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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Role of oceanic ozone deposition in explaining short-term variability of Arctic surface ozone" *by* Johannes G. M. Barten et al.

Anonymous Referee #2

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General Comments

In general, the paper is well presented, well written with a sound and detailed introduction, and with appropriate figures and tables. However, at first sight, results seem to be on a low side for Vd-O3 compared to other results found in the past literature (over the past 20 years or so). Moreover, with relatively little spatiotemporal variation in the High Arctic, for dry deposition velocity (0.012 $\pm$0.002 cm/s), the authors nevertheless claim a greater sensitivity of Vd with respect to environmental factors with COAREG vs DEFAULT. DEFAULT uses a constant for rs and no variability of surface resistance is allowed. The variability depends only on the aerodynamic and Rb resistances for

the latter. Therefore, it is not clear to what the word "sensitivity" and "high variability" refers to in this context for COAREG. For example, the standard deviation of COAREG (0.002) is smaller than DEFAULT (0.003) while the authors claim a greater sensitivity with COAREG. In comparison, other authors (see specific comments and references below) have shown a real and much larger sensitivity and variability than here over the same domain with respect to environmental conditions, for ozone and other gases. For CO2, many authors have shown a dependence on the square or cubic with windspeed for gas transfer to the ocean while here, the dependency of deposition velocity on windspeed seems small with respect to water-side turbulence and its impact on Vd-O3. Sensitivity tests with respect to environmental conditions (iodide conc., windspeed, SST, salinity, etc.) should be clearly presented with identification of which environmental factors contribute the most to the variability in COAREG. The authors should also clearly explain the little sensitivity of windspeed for ozone (as compared to other gases such as CO2, for example). Finally, the originality of the paper is questionable since many other authors have done the exercise of including mechanistic model such as COAREG in ACTM models. Therefore, one may question the science advancement brought by that paper since from the work of recent authors, it becomes obvious that a constant for surface resistance (rs =2000 s/m) is too high for northern regions (in summer) and this paper is just another confirmation. Finally, the authors question the value of rs in DEFAULT (2000 s/m) which results in Vd $\sim$ 0.05 cm/s. However, Ganzeveld et al. (2009) stated the following "Solely based on these comparable global annual mean VdO3 one could draw the conclusion that the commonly applied ConstRs approach (using an Rs of 2000 s m_1) seems to provide a good first-order estimate of global and long-term average oceanic ozone dry deposition for use in atmospheric chemistry and transport models". The presented paper here, seems to contradict this. Please explain and resolve this apparent major contradiction.

Specific comments

1) High variability/sensitivity of Vd-O3 over Arctic waters

-In the introduction, the authors correctly mentioned the sources of variability of dry deposition over oceans (lines 63-73). From this, the reader would expect a much larger variability than that of DEFAULT. However their results shown in the paper (Fig. 3c and table 1) rather indicate a rather small variability around the mean Vd-O3 = 0.012 cm/s. In fact, according to Table 1, the absolute variability in COAREG is actually less (0.002 cm/s) than that in DEFAULT (0.003 cm/s). In the conclusion, the authors repeat (line 373-375); "we show that Arctic surface O3 concentrations are very sensitive to the representation of O3 deposition". This claim is not supported from the results presented. Inter-seasonal variation of dry deposition velocity was shown to be greater than the spatiotemporal variation over the domain shown in the presented paper (compare with Figs 3a,b and Fig. 9 of Ganzeveld et al. 2009). Similarly, in other studies, the variability of Vd-O3 over oceans seem much larger (such as In-Bo Oh et al. 2008, Chang et al., 2004). Chang et al. (2004) (their Fig. 2) reports a large variability in ozone deposition velocity observations over the world oceans and a large sensitivity to windspeed (Vd about in the range 0.015 -0.07 cm/s; mean about 0.03 $\pm$ 0.015 cm/s from their Fig. 2), Again, how do you reconciliate that with your results: Vd = 0.012 $\pm$ 0.002 cm/s ?

2) Sensitivity of environmental factors

- The sensitivity with respect to wind is unclear in the paper. Wanninkhof (1992), McGillis et al. (2001a,b) have shown a strong dependency (U**2 or cubic root U**3 with windspeed) for air-sea gas exchange. Please comment more clearly about the sensitivity vs windspeed. Moreover, in the study presented, it seems that the biogeochemistry spatiotemporal changes do not impact much Vd-O3. For example, other authors have clearly really demonstrated a large variability (e.g. Table 2, Fig 3a,b, Fig. 4 and Fig.8, of Genzeveld et al. 2009). Helmig et al. (2012) provide a large variability for Vd-O3 from 0.01 to 0.1 cm/s (as mentioned by the authors Barten et al. 2020 in line 58 of their paper). Therefore, the variability shown by the authors here again appears much smaller for Arctic regions (Vd=0.012 $\pm$ 0.002 cm/s) than the above authors despite the authors claim high sensitivity. Please explain. My understanding is that the

