variation approaches the one-layer solution Eq. (18) and as δ_m increases this variation approaches

20 the diffusion-reaction limit Eq. (19).

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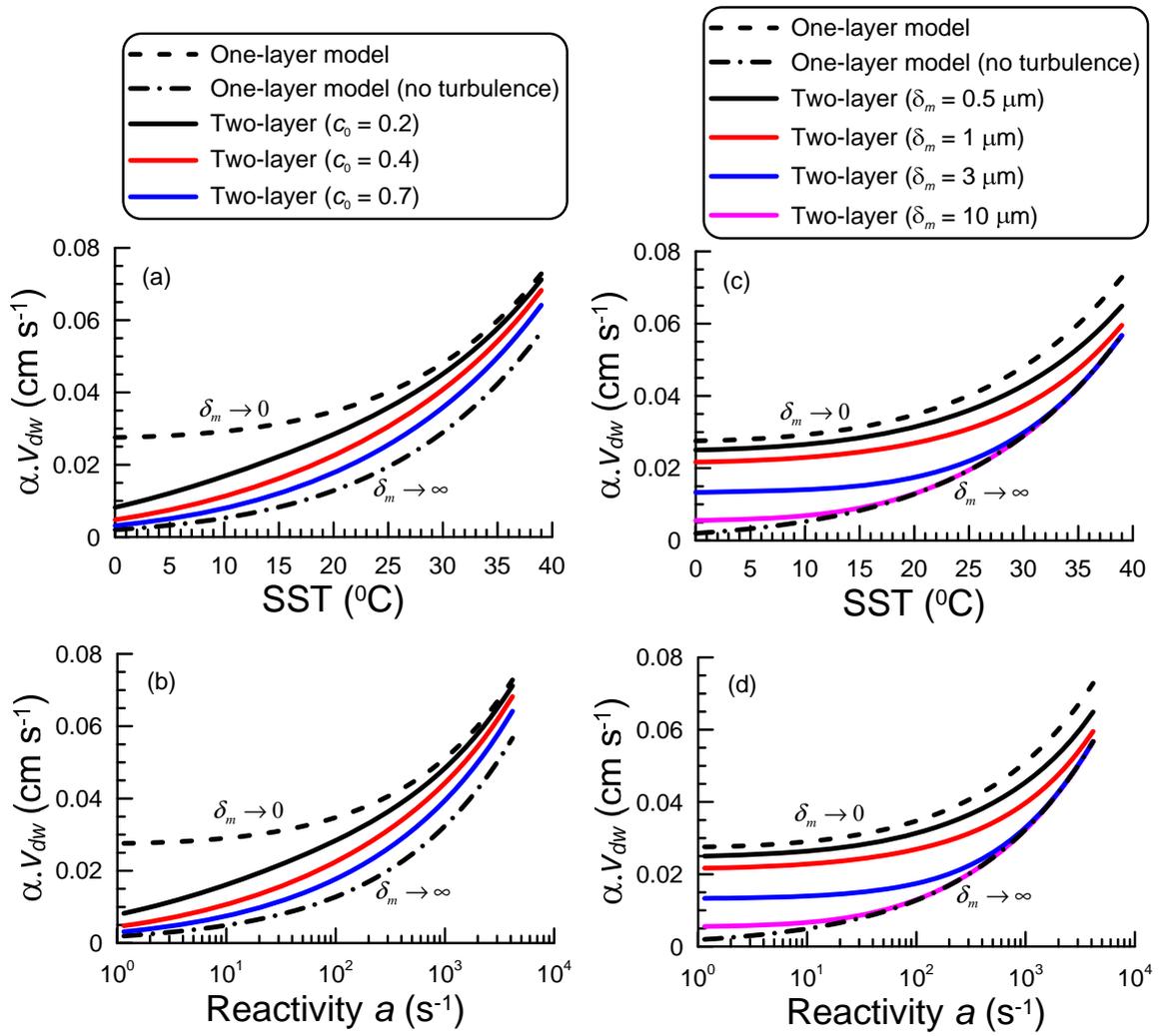
Figure 3: Variation of the waterside component of ozone dry deposition velocity multiplied by ozone solubility, αv_{dw} (= $1/r_c$), as a function of (a, c) sea surface temperature (SST, °C), (a, c); and (b, d) reactivity a (s^{-1}), (b, d). Curves determined using the two-layer deposition scheme (Eq. (16)) for (a, b) several c_0 values used in $\delta_m = c_0 \, l_m$, (a, b); and (c, d) several δ_m values, (c, d).

5   **The variations obtained using the one-layer deposition scheme with (Eq. (18)) and without (Eq. (19)) waterside turbulent transfer (i.e. reaction-diffusion only) are also shown. The waterside friction velocity (u_{*_w}) used was 0.01 m s^{-1}.**

There are further considerations to the parameterisations. There is uncertainty in the parameterisations (20)–(23), particularly in the second-order rate coefficient k for which there is a paucity of data. The expression (21) is based on the data from Magi

10   et al. (1997) which are plotted in Figure 4 with the associated uncertainty. Also, plotted are the single data points from Garland et al. (1980), Hu et al. (1995) and Liu et al. (2001). Clearly there is a large scatter in the data. Five optionseases are

considered (option 6 is discussed later) with regards to parameterising k via an exponential fit of the form Eq. (21): 1) only consider the data of Magi et al. (1997) (so the fit is the same as Eq. (21) with stated p and q values); 2) consider all the data (which gives $p = 2349.2$ and $q = 29.2$); 3) consider all the data except the data point of Hu et al. (1995) which is treated as an outlier (which gives $p = 5632.9$ and $q = 40.3$); 4) assume a constant $\delta_m = 3$ μm with k given by Eq. (21) using

5 only the data of Magi et al. (1997); and 5) assume a constant $k = 2 \times 10^9$ M^{-1} s^{-1} as in MacDonald et al. (2014). In Figure 3a and Figure 3b, all five curves fall within the two asymptotic limits (equivalent to $c_0 \rightarrow 0$ and $c_0 \rightarrow \infty$). The $c_0 = 0.4$ curve roughly lies in the middle of the two asymptotic limits and this value of c_0 was used in calculating $\delta_m = c_0 l_m$ in all the above options, except option (4) which does not need a specification of c_0 (but there will be an implied variation of c_0 through the relation $c_0 = \delta_m / l_m$). Figure 5 shows the variation of αv_{dw} calculated from Eq. (16) as a

10 function of SST for the above five options. All five options provide qualitatively similar variations of αv_{dw} with SST, but when compared with the cruise measurements of oceanic deposition velocities (v_d) discussed later (which themselves have substantial scatter) in Section 4.1, options (3) and (4) provide better agreement overall with the measurements compared to the other options (noting that v_d is dominated by the term αv_{dw} for water, with $v_d \leq \alpha v_{dw}$). Option (3) tends to underestimate the observed deposition velocities by roughly 15% for SSTs less than around 12°C whereas option (4) tends to

15 overestimate them by about the same degree. For higher SSTs, both options perform similarly, with option (4) being very slightly better for SSTs greater than 20°C, within the scatter of the measurements. In all the calculations below we have used option (4) for δ_m and k in ACCESS-UKCA.

We also include in Figure 5 an additional curve as option 6 which is the same as option 4 but using the Chance et al. (2014) parameterisation for iodide concentration (in molar)

$$[I^-] = [0.225(T_s - 273.16)^2 + 19] \times 10^{-9}. \tag{24}$$

20 Compared to option 4, option 6 results in larger αv_{dw} 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 and 33%, respectively. Consequently, option 6 would overestimate the observed ozone deposition velocity data presented later in Figure 7, 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

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deposition velocity obtained are comparable to those obtained using option 4 for the same δ_m. This is because a larger iodide concentration is compensated by a lower k in the expression for reactivity $a(=k.[I^-])$ which is what goes directly into the deposition velocity calculation.

Clearly there is significant uncertainty in the representation of iodide concentration $[I^-]$ and k, and certain choices of the input parameterisations can describe deposition velocity observations better. Overall, the calculation of ozone deposition velocity using the model presented here is a rather poorly constrained problem where multiple choices of input parameters can give the same or very similar calculated deposition velocity. The best constrained at this stage is the comparison of the calculated deposition velocity with that observed.

