

Interactive comment on “Hydrogen peroxide in the marine boundary layer over the southern Atlantic during the OOMPH cruise in March 2007” by H. Fischer et al.

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The paper describes analysis of an interesting dataset of an oceanic campaign during which more observations on some of the compounds relevant to the MBL photochemistry have been sampled. These data are evaluated also by comparison with the global chemistry-climate modelling system EMAC to further support the analysis on the role of the different sources and sinks of the peroxides (and ozone). Having anyhow more detailed analysis on some of these marine exchange and chemistry components is very relevant also to overcome some of the strong bias on continental chemistry analysis and therefore would strongly recommend publication of this paper in ACP. However,

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reading through some of the more detailed discussion on the role of the deposition process as represented also in the EMAC model system I am getting really concerned that there might be a serious flaw on some of these calculations in this modelling system. I need to further corroborate my observations and realize that also because of this, it is pity that I now only provided this feedback at the end of the discussion stage (but having been out of office last 3 weeks),

Below you can find my more specific comments.

Abstract: “An interesting feature during the cruise is a strong increase of hydrogen peroxide, methylhydroperoxide and ozone shortly after midnight off the west coast of Africa due to an increase in the boundary layer height, leading to downward transport from the free troposphere”. Is this a one time event or was this a re-occurring event? Would already be useful to make this also clear here in the abstract

Introduction: “These measurements are compared to the atmospheric chemistry global circulation model EMAC (Jöckel et al., 2006, 2010).” It would be good to indicate what you like to achieve with this comparison. Do you simply want to evaluate how well the model performs or is it also that you need the model to fill in some of the missing information not being included in the observations.

Results; page 30555. So it is mainly a one time event that H₂O₂ significantly increased associated with changes in BL dynamics

Page 30556: “As can be deduced from the time series (Fig. 4) the model tends to reproduce trace gas levels over the Southern Atlantic”. Are you referring here to the large-scale/long term concentrations that are in reasonable agreement with the observations. You discussed before some of the discrepancies that clearly exist between the model and the observations for O₃ and H₂O₂.

Page 30557: Given the fact that model underestimates both O₃ and H₂O₂ during the first part of the cruise, for the southern Atlantic and that the chemical precursors seem

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to be well represented by the model you conclude that it must be a misrepresentation of the sinks that explains the discrepancy. But it could also be a misrepresentation of the other source, which is entrainment of FT air masses enhanced in O3 and H2O2.

Page 30558: "Kerkweg et al. (2006) according to an implementation of the dry deposition scheme of Ganzeveld et al. (JGR, 1995, JGR, 1998) partly following Wesely's 1989 concept"

(The dry deposition scheme of Wesely 1989 was mainly developed to consider land surface deposition and some of its components have been adopted in the dry deposition algorithm's ultimately included in EMAC)

"It strongly depends on the wind speed, which determines the transfer velocity to the ocean surface. The loss itself is determined by the solubility of the species under investigation, defined by its Henry's law coefficient."

Since you refer here to the dry deposition process in general and not specifically to that for H2O2; For H2O2 dry deposition strongly depends on wind speed because of its high solubility, which results in the use of an estimated negligible ocean surface uptake resistance but it is definitely not the case for O3 and other gases (e.g., MHP) for which solubility/reactivity is much smaller and resulting in the use of significant surface uptake resistances which dominate the small dry deposition velocities.

Based on the following text I suggest you to remove the text of lines 8-11 at 30558: "It strongly depends on the wind speed, which determines the transfer velocity to the ocean surface. The loss itself is determined by the solubility of the species under investigation, defined by its Henry's law coefficient."

"Ozone has an intermediate role, since its solubility is in between these two extremes. The deposition velocity calculated by the model for O3 does not depend on the wind speed and is about 0.5 cm s⁻¹, indicating that the deposition loss is limited by the solubility of O3". This statement should also be changed. Ozone solubility might be in

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between those two (didn't check that) but the oceanic ozone deposition velocity should be <0.05 cm s⁻¹ (and not 0.5!). This is also based on a selected oceanic surface uptake resistance of 2000 s m⁻¹ (also included in EMAC) based on the Ganzeveld et al. 1995 review of observed O3 dry deposition velocities over water surfaces. Actually, the O3 oceanic dry deposition velocity based on its solubility is 40 times smaller than the typically observed VdO3 implying that there is a significant chemical enhancement of oceanic O3 deposition due its reaction with Iodide and DOM (Ganzeveld et al. GBC 2009).

Reading further through the discussion about the issues of too high H2O2 dry deposition with simulated values large at 18 cm s⁻¹, you wonder if this is indeed physically feasible. There might be an extremely efficient uptake in the water but then the turbulent transport and molecular diffusion become the limiting term. I conducted some calculations with a water dry deposition algorithm (including the dependence of roughness on wind speed, Charnock) calculating the maximum feasible Vd that would only be limited by turbulent transport and that gives a maximum Vd of ~5 cm s⁻¹ for wind speeds large as 25 m s⁻¹. For a wind speed of 5 cm s⁻¹, this is about 1 cm⁻¹. I will further corroborate these calculated values with some experts on ocean-atmosphere exchange processes since if this is correct it might point at a problem with the implementation of oceanic dry deposition in EMAC.

Page 30560: "Due to the limited resolution of the model the data points here are extrapolated between an oceanic and a continental cell, leading to a diurnal evolution of the boundary layer height that resembles that of a continental boundary layer instead of the marine boundary layer". It is good that you mention this specific explanation why the shown BL depth become so large since a MBL depth is typically around 500-800m and not as deep as the shown 1500m. I would therefore put this statement directly after you have introduced Figure 7. But also the fact that the model resolution is still rather coarse compared to the scale of the observations, resulting in this much deeper BL depth of the simulations might result in a simulated overestimation of the entrainment

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term (but that would be needed to compensate for the way too high deposition term)

Summary: "Quantitatively, the model tends to UNDERestimate H₂O₂ mixing ratios during the first part of the cruise"

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30547, 2014.

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