intra-annual amplitude of dry deposition for ozone is large at high latitudes (e.g. Fig.3,b and Fig.4 of Genzeveld et al. 2009). The authors should state clearly state that the variability for Vd-O3 presented applies only in summer and under special conditions so that readers would not be tempted to extrapolate the results to other seasons or to lower latitudes, or anywhere else. In the literature, the inter-annual variability is up to 0.15 cm/s in the North Atlantic. The authors reports a summer variability of only 0.002 cm/s for dry deposition velocity. - According to Clifford et al. (2008), ozone deposition velocity is up to 0.1 cm/s in high chlorophyll (found in coastal waters in North Atlantic and Arctic in concentration up to 3-4 mg/m3). This dry dep. velocity range seems to agree with Chang et al. 2004 (range 0.015 cm/s to 0.07 cm/s), although the latter study dealt with lower latitudes. What are the levels of chlorophyll in your domain here ? The authors have to explain more clearly why they divert drastically from past literature and why chlorophyll-alpha is not important here. Moreover, Gallagher et al. (2001) proposed an average value of surface resistance of 950 s/m (corresponding to about Vd = 0.1 cm/s) for coastal UK. Do you obtain similar values ? if not, this means significant sensitivity to u* greater than shown in the paper here. Chang et al (2004) has shown a factor of 5 for deposition velocity of ozone with windspeed increasing from 0 to 20 m/s. Similarly, In-Bo Oh et al. (2008) reported values of surface resistance decreasing rapidly for [I-]=100nM from 5000 sm-1 at zero wind speed to about 1000 sm-1 at 20 m/s windspeed (their Fig. 4). For turbulent air (aerodynamic resistance negligible), this corresponds to dry deposition of 0.02 to 0.1 cm/s respectively. Therefore, I have some trouble re-concialiting this with the conclusions of the paper presented here. In any cases, authors should not claim high sensitivity for summer in Arctic region but rather a large discrepancy with the DEFAULT constant value for rs vs COAREG with small variability around the value 0.012 cm/s. More importantly, the authors should present a table showing the sensitivity of each environmental conditions in COAREG and show the results of sensitivity tests to support and clarify their claim. I suggest that the authors first present a table describing basic simulated statistics about environmental conditions, windspeed, SST, iodide conc, salinity, aerodynamic resistance (Ra),

boundary layer resistance (Rb), surface resistance, etc. to better understand the link with Vd in the Arctic and O3 mixing ratio and also provide sensitivity tests (as already discussed above).

3) Originality/added value

-Overall, I did not found that the results are of significant impact and have substantial originality vs existing literature. Other authors have modified ATCM models with mechanistic dry deposition scheme over water (Pound et al., 2020; Helmig et al. 2012; Fairall et al., 2011; Luhar et al., 2011; Coleman et al., 2010; Ganzeveld et al., 2009; In-Bo Oh et al., 2008; etc.). Perhaps, the authors should clearly provide a statement discussing the added value to the existing literature. The case presented seems a special case where there is a limited role of water-side turbulence, iodide variation, impact of halogen chemistry influence, chlorophyll and organic matter, etc. A comparison of winter versus summer case would have been more interesting.

Line 35: Ozone has also significant impact on destroying materials by oxidation, see https://www.sciencedirect.com/science/article/pii/1352231095004076 or https://www.worldscientific.com/doi/abs/10.1142/9781848161283_0009 I think a word about impact on materials should also be mentioned there for completeness.

Line 43-44: Changes in deposition velocities (linked with changing meteorological and oceanic conditions, stomata closure, droughts, etc.) may also contribute to these trends in mid-latitude.

Line 57-58. Over oceans, Clifford et al. (2008) suggest values of Vd-O3 up to 0.1 cm/s, Chang et al. (2004) had Vd-O3 in the range: 0.015 cm/s to 0.07 cm/s. Gallagher et al. (2001) had Vd-O3 up to 0.1 cm/s near coastal waters. Perhaps these references deserved to be mentioned for oceans and coastal waters as well to give more background about the real variability of Vd-O3.

Line 62. It would be very interesting for the reader to know where this value of rs cm/s

(DEFAULT) comes from. Ganzeveld et al. 2009 seems to agree with the constant for northern latitude (rs=2000 s/m) as stated above.

Line 93-96. The reaction ozone + iodide is a fast reaction why it doesn't affect short time scales as well ?