In the calculations below, unless otherwise stated, we have used option 4 for δ_m and k. In Section 4.1, this option 4 is used for calculating v_d in ACCESS-UKCA and comparing the modelled v_d values with measurements and with other deposition schemes/configurations. In Section 5.3 we estimate a measure of uncertainty in our deposition flux estimates taking into account the scatter in the ocean deposition velocity data used.
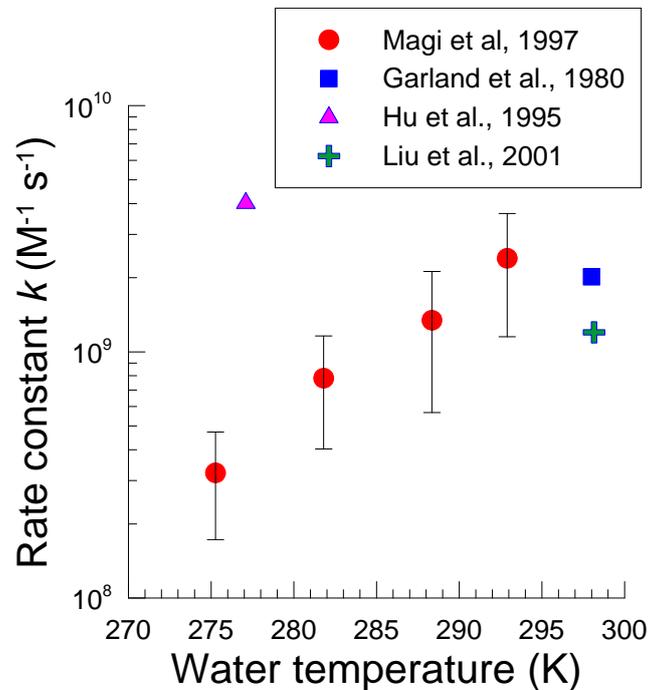
Figure 4: The second-order rate coefficient (*k*) for the ozone-iodide reaction as a function of water temperature. Data from various studies are shown.
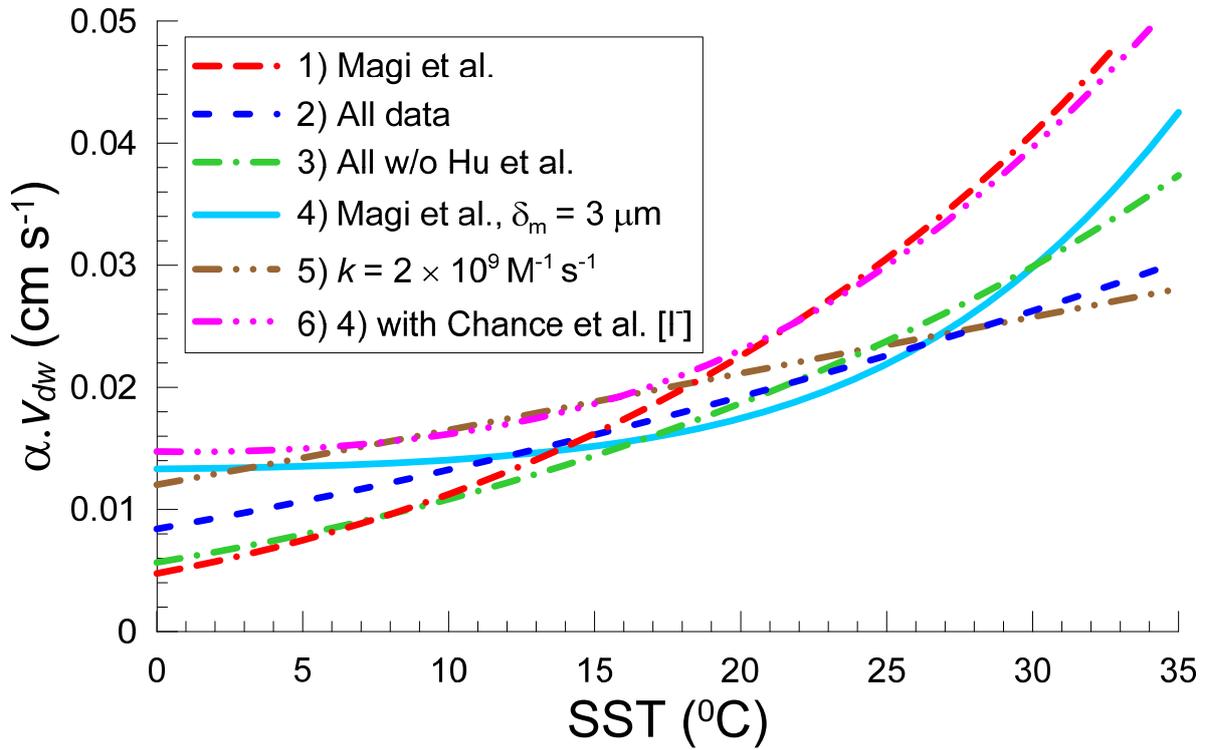
Figure 5: Variation of the oceanic component of ozone dry deposition velocity multiplied by ozone solubility, αv_{dw} ($= 1/r_c$), as a function of sea surface temperature (SST, °C). Curves determined using the two-layer deposition scheme (Eq. (16)) for various options for parameterising the second-order rate coefficient (*k*) (see text). The waterside friction velocity (u_{*w}) used was 0.01 m s⁻¹.

2.3 Impact of ozone reaction with dissolved organic carbon (DOC)

Some studies have considered the impact on dry deposition of ozone reaction with dissolved compounds other than iodide. In general, the inclusion of additional reactions in the deposition mechanism enhances the ozone loss to the ocean and thus increase deposition velocities. 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 (hence most important) in most cases. In their global modelling, Ganzeveld et al. (2009) included ozone reaction with chlorophyll-a as a first order approximation to

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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) (a measure 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 studies that have compared modelled deposition velocities involving the impact of the aqueous O_3-DOC reaction with the open-ocean observations of Helmig et al. (2012) and their dependence on SST. ~~model data later~~ It is instructive to carry out a simple sensitivity analysis involving ozone reaction with DOC. (Our new two-layer parameterisation is applicable to any other chemical compounds that are taken up by the oceanic mixing layer.)

For open ocean surface waters, Hansell et al. (2009) report DOC concentration values of 70–80 µM 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 DOC-O_3 reaction. Coleman et al. (2010) empirically derived $k = 3.44 \times 10^6$ M^{-1} s^{-1} based on data fitting, whereas Sarwar et al. (2016) used $k = 4.0 \times 10^6$ M^{-1} 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). This reactivity value lies within the range of iodide-O_3 reactivity in Figure 3.

Clearly there is considerable uncertainty in k for the DOC-O_3 reaction, and in the DOC concentration and its variability. Dependencies of k, such as how it may vary with SST, are not known. For our purposes, we use a mean $k = 3.7 \times 10^6$ M^{-1} s^{-1} (which lies is in the middle of the two values noted above) and a DOC concentration of 52 µM (Massicotte et al., 2017) in our two-layer scheme, together with an integrated chemical loss rate $a = \sum k_i C_i$, where the summation is over the iodide and DOC reactions with ozone ($i = 1, 2$).

Figure 6 shows the variation of αv_{dw} as a function of SST determined using our two-layer deposition scheme incorporating the ozone reaction with: (1) only iodide (this curve is the same as option 4 in Figure 5, with $\delta_m = 3$ µm), (2) only DOC, and

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(3) 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 has no impact on αv_{dw} (not shown). When only DOC is considered, αv_{dw} decreases with SST. Given that the αv_{dw} term dominates in the determination of v_d, the behaviour of the former represents that of the latter. In

5 Section 4.1 below, we show that the addition of DOC in the deposition scheme deteriorates the model-data agreement for deposition velocity. (We note that for coastal waters, not explicitly investigated here (see Section 4.2), the case may be different.) 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 k value for the DOC-O_3 reaction that decreases with SST (like that for the iodide-O_3 reaction) could explain the deposition velocity data better but any such k observations are lacking at present. ~~explicitly~~

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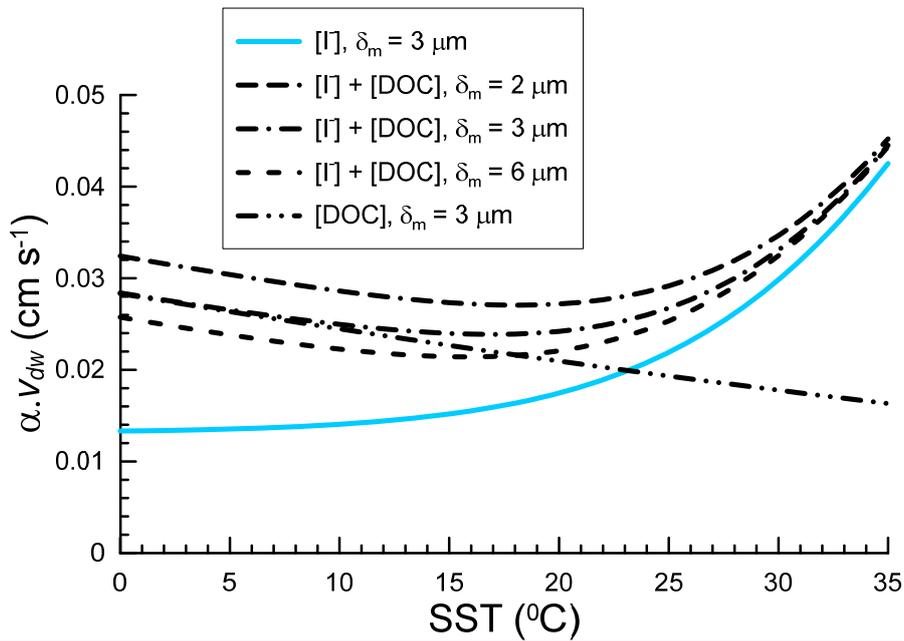
Figure 6: Variation of the oceanic component of ozone dry deposition velocity multiplied by ozone solubility, αv_{dw} ($= 1/r_c$), as a function of sea surface temperature. Curves determined using the present two-layer deposition scheme incorporating the ozone reaction with iodide [I-], dissolved organic carbon [DOC], and the two reactions together ([I-] + [DOC]). The waterside friction
15 **velocity (u_{*w}) used was 0.01 m s⁻¹.**

3 ACCESS-UKCA chemistry-climate modelling system

The two-layer dry deposition scheme developed above was incorporated into the UKCA ~~Chemistry and Aerosol (UKCA,~~ (http://www.ukca.ac.uk) global atmospheric composition model (~~at UM vn8.4; see~~ Morgenstern et al., 2009; Abraham et al., 2012; O'Connor, 2014) which is a component in ~~the Australian Community Climate and Earth System Simulator (~~ACCESS

5 (Bi et al., 2013; Woodhouse et al., 2015). The physical atmosphere component of ACCESS-UKCA is the same as the UK Met Office's Unified Model (UM) (at UM vn8.4; Walters et al., 2014). In our simulations, ACCESS-UKCA is essentially 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. The particular UKCA configuration used here (at UM vn8.4) is the so-called Chemistry of the Stratosphere and Troposphere

10 (CheST)~~, which includes O$_x$, HO$_x$, NO$_x$ and volatile organic carbon chemistry in addition to bromine and chlorine chemistry relevant for stratospheric ozone~~. ACCESS-UKCA uses ~~an atmosphere only configuration with~~ the monthly-mean sea surface temperature and sea ice fields prescribed from the Atmospheric Model Intercomparison project (AMIP). The atmospheric model has a horizontal resolution of 1.875° in longitude and 1.25° in latitude, and 85 levels extending from the surface to approximately 85 km (the N96L85 configuration). The model was nudged to the ERA-Interim meteorological

15 reanalyses (Dee et al., 2011), given on pressure levels, for the horizontal wind and potential temperature in the free troposphere (Uhe and Thatcher, 2015). Other model setup details including monthly-varying emissions are as in Woodhouse et al. (2015)~~, except that the GFED4s (http://www.globalfiredata.org; van der Werf et al., 2017) rather than the ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) biomass burning emissions were used in the present study to incorporate interannual variability of these emissions~~.

20 There are nine surface types in the model, namely broad-leaf trees, needle-leaf trees, C3 grass, C4 grass, shrub, urban, water, bare soil, and land ice. For every ~~any particular~~ surface grid box the three resistances r_a, r_b and r_c are calculated for each surface type and a corresponding v_d is then computed. For the water surface, standard expressions for r_a and r_b are used by ACCESS-UKCA in Eq. (2) (see Abraham et al., 2012; Luhar et al., 2017) and r_c is computed using Eq. (17) together with Eq. ~~the new expression~~ (16). Currently there is only one water surface type in the model, so the same deposition scheme

25 is used for both seawater and freshwater. The SSTs prescribed in the model for every grid box vary with time and are used in the input parameterisations (20)–(24). A grid-box mean deposition velocity and the corresponding loss rate ~~is~~ are ~~then~~ calculated using the individual deposition velocities weighted by the fractions of the surface types present in the grid box and this loss rate is applied to the lowest model grid box in the species mass conservation equation. For a coastal grid box that also includes fractions of non-water surfaces, we use the two-layer deposition scheme when the fraction of the water surface

30 in the grid box is greater than 60%. In all other cases the default Wesely (1989) scheme for v_d is used, including the use of

r_c = 2200 s m^{-1} for the water surface.

19

The ozone dry deposition velocity in the model is solely a function of parameters of the physical component of the model (e.g., SST, flow properties and turbulent mixing, and surface characteristics) and prescribed input parameters (e.g., reactivity, ozone molecular diffusivity and solubility in water), and is unrelated to the tropospheric ozone chemistry within the model.

5 Ozone dry deposition budgets can be better constrained by using tropospheric ozone reanalyses which are taken as a more reliable source of ozone data than those obtained by models alone. Below, we follow this approach, in which the gridded 3-hourly MACC global reanalyses of near-surface ozone for the period 2003–2012 (Inness et al., 2013; http://apps.ecmwf.int/datasets/data/macc-reanalysis) are multiplied by the gridded 3-hourly dry deposition velocities obtained from ACCESS-UKCA to calculate ozone deposition flux (and hence the annual deposition loss). Because we use
10 the MACC ozone the derived deposition fluxes do not depend on ACCESS-UKCA's ozone chemistry.

4 Ozone dry deposition velocity to the ocean

4.1 Comparison with observations

We use the ozone dry deposition velocity measurements of Helmig et al. (2012) taken over the open ocean from a ship-based eddy-covariance ozone flux system during 2006–2008 which spanned 45°N to 50°S. Additional details of these data are
15 given by Bariteau et al. (2010). Surface based ozone flux stations employing the eddy-covariance technique enables a direct measurement of ozone dry deposition velocity. The data of Helmig et al. (2012) are the only such measurements available to date over the open ocean. These authors also summarise deposition velocity measurements reported in earlier studies, which are very sparse and none of these studies involved a surface-based eddy-covariance technique over the open ocean (there were a few data points for coastal locations and from aircraft-based systems using such a technique). Given the substantially
20 larger sample size for a range of SST, and the (perceived) use of improved instrumentation and analysis techniques in the cruise measurements of Helmig et al. (2012) compared to those reported by earlier studies, we only consider the cruise data.

The ship-based experiments were conducted on five cruises, namely: (1) TexAQS06 (July 7 to September 12, 2006), (2) STRATUS06 (October 9–27, 2006), (3) GOMECC07 (July 11 to August 4, 2007), (4) GasEx08 (February 29 to April 11, 2008), and (5) AMMA08 cruises (April 27 to May 18, 2008). The respective areas covered were: (1) North-western Gulf of
25 Mexico, (2) the persistent stratus cloud region off Chile in the eastern Pacific Ocean, (3) the Gulf of Mexico and the US east coast, (4) the Southern Ocean, and (5) the southern and northern Atlantic Ocean. Helmig et al. (2012) present bin-averaged deposition velocity data as a function of SST and wind speed for each of the five cruises. As in Luhar et al. (2017), the v_d versus SST cruise data used for comparison with the model are those with the wind speed dependence retained (Ludovic Bariteau, personal communication, 2016) and not the data originally reported by Helmig et al. (2012) in which the wind-
30 speed dependence was removed. While this approach is logically correct, there is not a large difference between the data with and without the wind-speed dependence.

ACCESS-UKCA output including dry deposition parameters is available at 3-h time intervals and also as monthly averages over the period 2003–2012, which covers the time period of the Helmig et al. (2012) observations. Because the data are averaged with respect to SST or wind-speed bins for each cruise and as a result there is no explicit dependence present as to the exact timings and locations of the data along a cruise track, we used the same methodology as that in Luhar et al. (2017)

5   for comparing the v_d data with ACCESS-UKCA. In summary, as the months corresponding to the cruise experiments are known, the model monthly averages matching the experimental months were selected. For a given month, the monthly-averaged model output was extracted at a series of grid-boxpoint locations (fully covered by water) with almost uniform spacing along the tracks of the experimental cruises, and the modelled values at these locationspoints were used for comparison with the measurements. This is an approximate matching of the deposition velocity data and the modelled values

10   in terms of time and location.

Figure 7 shows the observed ozone dry deposition velocity (v_d) as a function of SST from the five field experiments and the corresponding values obtained from the ACCESS-UKCA model using the new two-layer scheme (Eq. (16)). The SST range for the measurements is 2–33 °C with the lowest values being for GasEx08 and the highest for TexAQS06 and GOMECC07. Despite the large fluctuations within the field data, an increasing trend of v_d with SST is clearly noticeableidentifiable.

15   Helmig et al. (2012) compiled a historical record of ozone deposition velocities over water (their Figure 4) starting from 1969 which lie within the range 0.01–0.15 cm s^{-1}. The range of the cruise measurements in Figure 7, which are the only direct, open-ocean flux measurements, is 0.005 – 0.06 cm s^{-1} which is on the lower end of the range of the historical data. As stated by Helmig et al. (2012), the earlier experiments, lacking ocean-deployable measurement techniques, are biased toward coastal waters which may carry higher concentrations of ozone reactants that lead to increased deposition velocities. Another

20   reason for the difference could be the use of improved experimental techniques in the cruise measurements.

Figure 8 presents a scatter plot of the observed deposition velocities averaged over the data from each of the five cruise experiments versus the corresponding values obtained from the model (with the error bars representing one standard deviation variation). The correlation between the modelled v_d and data is good ($r^2 = 0.86$). Although In Figure 7 and Figure 8, ACCESS UKCAshow that the model is able to describe the absolute magnitude and the sea surface temperature

25   dependence and the absolute magnitude of the field measurements, with the modelled variation almost passing through the middle of the data. However, it is clear that there are some significant fluctuations in the measurements, particularly for SSTs within the range 8–24 °C, that are not present as prominently in the modelled values. There could be a number of possible reasons for this: 1) the monthly-averaged modelled deposition values used and the approximate method followed for matching the data and for time and location; 2) the dissolved iodide concentrations are not directly available and the

30   parameterisation used here only depends on SST; and 3) the observed SSTs used in our atmosphere-only model set up are monthly averaged—a model setup with a coupled ocean model that interacts with the atmosphere at sub-diurnal intervals would provide a better SST variability which would in turn influence the variability in the iodide concentration and thus impact the modelled deposition velocity. Needless to say, additional measurements of ozone dry deposition velocity and

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governing parameters (e.g. iodide concentrations, SST, DOC, nitrate etc.) with greater temporal and spatial coverage would help to further assess the scheme.