Line 125. The choice of the period is well supported according to the authors (end of summer 2008). However, the reader should be reminded that the conclusions of this study only strictly applies for summer 2008. Waves height are highly variable in the north Atlantic and therefore the water-side turbulence in other seasons. Under high chlorophyll conditions (as seen by MODIS instrument), algae bloom, etc., the fate of ozone is possibly more in other seasons. Therefore, there will be cases when the net dry deposition would be much higher than 0.012 cm/s. The authors should not leave the reader under the impression that vd=0.05 cm/s currently used in model is too high everywhere in any seasons. I wonder about any contribution of ozone subsidence for higher altitudes in the High Arctic ?

Line 125-126. Is halogen chemistry limited only to spring time ?

Line 154. "Extension for a two-layer scheme vs Fairall et al. 2011". The authors should provide briefly more details on how these two layers are structured for the benefit of the reader.

Line 158. It is not clear why chlorophyll-alpha from MODIS as proxy for iodide and organic matter is ignored. Such proxy has been used with success in previous literature (In-Bo Oh et al., 2008). A good linear correlation was found between iodide and chlorophyll-alpha. The advantage of using MODIS is to obtain a very good spatial coverage (not the case with ground point measurement).

Line 173. About machine learning (ML) approach. It needs more details. ML is a generic term. Which ML was used ?

Section 2.2.1 and 2.3 Ozone could be destroyed by chemical reaction with snow. Not

clear how it is taken into account in the study presented. Please provide more details here or refer to a discussion later in the paper. The authors do not provide clear scientific reasons to why they decrease Vd-O3 for snow/ice from 0.03 to 0.01 cm/s (although it fits better the observations). Writing “Based on Helmig et al.” is not sufficient . Please add-up a bit more details.

Line 238-239. Variability of O3 deposition of 20% in turbulent transport looks small. Other authors have found a factor of 5 with windspeed (Chang et al. 2004).

Line 160. Nitrate is used as a proxy for iodide concentration. Chlorophyll-alpha is another proxy available from satellite (MODIS). Again, why not considering satellite measurement of chlorophyll since the spatial coverage is much better ? Anyways, a comparison of the two methods would be of interest.

Line 226. VD increases over warmer water (Fig. 4) but the solubility of ozone and other gases (such as CO2) generally decrease with increasing sea surface temperature. Therefore, in principle, this produces less ozone uptake by ocean if everything else is equal. Your results show the opposite: increase from 0.01 to 0.018 cm/s from cold to warm waters. What is the impact in % of the solubility effect on Vd-O3 vs other factors. Perhaps the effect of iodide counteracts effect of solubility. Please discuss.

Figure 3b,c. -The result of the authors show rather low deposition velocity (0.012 cm/s) with relatively low variability (0.002, i.e. less than 20% variability). In fact the variability (e.g. Fig 3c) is less than the default (the latter having a surface resistance taken as constant). Compared to the literature, the results obtained by the authors are among the lowest Vd and among the lowest variability found. Please indicate which authors, and which paper would support the results found ? For example, Coleman et al. (2010) using different scenarios computed much higer VD = 0.0547 cm/s (for iodide conc. of 100 nM) for the North Sea. Ganzeveld et al (2009) shows a worldwide map of deposition velocity of ozone over oceans for January and July. The simulation for summer (their Fig. 3b) shows a minimum of 0.025 cm/s (range 0.025-0.045 cm/s) for the do-

main of the study presented here for dry dep ozone. Moreover, although the location is significantly different, Chang et al. (2004) mentioned a high variability of VD (ozone) of at least 50% (compared to less than 20% in the authors study). Therefore, a question arises: what particular conditions of Arctic at that period of the year 2008 in summer would produce such low variability and low deposition velocity?. I understand iodide conc. is low, in the context of the paper presented, moreover the authors neglected halogen chemistry, etc. but still, I think the authors should explain better why their Vd are so low and their variability not so high as well although the authors claim a high sensitivity. I also suggest that Fig. 3c should show the time series at various locations not only at a single one.

Figure 4. Concerning differences between CAMS and COAREG over land: could it be explained by modification of the Wesely scheme (1989) over land to take into account LAI (i.e. bug in Wesely, 1989; see correction in Val-Martin et al, 2010) ? I suspect one model has integrated the Val-Martin’s correction and the other not (e.g. to explain differences over Scandinavia, Russia and Northern Europe between the two models CAMS and COAREG). Please comment or check on this.

Line 273. Vd (ocean) is about 0.012 cm/s and over snow/ice about the same. i.e. 0.010 cm/s (small gradient) Therefore, why is there a sharp gradient from Greenland vs sea (Figure 4). Authors should perhaps say a word about it (altitude effect, accumulation of ozone over Greenland, descent of ozone from higher altitudes over Greenland, etc. or any other reasons ?).

Line 275 and Figure 4d. The COAREG distribution is closer to a Gaussian distribution than that of DEFAULT. I think it is worth to briefly mention it.