~~Overall, t~~The model results in Figure 7 are very similar to those obtained by Luhar et al. (2017) using their two-layer reactivity scheme (their Figure 6), but unlike the old two-layer scheme the new two-layer scheme performs well for the right reasons—as discussed earlier the old scheme artificially limits chemical reactivity to the reaction-diffusion sublayer in order to compensate for the overestimation of the impact of waterside turbulence due to a turbulent diffusivity parameterisation that is not appropriate very close to the water surface. ~~The model performance presented in Figure 4 leads us to conclude that new scheme performs as well as the two-layer reactivity scheme in Luhar et al. (2017) but unlike the latter the new scheme does not unrealistically/artificially limit the chemical reactivity to within a fixed depth of the order of a few micrometres and has consistent asymptotic limits.~~
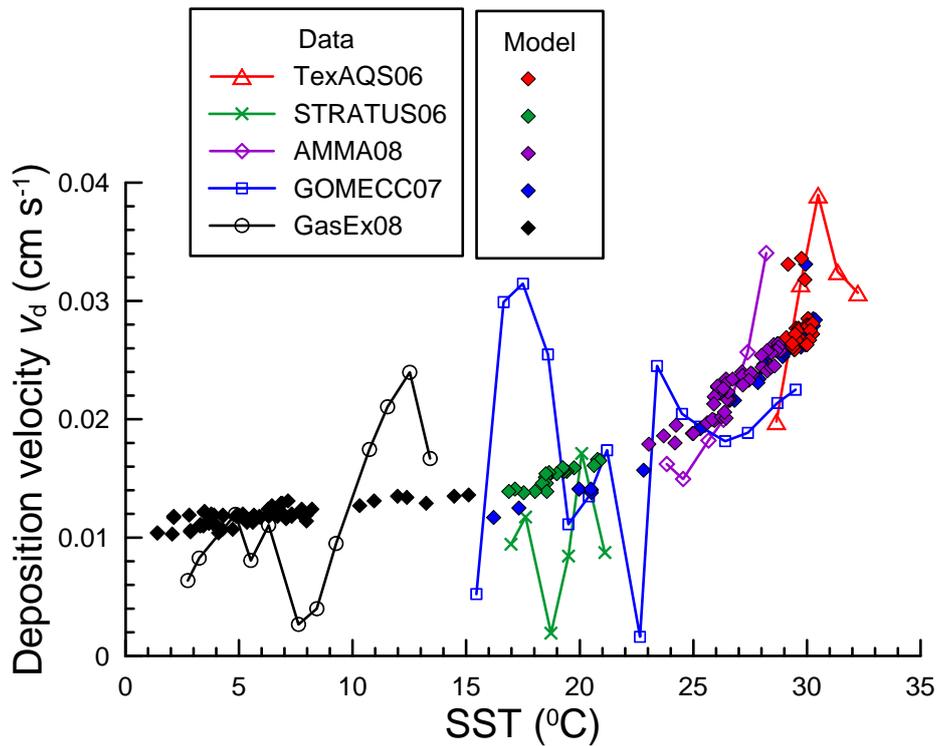
Figure 7: Ozone dry deposition velocity (v_d) as a function of sea surface temperature (SST) from five field experiments (Helmig et al., 2012; Ludovic Bariteau, personal communication, 2016) and the corresponding values obtained from the ACCESS-UKCA model using the new two-layer scheme (Eq. (16)) for ozone deposition to the ocean.
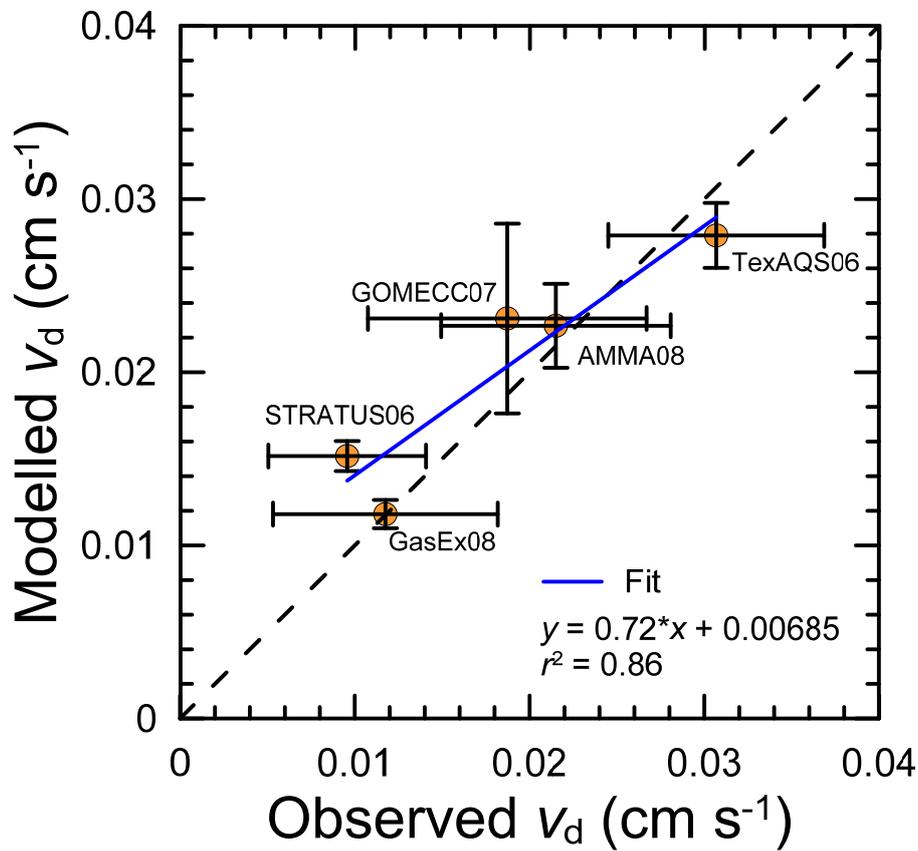
The performance with ranking of the various ozone dry deposition velocity schemes/configurations for seawater discussed above compared to the observations shown in Figure 7 is summarised in Table 1 in terms of some commonly used performance measures, which were calculated using the bin-averaged modelled and observed v_d values within SST bins of 5°C lying within the range 1–35°C (sample size = 7). The measures used are the ratio of modelled mean to observed mean ($\overline{M} / \overline{O}$), fractional bias (*FB*, varies between +2 (underestimation) and -2 (overestimation)), normalised mean square error (*NMSE*), and index of agreement (*IOA*, varies between 0 and 1). For a perfect agreement, the values of these parameters should be 1, 0, 0 and 1, respectively. Unlike the correlation coefficient (r^2), IOA is sensitive to differences between the observed and model means as well as to certain changes in proportionality, and is thus preferred.

In the schemes in Table 1, unless stated otherwise, $\delta_m = 3$ µm, the second-order rate coefficient is given by Eq. (21) using only the data of Magi et al. (1997), and the MacDonald et al. (2014) iodide parameterisation (20) is used. In Table 1, the two-layer scheme (used in the model-data comparison plots above and in all the calculations below) performs the best, followed by the same scheme with the Chance et al. (2014) iodide parameterisation (24) which overestimates the v_d data.

5   The next two schemes in the ranking are the one-layer scheme of Fairall et al. (2007) without waterside turbulence, Eq. (19), which is equivalent to the diffusion-reaction formulation considered by Garland et al. (1980)) and the two-layer scheme that also includes DOC – these two schemes underestimate and overestimate, respectively, the deposition velocity measurements. The largest overestimation of the v_d data is through the use of constant $r_c = 2200$ s m^{-1} and to a slightly lesser extent by the one-layer scheme of Fairall et al. (2007), Eq. (18). The above model-data comparison suggests that our two-layer scheme

10   with the soundly based iodide mechanism is able to describe well the deposition velocity measurements for the open ocean and we use this setup subsequently.

Table 1: Performance statistics of various ozone dry deposition velocity schemes for seawater compared to the observations shown in Figure 7[1].

Scheme	$\overline{M}/\overline{O}$	FB	NMSE	IOA	Ranking
Two-layer scheme	0.99	0.01	0.06	0.92	1
Two-layer scheme with Chance et al. (2014) $[I^-]$	1.20	-0.19	0.09	0.88	2
Two-layer scheme with DOC	1.30	-0.26	0.14	0.73	4
One-layer scheme of Fairall et al. (2007)	1.63	-0.48	0.29	0.65	5
One-layer scheme of Fairall et al. (2007) without waterside turbulence	0.73	0.32	0.18	0.87	3
Wesely's (1989) scheme with $r_c = 2200$ s m^{-1}	1.90	-0.62	0.51	0.45	6

5

[1]Observed mean ($\overline{O}$), modelled mean ($\overline{M}$), fractional bias (FB) = $2(\overline{O}-\overline{M})/(\overline{O}+\overline{M})$, normalised mean square error

(NMSE) = $\overline{(M-O)^2}/(\overline{M}.\overline{O})$, and index of agreement (IOA) = $1-[\overline{(M-O)^2}/\overline{(|M-\overline{O}|+|O-\overline{O}|)^2}]$.

4.2 Global distribution

10   Figure 9 shows the distribution of ozone deposition velocity (cm s^{-1}) to the ocean (not including sea ice) obtained using the new two-layer scheme within ACCESS-UKCA for the year 2005. The year 2005 is chosen to illustrate the spatial variability because, as will be discussed later, the MACC ozone reanalysis has the least bias for this year (however, we note that the interannual variability of the modelled deposition velocity fields is small). The largest open-ocean deposition velocities occur in the tropics where both the observed (Chance et al., 2014; MacDonald et al., 2014) and parameterised iodide

15   concentrations, which are proportional to SST, are the largest, and the magnitude of deposition velocities decreases with increasing latitude.
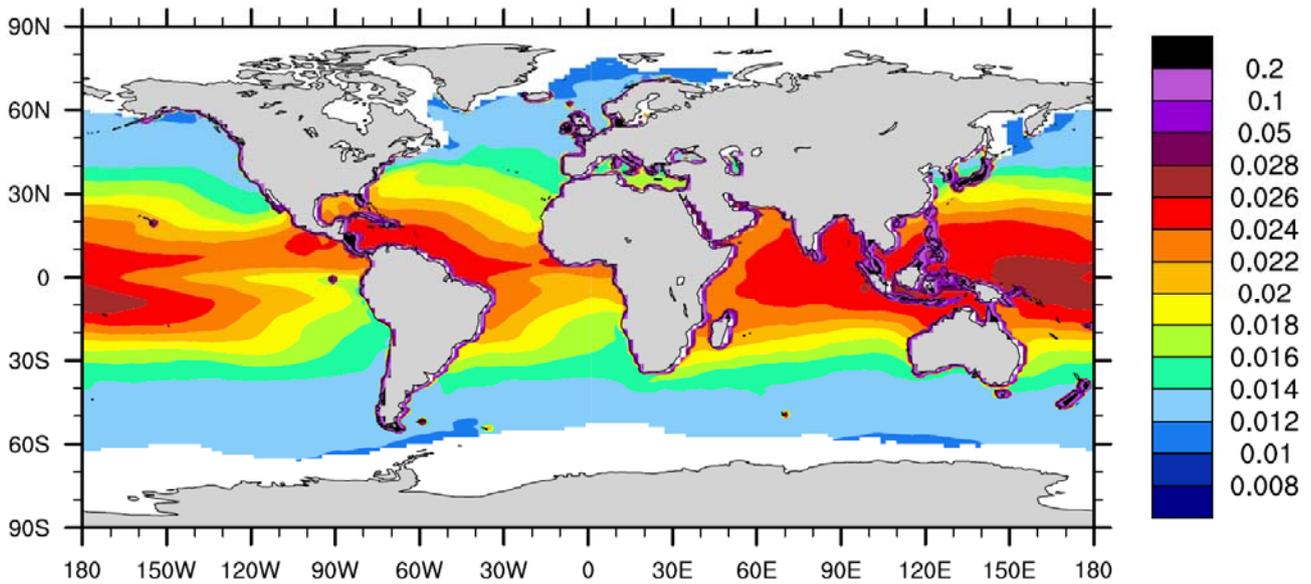
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Figure 9: Annual mean ozone dry deposition velocity (v_d, cm s^{-1}) to the ocean for the year 2005 obtained from the ACCESS-UKCA model incorporating with the oceanic dry deposition scheme proposed in this paper. Deposition velocities over coastal grid boxes are also shown.

Figure 9 also shows the modelled deposition velocities over the coastal grid boxes that contain some fractions of both water and land surfaces. For such grid boxes, the modelled deposition velocities are typically 0.1–0.2 cm s^{-1} which are much greater than those for grid boxes fully covered by water. This is because terrestrial surfaces have higher deposition velocities than water and also partly because of the use of the larger deposition rate through the use of r_c = 2200 s m^{-1} for the water surface tile when its fraction is less than 60%. There is some evidence that the measured ozone deposition velocities over coastal waters are larger than those over open oceans (e.g. Coleman et al., 2010; Bariteau et al., 2010), which could be due to factors such as stronger chemical reactivity and turbulence, and advection from land if the distance between the monitor and coastline (i.e. fetch) is limited. Our approach for treating coastal water grid boxes is qualitatively consistent with ozone deposition velocities over coastal waters being larger than over the open sea, but here we have not examined or included any particular mechanistic processes that are relevant for coastal waters. High resolution, regional- or small scale-modelling could be useful in exploring such processes and their spatial and temporal scale and variability.

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5 Dry deposition budgets using the MACC ozone reanalysis

Ozone deposition fluxes are calculated from ozone concentrations in near-surface air and associated ozone deposition velocities. In this study, the MACC near-surface ozone data are used.

The global model used for deriving the MACC reanalysis consists of the European Centre for Medium-Range Weather Forecasts' (ECMWF) Integrated Forecast System (IFS) coupled to the MOZART (Model for OZone And Related chemical Tracers) chemistry transport model (Kinnison et al., 2007). The modelling system makes use of four-dimensional variational data assimilation to combine satellite retrievals of carbon monoxide, ozone, nitrogen oxides as well as the standard meteorological observations with the numerical model in order to produce a reanalysis of atmospheric composition. For ozone, profile, total column and partial column data are assimilated.

The MACC reanalysis has been evaluated against multiple observational networks of ground-based measurements, ozonesondes, and aircraft and satellite data (Inness et al., 2013; Gaudel et al., 2015; Giordano et al., 2015; Katragkou et al., 2015; http://macc.copernicus-atmosphere.eu/documents/maccii/deliverables/val/MACCII_VAL_DEL_D_83.6_REAreport04_20140729.pdf). These evaluation studies suggest that the assimilation of composition data generally improves the modelled tropospheric ozone fields, noting that there are some exceptions which highlight the fact that assimilation does not always yield a close match with observations and that the results depend on several factors such as the quality and quantity of data being assimilated, and the type of modelling system and the data assimilation methodology used.

The MACC composition reanalysis is given at 60 hybrid sigma-pressure levels, from near the surface (1012 hPa, 10 m Geometric Altitude) to 0.1 hPa (~ 65.6 km) covering both the troposphere and the stratosphere. The global MACC ozone concentration data (given as mass mixing ratios) at the 10-m level (L60) were extracted at a horizontal resolution of $1.125° × 1.125°$ at 3-h time intervals, and were re-gridded to the ACCESS-UKCA N96 horizontal grid using bilinear interpolation. These data were then multiplied by the time-matched 3-h deposition velocity fields obtained from ACCESS-UKCA (with the new two-layer ocean deposition scheme) to calculateobtain the deposition flux and total global deposition loss. The use of a 3-hourly temporal resolution, which is the finest available for the MACC reanalysis, ensures that anythe (e.g. diurnal) covariance of near-surface ozone and deposition velocity is accounted for in calculating total dry deposition. We find that this This diurnal covariance based on the 3-h fields for the ocean is likely to be small and leads to a small increase of 1.4% in the annual deposition flux to the ocean compared to when monthly averaged fields of deposition velocity and ozone concentration are used. On the other hand, this increase is about 28% over land surfaces, demonstrating a considerable degree of covariance. The likely reason for the small covariance over the ocean surface is that the near-surface ozone is influenced more by vertical turbulent exchange than by dry deposition due to the relatively small values of v_d over such surfaces. On the other hand, deposition velocities to land surfaces are large and they influence the near-surface ozone to a greater degree than turbulent vertical air exchange particularly during stable conditions. as parameterised in our model

The MACC data for all ten years were used, which is useful for examining interannual variability of deposition.

5.1 Global distribution of surface ozone and dry deposition flux

As an example, Figure 10a shows the mean surface ozone ~~concentration~~ mixing ratio (ppbv) based on the MACC reanalysis for 2005. It is apparent that relatively high ~~concentrations~~ values occur in the Northern Hemisphere, particularly in the mid latitudes which can be attributed to the larger precursor emissions in these areas. The ~~concentrations~~ mixing ratios over the ocean are generally greater than those over the land, which can be partly attributed to the smaller dry deposition velocities to the ocean and hence lower deposition. There are ozone minima around the Equator, especially over the Pacific Ocean.

The annual oceanic ozone dry deposition flux obtained using the MACC ozone reanalysis coupled with the deposition velocities from ACCESS-UKCA averaged over 2005 presented in Figure 10b indicates that the largest flux values between 0.014–0.02 μg m^{-2} s^{-1} are observed within latitudes 10–40°N. The flux in the Southern Hemisphere is lower than that in the Northern Hemisphere and decreases with latitude.
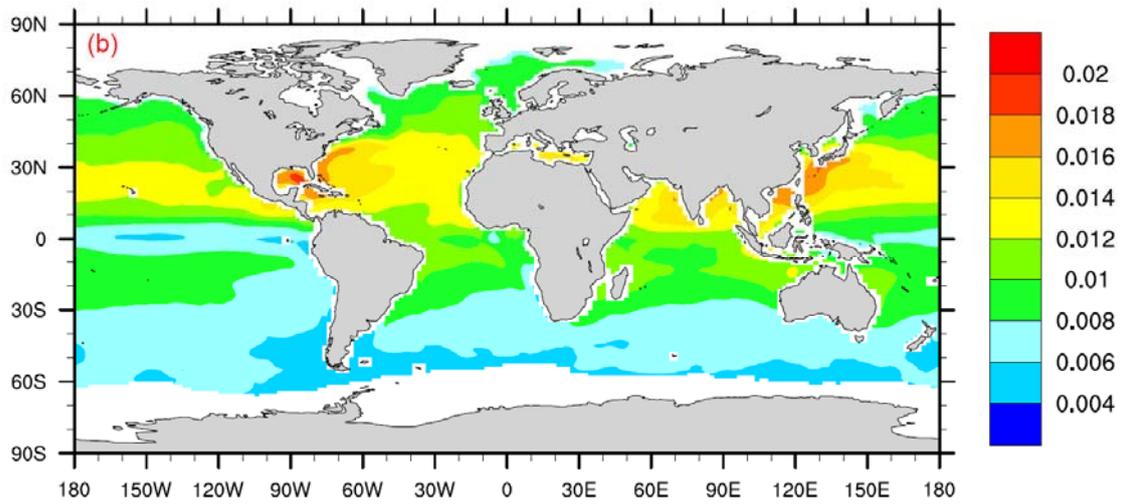

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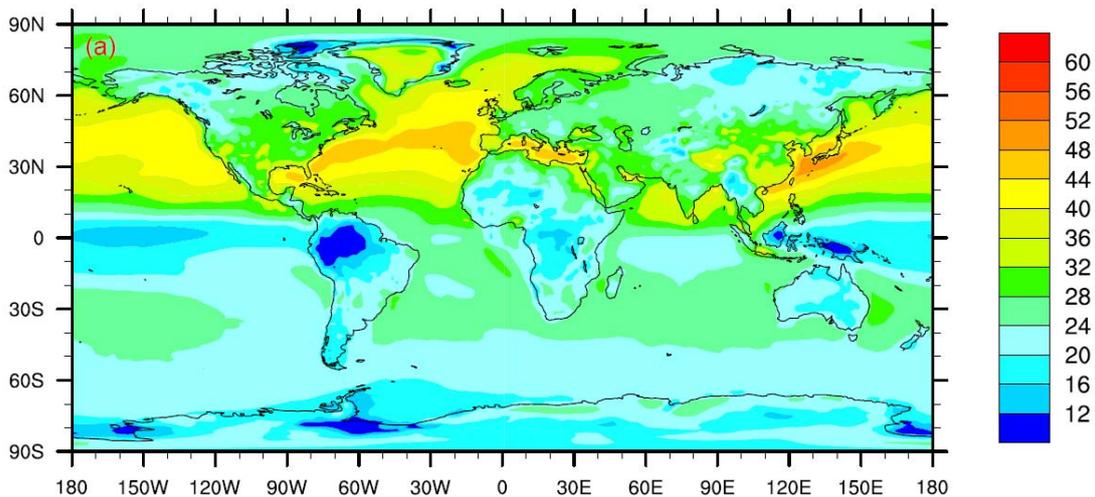
Figure 10: (a) Mean surface ozone ~~concentration~~ <u>mixing ratio</u> (ppbv) and (b) mean oceanic ozone dry deposition flux (μg m⁻² s⁻¹), for 2005 obtained from the MACC reanalysis.