Table 2. Note that bias, MAE and R are somehow redundant metrics (show similar information). I think the authors should consider adding up another metric which is entirely orthogonal to bias such as the standard deviation of O-P (Observations minus model prediction) or any other metrics showing the random error. Bias and MAE both

show systematic errors (i.e. Table 2 either give information on the systematic error or on the degree of correlation). See Chang and Hanna (2004) for metric redundancy.

Line 374. What is your criteria to conclude about the high sensitivity ? To which environmental conditions Vd-O3 is very sensitive: windspeed, temperature, salinity , iodide concentration ?. Again, I would suggest providing evidence of sensitivity by making sensitivity tests and showing the results as a form of a Table. DEFAULT was driven by a constant which is too high and likely not applicable for arctic regions in summer. COAREG does not use this constant but shows little variability around the mean, i.e 0.012 $\pm$0.002. Please re-word or add specific evidence for high sensitivity.

Line 496. "It corroborates findings of which study on global scale" ? The authors should give references to that statement. As mentioned above, values shown for Vd are lower w.r.t to previous literature in general. Conclusion: I think somewhere, the author should comment about the need for open ocean measurements (for iodide, DOM, halogen, ozone, weather variables and other relevant environmental variables) and/or of flux measurements. These measurements are needed to validate models and quantify better open ocean chemistry near-surface. Observations shown are limited and conclusions should be taken with care. Authors should recognize the limitations of their study (no halogen chemistry included; results cannot extrapolated to other seasons, lower latitude, etc.).

Technical corrections

Line 12 and 465: "we have coupled the Coupled-": redundant words.

Line 29: "is used" –> "be used"

Line 36: ozone lifetime differs according to NOx source proximity or altitude. Should indicate that it is the corresponding lifetime in the free troposphere (not near surface or in the upper troposphere or stratosphere which differs substantially).

Line 194 and 488. (sea-)ice –> sea-ice

Line 225 and 227 deposition –>deposition velocity (figure 3 deals with deposition velocity, not deposition)

Line 234. Up to 8% reduction ? Seems a bit small to me. Say Ra = 2000 (under temp. inversion), Rs =2000 (default) ,–> Vd=0.025 cm/s a 50% reduction. Please verify.

Line 239-240. Reduction from 0.03 to 0.01 cm/s gives a reduction 66% , not 30% !

Line 258. I suggest re-wording "We find a limited effect. . ." –> "As expected, we find a limited effect. . ."

Line 278-279. Improve in what sense ? model predictions scores improvement ?

Line 278. Improve short-term –> increase the short-term

Line 280 such a oceanic –> such an oceanic

Line 364,372, 495. role –> impact

Line 374. address or include ? not both.

Line 403-420. Much of the stuff should go in the Methods section 2.

Line 439. meteorolog -> meteorology

Line 478-480. This is not clear. What is dominant, sensitivity to iodide, solubility, temperature or windspeed ? Showing a table with sensitivity tests would be appreciated.

Line 483, 484. I suggest you replace % –> reduced by a factor of 3.4 (ocean) and 2.6 (ice).

Line 496. It corroborates which findings ? (needs a reference)

Author contributions: what is the precise role of Maarten Knol in the study ? Please specify.

Reference (in support to the above)

Chang et al. 2004; (see line 531 of the paper)

Chang and Hanna (2004). Air quality model performance evaluation. Meteorol Atmos Phys 87, 167–196 (2004). https://doi.org/10.1007/s00703-003-0070-7

Clifford et al. (2008) (see line 535 of the paper)

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Fairall et al., 2011; (see line 544 of the paper)

Gallagher, M.W., Beswick, K.M., McFiggans, G. et al. Ozone Dry Deposition Velocities for Coastal Waters. Water, Air, & Soil Pollution: Focus 1, 233–242 (2001). https://doi.org/10.1023/A:1013119524952

Ganzeveld et al. 2009 (see line 549 of the paper)

Helmig et al., 2012; (see line 570 of the paper)

In-Bo Oh et al. 2008. Modeling the effect of iodide distribution on ozone deposition to seawater surface. Atmospheric Environment. Doi: 10.1016/j.atmosenv.2008.02.022

Kawa, S. R., and R. Pearson Jr. (1989), Ozone budgets from the dynamics and chemistry of marine stratocumulus experiment, J. Geophys. Res., 94, 9809– 9817, doi:10.1029/JD094iD07p09809.

McGillis, W. R., J. B. Edson, J. E. Hare, and C. W. Fairall (2001a), Direct covariance airâĂŘsea CO2 fluxes, J. Geophys. Res., 106, 16,729– 16,745.

McGillis, W. R., J. B. Edson, J. D. Ware, J. W. H. Dacey, J. E. Hare, C. W. Fairall, and R. Wanninkhof (2001b), Carbon dioxide flux techniques performed during GasExâĂŘ98, Mar. Chem., 75, 267– 280.

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