5

5.2 Dry deposition budgets

Figure 11 presents the annual ozone dry deposition obtained using the MACC reanalysis as a function of year. The oceanic deposition (Figure 11a) lies between 86.5–108.3 Tg O_3 yr⁻¹ with the average being 93.9 ± 7.5 Tg yr⁻¹ ~~(see Table 1)~~ where the ~~uncertainty~~ <u>error bounds</u> correspond~~s~~ to one standard deviation and <u>are</u>~~is~~ solely due to interannual variation. <u>(In our</u>

10 <u>calculations, the oceanic component excludes sea ice and coastal grid boxes and on average covers 62.4% of the Earth's surface.)</u> The largest deposition occurs for 2005–2007. Oceanic deposition in the Northern Hemisphere (49.0 ± 3.4 Tg yr⁻¹) is somewhat larger than that in the Southern Hemisphere (44.9 ± 4.5 Tg yr⁻¹) due to the higher O_3 concentrations and slightly larger oceanic deposition velocities in the former, although the Earth's area covered by the ocean is larger by approximately 30% in the Southern Hemisphere. <u>The main reason why the dry deposition velocities to the ocean in the Northern</u>

15 <u>Hemisphere are larger (e.g. 0.020 vs. 0.017 m s⁻¹ on average for the year 2005) is that the SSTs for the Northern Hemisphere are warmer than those for the Southern Hemisphere (e.g. 295.3 K vs. 291.2 K on average for the same year). In our formulation, deposition velocity to the ocean is dominated by the surface-resistance term (r_c) which in turn depends on SST. Overall the higher the SST the higher the oceanic deposition velocity.</u> There is a hint in Figure 11a that the pattern of interannual variability of the global oceanic deposition follows that for the Southern Hemisphere more closely.
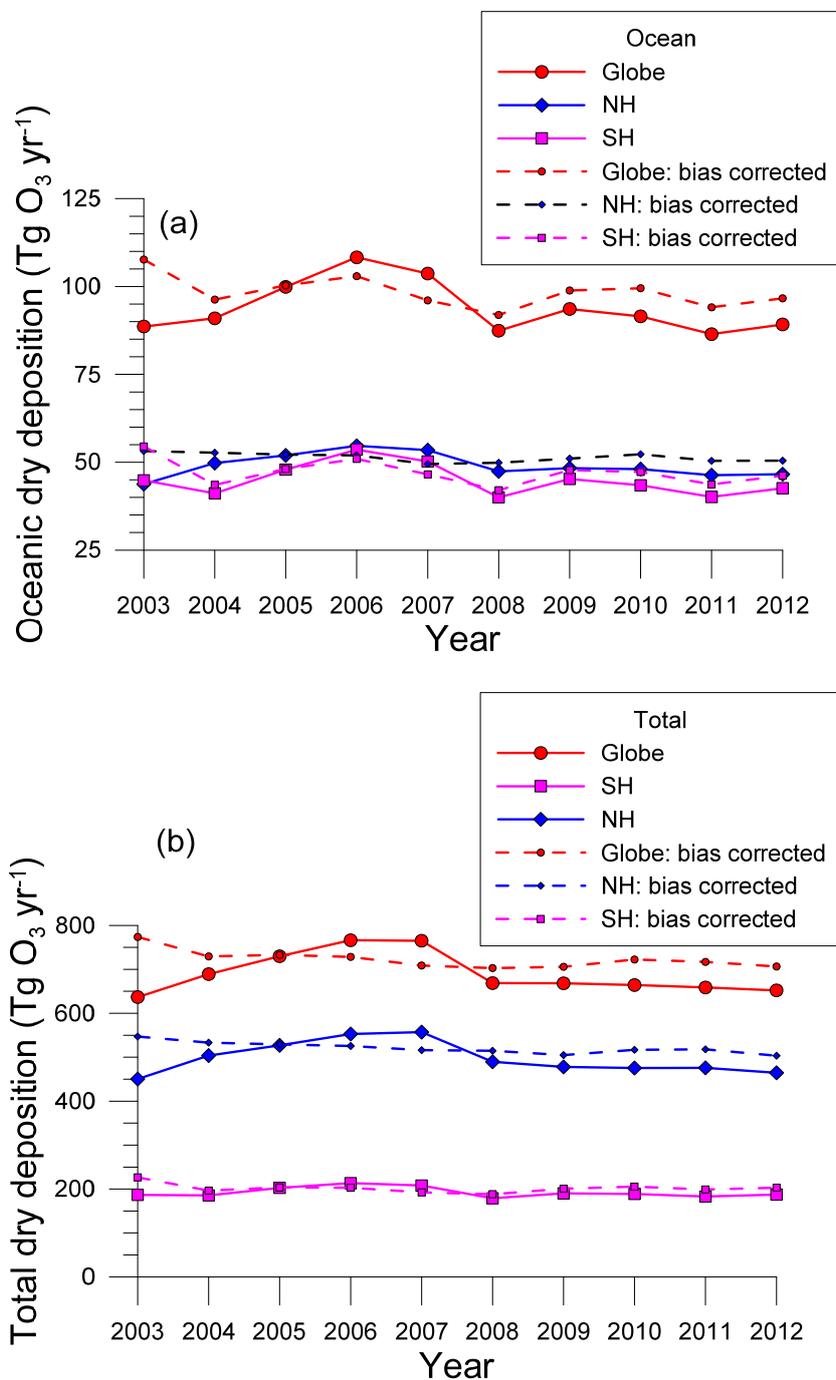
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Figure 11: Annual variation of the dry deposition of ozone (Tg O$_3$ yr^{-1}) obtained using the ACCESS-UKCA model (dotted lines) and the MACC reanalysis (solid lines): (a) the ocean component and (b) total. (NH = Northern Hemisphere, SH = Southern Hemisphere).

5

The variation of the global total deposition obtained using the MACC reanalysis in Figure 11b is in the range 636.9–766.3 Tg yr^{-1} and the mean value is 689.9 ± 47.0 Tg yr^{-1} ~~(see also Table 1)~~ with the largest deposition amounts for 2005–2007. The total deposition to the Northern Hemisphere (497.5 ± 36.9 Tg yr^{-1}) is 72% of the total deposition and is two and a half times larger than that to the Southern Hemisphere (192.4 ± 11.4 Tg yr^{-1}) because in the former the O$_3$ concentrations are larger coupled with the larger coverage of the Earth's area by land for which deposition velocities are larger than for water. On average, deposition to the ocean is approximately 14% of the total deposition. The pattern of interannual variability of the global deposition is dominated by that for the Northern Hemisphere. This variability is driven by MACC ozone concentration changes rather than changes in deposition velocity.

The MACC reanalysis is not free from bias as demonstrated in a number of studies (e.g., Inness et al., 2013; Gaudel et al., 2015; Giordano et al., 2015; Katragkou et al., 2015). With regards to global bias in surface ozone, Figure 12 presents the annual averaged normalised median bias (%) of the MACC ozone mixing ratios relative to the Global Atmosphere Watch (GAW) surface observations (http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html) for the years 2003–2012. We have derived this bias using the seasonal bias data taken from Benedictow et al. (2014) (http://macc.copernicus-atmosphere.eu/documents/maccii/deliverables/val/MACCII_VAL_DEL_D_83.6_REAreport04_20140729.pdf). Figure 12 shows that except for the first year the bias has remained within ±10%, and has been negative since 2008. The bias is the smallest for the year 2005. The total deposition for that year is 729.8 Tg yr^{-1} of which 527.1 Tg yr^{-1} is to the Northern Hemisphere and 202.7 Tg yr^{-1} is to the Southern Hemisphere. The total oceanic deposition for that year is 99.9 Tg yr^{-1} of which 52.0 Tg yr^{-1} is to the Northern Hemisphere and 47.9 Tg yr^{-1} is to the Southern Hemisphere. Thus the total deposition to non-water surfaces is 629.9 Tg yr^{-1}.

Interestingly, the shape of the interannual variation of total deposition in Figure 11b (and also the interannual variation of total oceanic deposition in Figure 11a) is similar to that of the bias in Figure 12, suggesting that the interannual variability of dry deposition may at least partly be due to the interannual variability of bias in the MACC ozone. Figure 13 is a scatter plot of the annual averaged bias (%) in the MACC ozone versus the total global deposition and total oceanic deposition determined based on the MACC data for the years 2003–2012. The annual bias and deposition appear well correlated, with a liner correlation coefficient of $r^2 = 0.83$ for the total deposition and $r^2 = 0.65$ for the oceanic deposition. Based on the linear fits, the annual ozone deposition value corresponding to zero bias is 717.6 Tg yr^{-1} for the globe and 97.8 Tg yr^{-1} for the ocean.
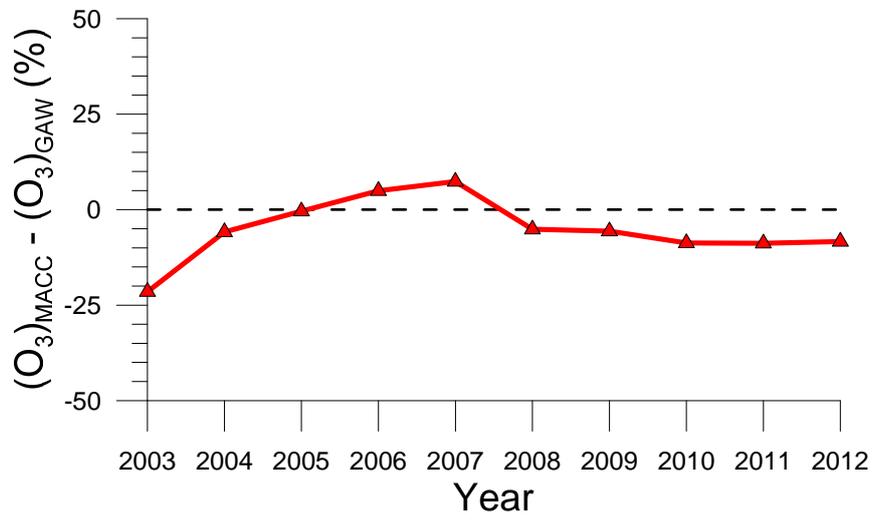
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Figure 12: Annual averaged normalised median bias (%) of the MACC ozone reanalysis mixing ratios relative to the Global Atmosphere Watch (GAW) surface observations for the years 2003–2012.
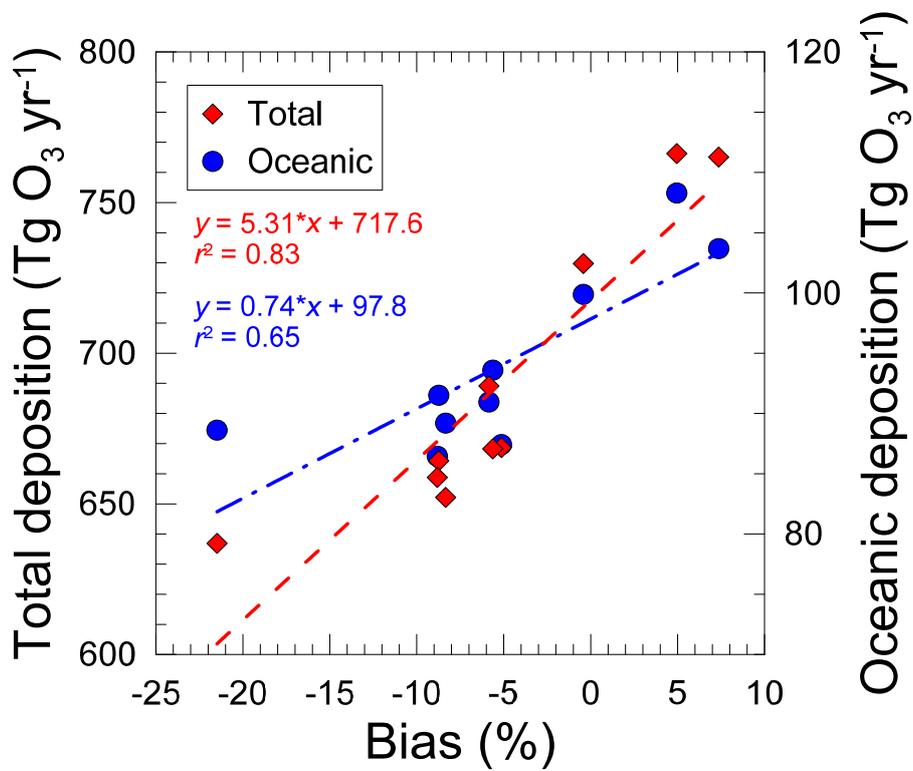

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Figure 13: Scatter plot of annual averaged normalised median bias (%) in the MACC ozone reanalysis mixing ratios relative to the Global Atmosphere Watch (GAW) surface observations for the years 2003–2012 versus the total global deposition and total deposition to the ocean determined based on the MACC reanalysis. The best fit lines are also shown.

The above bias correction does not provide information ~~to~~ on annual variability without bias. A simple (but rather crude) way to correct the MACC based deposition (d_{p0}) for each year for the bias (b_s) is to calculate a new annual deposition

$$d_p = d_{p0}(1 - b_s/100)$$ and then calculate the average over the ten years and the corresponding standard deviation. By

5 assuming that the observed global bias is uniform over the land, ocean and hemispheric components, averages and standard deviations for these components can also be derived. The bias corrected deposition values are plotted in Figure 11 ~~and presented in Table 1~~. Based on these, ~~t~~The average oceanic deposition is 98.4 ± 4.5 Tg yr^{-1} and the average total global deposition is 722.8 ± 20.9 Tg yr^{-1}. The total deposition to non-water surfaces is 624.4 ± 17.4 Tg yr^{-1}. These averages are very similar to those for the year 2005 and those corresponding to the zero bias in Figure 13. The 1σ uncertainties on these figures

10 are due to interannual variability alone.

Table 2: Mean ozone dry deposition based on the MACC data for the years 2003–2012 (Tg O₃ yr⁻¹)[1], and from other studies that also report the oceanic component. The uncertainties are ±1σ.

Method	Ocean			Land			Total		
	NH	SH	Global	NH	SH	Global	NH	SH	Global
Galbally and Roy (1980)[2]	191	300	491	459	141	600	650	441	1091
Ganzeveld et al. (2009)[3]	-	-	291.5	-	-	543.5	-	-	835
Hardacre et al. (2015)[4]	-	-	340	-	-	638	646	332	978 ± 127
~~MACC~~	~~49.0 ± 3.4~~	~~44.9 ± 4.5~~	~~93.9 ± 7.5~~	~~448.5 ± 33.6~~	~~147.5 ± 7.2~~	~~596.0 ± 40.0~~	~~497.5 ± 36.9~~	~~192.4 ± 11.4~~	~~689.9 ± 47.0~~
~~MACC (bias corrected)~~	~~51.3 ± 1.3~~	~~47.1 ± 3.7~~	~~98.4 ± 4.5~~	~~469.6 ± 12.3~~	~~154.8 ± 7.3~~	~~624.4 ± 17.4~~	~~520.9 ± 13.2~~	~~201.9 ± 10.2~~	~~722.8 ± 20.9~~
Present study	51.3	47.1	98.4 ± 30.0	469.6	154.8	624.4 ± 82.0	520.9	201.9	722.8 ± 87.3

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[1]The ocean component excludes sea ice and coastal grid boxes~~cells~~ (which are included in the land component) and on average covers 62.4% of the Earth's surface; [2]In Galbally and Roy (1980), the oceanic component includes ice and there is an uncertainty of ±50% in their estimates; [3]average values from two model runs; [4]the oceanic component is based on the

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average of values from two different land-cover schemes, and the NH and SH components based on Hardacre (2017, personal communication); NH = Northern Hemisphere, SH = Southern Hemisphere.

The above MACC based deposition amounts can be compared with other studies, going as far back as Galbally and Roy (1980) (see Table 2). The total land-based deposition in Galbally and Roy (1980) is similar to the present estimates but their oceanic deposition is five times as large. This may ~~partly~~ be due to the fact that at that time there were only coastal measurements of ozone uptake by seawater with larger deposition velocities than for the open ocean.

More recently, Hardacre et al. (2015) analysed monthly ozone dry deposition fluxes from 15 global chemistry transport models (not including UKCA) driven by meteorological fields for the year 2001. These models use Wesely's scheme (1989) for the deposition velocity calculation for both water and terrestrial surfaces. ACCESS-UKCA also uses Wesely's scheme for terrestrial surfaces. A comparison of observed dry deposition fluxes with those obtained from the above global chemistry transport models for terrestrial surfaces is presented by Hardacre et al. (2015). These authors noted that differences in ozone dry deposition flux to the ocean, driven by small absolute differences in dry deposition velocity but with large areal coverage by the ocean, are the largest contributor to differences in the total global O_3 deposition compared to any other surface type. They determined that the mean total global deposition was 978 ± 127 Tg O_3 yr^{-1} where the range corresponds to one standard deviation. By using two different land-cover schemes for partitioning fluxes, they determined that deposition to the ocean was in the range 250–591 (average 361) Tg yr^{-1} across the model ensemble using one land-cover scheme that had 71.2% of the Earth's surface covered by water, and 209–538 (average 319) Tg yr^{-1} using the other that had 68.6% of the global surface covered by water. The modelling study by Ganzeveld et al. (2009) points to an oceanic dry deposition estimate of 283–300 Tg yr^{-1} and a global total of 833–837 Tg yr^{-1} (Table 2). The oceanic deposition budgets in all these studies are more than three times larger than the 98.4 Tg yr^{-1} value obtained in the present study. This much of difference cannot be explained by the slightly lower fraction of the global surface covered by water in the present calculations (i.e. 62.4%). The primary reason for this difference, as alluded earlier, is that the global chemistry transport models in these studies are all largely based on Wesely's (1989) deposition scheme which uses a constant surface resistance for water. As shown by Luhar et al. (2017) the use of $r_c = 2200$ s m^{-1} overestimates open ocean deposition velocity compared to the open-ocean measurements of Helmig et al. (2012) by a factor of 2 to 4 for cooler SSTs. The smaller oceanic deposition budget presented in this paper is consistent with these currently best available open-ocean measurements. The total deposition to non-water surfaces based on the MACC data is 624.4 Tg yr^{-1}, which is similar to 638 Tg yr^{-1} obtained by Hardacre et al. (2015) (using an average oceanic deposition of 340 Tg yr^{-1} in their calculations) and 600 Tg yr^{-1} obtained by Galbally and Roy (1980).

There are other studies that report on the total global dry deposition. Stevenson et al. (2006) report an average global ozone dry deposition of 1003 ± 200 Tg yr^{-1} for the year 2000 based on 21 models. The average deposition calculated by Wild ~~et al.~~ (2007) using 17 post 2000 modelling studies is 949 ± 222 Tg yr^{-1}, whereas that reported by Young et al. (2013) for the year

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2000 based on a subset of six models participating in the ACCMIP intercomparison study is 1094 ± 264 Tg yr^{-1}. However, these studies do not report values of the oceanic deposition separately.

It is clear from the above comparison that the land component of the total deposition remains similar in all the studies (after subtracting an oceanic contribution of ~ 300 Tg yr^{-1} from the total in the previous studies). The new estimate of dry deposition to the ocean of ~ 100 Tg O$_3$ yr^{-1} is approximately a third of the current model estimates. This reduction corresponds to an approximately 67% decrease in the modelled oceanic dry deposition and 20% decrease in the modelled total dry deposition.

Based on a simple calculation involvingUsing the tropospheric ozone budgets given in IPCC (2013) based onfollowing Young et al. (2013), we estimate that the reduction in the modelled dry deposition rate by ~ 200 Tg O$_3$ yr^{-1} over the ocean presented here (with all other factors being unchanged) results in roughly 5% increase in modelled tropospheric ozone burden and an equivalent increase in tropospheric ozone lifetime. In the marine boundary layer at mid to high latitudes, the effect of the ozone increase would be expected to be larger.

5.3 Uncertainty in annual ozone dry deposition

The (1σ) uncertainty in the global ozone deposition of 1003 ± 200 Tg yr^{-1} reported by Stevenson et al. (2006), 949 ± 222 Tg yr^{-1} by Wild (2007), 1094 ± 264 Tg yr^{-1} by Young et al. (2013) and 978 ± 127 Tg yr^{-1} by Hardacre et al. (2015) based on multi-model runs is by and large all due to model to model variations. Here we attempt a comparable uncertainty estimate.

Our modelling yields an ozone deposition loss to the ocean of 98.4 ± 4.5 Tg yr^{-1} and a total global deposition of 722.8 ± 20.9 Tg yr^{-1}, with the 1σ error bounds in these estimates only representing the 10-year interannual variability in the modelled deposition velocity and MACC concentration fields. These error bounds do not include any uncertainties that may arise due to the approximations and assumptions used in the deposition velocity (e.g. iodide concentration, reaction rate constant etc.) or MACC ozone reanalysis methodologies.

In earlier discussion of the oceanic dry deposition velocity in Section 2.2 it was identified that calculations of the reaction-diffusion length scale ($l_m = \delta_m/c_0$) based on oceanic observations of iodide and SST give results varying between 24.0–1.2 µm for the SST range 2–33°C, and it is 3 µm at 23°C. In the subsequent work in this paper a value of 3 µm is used for the depth of the reaction-diffusion sublayer (δ_m). Considering Figure 3c and Figure 3d, the waterside deposition velocity varies by at most a factor of 2 for the range of variations in δ_m that lie between the two extreme physical limits of a one-layer diffusive model and a one-layer turbulent model. These limits implicitly encompass the uncertainties in the rate constant and iodide concentrations. Assuming these limits can be described as three-sigma, we estimate that the one-sigma uncertainty in δ_m is approximately ±30%. This uncertainty can directly feed into the uncertainty of the global ozone deposition rates.

Combining it with the 1σ error bounds in the MACC ozone reanalysis gives a combined relative uncertainty of ±31% or our total oceanic deposition of 98.4 Tg yr^{-1} with an uncertainty ± 30.5 Tg yr^{-1}.

An alternate approach to estimate uncertainty for the oceanic component, which is the main focus here, is to consider the scatter in the deposition velocity observations of Helmig et al. (2012) in Figure 7, which show some large fluctuations in the v_d data that are not present in the modelled values. We take the difference between the amount of scatter in the v_d data and that in the modelled values as a measure of uncertainty that is not captured by the model. We call this difference residual uncertainty (σ_{vdr}) which we aim to account for. In order to quantify σ_{vdr}, four SST ranges, namely < 15, 15–21, 21–28 and > 28 °C were considered, which approximately correspond to the SST ranges of the cruise experiments shown in Figure 7. For each SST range, the v_d data were detrended by fitting a linear v_d versus SST regression line and the variance (σ_{vdo}^2) of the detrended data was calculated. Similarly, the variance (σ_{vdm}^2) of the detrended modelled v_d values was calculated for the same SST range. Thus $\sigma_{vdr} = (\sigma_{vdo}^2 - \sigma_{vdm}^2)^{1/2}$, and its value was 0.0046, 0.0093, 0.0049 and 0.0056 cm s^{-1} for the above SST ranges, respectively.

To calculate the uncertainty in oceanic deposition flux due to σ_{vdr}, the 3-h modelled depositions velocity at each grid point was perturbed by $\pm \sigma_{vdr}$ (which is selected from one of the above four values depending on which SST range the SST at the grid point falls into) and then multiplied with the 3-h MACC ozone fields. This was done for all 10 years which yielded the uncertainty in the oceanic ozone deposition flux due to $\pm \sigma_{vdr}$ to be ± 30.0 Tg yr^{-1} (which includes the small interannual variability of ± 4.5 Tg yr^{-1} stated earlier).

Thus for our total oceanic deposition of 98.4 Tg yr^{-1} we have two uncertainty estimates of ± 30.5 Tg yr^{-1} based on the uncertainty in the deposition velocity model and the uncertainty ± 30.0 Tg yr^{-1} based on the random differences between the model and observations for the available data. While these independent estimates agree very well, the wider issue is that the world's oceans are under-sampled with regard to ozone uptake measurements, it cannot be assumed that the available measurements are a representative sample of the ozone uptake over the world's oceans and the uncertainties, consequently, are probably underestimates.

The total oceanic deposition and uncertainty estimates calculated here can be contrasted with the value 340.0 ± 98.6 Tg yr^{-1} obtained by Hardacre et al. (2015). It is interesting to note that our mean and standard deviation are both approximately a third of the respective values obtained by Hardacre et al. (2015). There would also be uncertainty in the MACC ozone data apart from their interannual variability which we have not considered.

With regards to the uncertainty in deposition to non-water surfaces, since our model uses the same Wesely (1989) deposition scheme as most other global models for such surfaces, we assume that the corresponding uncertainty would be similar to that in those models. Only Hardacre et al. (2015) report uncertainties in deposition fluxes to both water and non-water surfaces, with the latter calculated to be ± 80.0 Tg yr^{-1}. This value when combined with the interannual variability of ± 17.4 Tg yr^{-1} for non-water surfaces obtained here leads to a total uncertainty of ± 82.0 Tg yr^{-1} for such surfaces. Hence the total uncertainty combining this non-water component (± 82.0 Tg yr^{-1}) and the water component derived above (± 30.0 Tg yr^{-1}) is ± 87.3 Tg yr^{-1}.

The global oceanic and total deposition fluxes with the revised uncertainty are 98.4 ± 30.0 Tg yr^{-1} and 722.8 ± 87.3 Tg yr^{-1}, respectively (Table 2). The reduction in the total uncertainty compared to Hardacre et al.'s (2015) value of ± 127 Tg yr^{-1} is due to due to the reduction in the magnitude of the water component of deposition flux.

6 Conclusions

The ocean phase surface resistance term dominates over aerodynamic and atmospheric viscous sublayer resistances in commonly used parameterisations of ozone dry deposition velocity at the oceanic surface. Recent mechanistic schemes used to parameterise the oceanic surface resistance include the simultaneous effects of ozone solubility in water, waterside molecular diffusion and turbulent transfer, and first-order chemical reaction of ozone with dissolved iodide and other compounds. Luhar et al. (2017) formulated a semi-empirical scheme that described existing deposition velocity data well, but in order to compensate for the impact of overestimation of turbulent transfer within the waterside viscous sublayer it put an artificial limit on the iodide concentration to a fixed depth of the order of a few micrometres from the water surface whereas in reality iodide is present through the depth of the oceanic mixing layer. Here we presented a simple, new analytical two-layer formulation for the oceanic surface resistance that avoids making this limiting assumption. Instead, it makes the valid assumption that the influence of turbulent transfer can be neglected compared to the influence of chemical reaction within the top layer of water that is of the order of the reaction-diffusion length scale (typically a few micrometres). In the water layer below, both chemical reaction and turbulent transfer act together and are accounted for. The new scheme has an asymptotic behaviour that is consistent with the current limits of ozone dry deposition when either chemical reaction or turbulent transfer dominate. When compared against the available observed deposition velocity dependencies on sea surface temperature, the performance of the new two-layer dry deposition scheme as realised within the global chemistry-climate model ACCESS-UKCA (at UM vn8.4) was found to be satisfactorygood. with the inclusion of only the aqueous iodide-O$_3$ reaction. However, additional ocean-based measurements are needed for further development and evaluation of ozone deposition parametrisations with an aim of reducing uncertainty in ozone modelling.

The mean ozone deposition calculated using the new oceanic deposition scheme in ACCESS-UKCA for 2003–2012 is 86.1 ± 0.9 Tg yr^{-1} for the ocean and 566.7 ± 4.9 Tg yr^{-1} for the globe (the oceanic surface excludes sea ice and coastal grid cells

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and on average covers 62.4% of the Earth's surface). The tendency for ACCESS UKCA to underestimate observed tropospheric ozone concentrations leads to a lower estimate of the dry deposition flux and hence its budget. By using the 3-h MACC reanalysis for ozone concentration for the years 2003–2012 and the corresponding modelled 3-h deposition velocity values obtained from ACCESS UKCA (using the new dry deposition scheme for the ocean presented here and the default scheme for the other surface types), the deposition budget has been recalculated and quantified. The MACC based average global oceanic deposition of ozone is 93.9 ± 7.5 Tg yr⁻¹ and the average total global deposition is 689.9 ± 47.0 Tg yr⁻¹ with the largest deposition amounts for the years 2005–2007. The interannual variability in deposition is correlated with bias in the MACC ozone mixing rations. When deposition is selected for the minimum bias tThe annual ozone deposition value is $722.8 \pm 87.3\text{20.9}$ Tg O_3 yr^{-1} for the globe and $98.4 \pm 30.0\text{4.5}$ Tg O_3 yr^{-1} for the ocean. This new estimate of oceanic dry deposition represents a reduction of approximately 67% over the current estimates of oceanic deposition. This reduction leads to a 20% decrease in the modelled total global dry deposition, an increase of approximately 5% in the modelled tropospheric ozone burden, and an equivalent increase in tropospheric ozone lifetime.

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