

Detailed point-by-point response to all referee comments and specification of all changes in the revised manuscript. Referee comments are shown in black, our replies in blue and changes made to the manuscript in red:

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I would like to point out that further ozone measurements were performed over the South Atlantic during the Polarstern cruise ANTXVI/2 from Neumayer Station to CapeTown. Between 37 and 70°S we observed an average of 17.3 ppb ozone in the marine boundary layer during the period from 2 to 15 March 1999 (see Figure 2 in the reference below). This adds a further point regarding ozone observations in this region. Still, I agree with the authors that these limited observations do not enable to determine a trend in ozone over the South Atlantic.

Reference:

Jacobi, H.-W., and O. Schrems, Peroxyacetyl nitrate (PAN) distribution over the South Atlantic Ocean, *Phys.Chem.Chem.Phys.* 1, 5517-5521, 1999.

Dear Dr. Jacobi,

Thank you very much for your comment. In the revised version of the manuscript we have included a reference to the Jacobi and Schrems, 1999 paper

Revised manuscript line 206-210:

Similar O<sub>3</sub> mixing ratios of the order of 20 ppbv were also observed in the southern Atlantic south of 40° S during three Polarstern cruises in November 1990 (Slemr and Tremmel, 1994), October/November 1994 (Junkermann and Stockwell, 1999) and March 1999 (Jacobi and Schrems, 1999).

The following reference was added to the revised manuscript (line 488-489):

Jacobi, H.-W., and Schrems, O.: Peroxyacetyl nitrate (PAN) distribution over the South Atlantic Ocean, *Phys. Chem. Chem. Phys.*, 1, 5517-5521, 1999.

Anonymous Referee #1

Received and published: 1 January 2015

Review of Fischer et al.

Summary

The authors present an analysis of H<sub>2</sub>O<sub>2</sub> (HP) and CH<sub>3</sub>OOH (MHP) during the OOMPH cruise in the S. Atlantic. They compare the results to model output and make inferences regarding the model representation of HP & MHP sinks.

Their chemical transport model has a tendency to underestimate the observed HP during the first part of the campaign, but not the second part, while overestimating MHP throughout. The authors argue that the model HP underestimate is unlikely to reflect sources, and instead indicates that HP sinks in the model are too strong – and in particular dry deposition. A sensitivity simulation in which they impose a lower deposition velocity improves agreement for HP, while not affecting MHP much because of the lower solubility.

They point out that the MHP overestimate in the model could reflect a number of factors, including the collection efficiency, which was not quantified but estimated at 60%, as well as chemical reactions (i.e. CH<sub>3</sub>O<sub>2</sub> + OH) that were not included in their baseline simulation.

The argument that the model H<sub>2</sub>O<sub>2</sub> bias arises from dry deposition is plausible but far from definitive. In my opinion they need to do more quantitative analysis to justify this assessment. They state that the model accurately simulates HO<sub>2</sub>, and that therefore the discrepancy is unlikely due to misrepresentation of the H<sub>2</sub>O<sub>2</sub> source. But specifically, how good is the agreement for HO<sub>2</sub>, and how does that error propagate onto the predicted H<sub>2</sub>O<sub>2</sub>? Measurements of HO<sub>2</sub> are themselves far from perfect, and in at least some FAGE measurements include an interference from some RO<sub>2</sub>. Is that an issue here? Once you consider both measurement and model uncertainty in terms of HO<sub>2</sub>, what is the resulting error bar imparted to the H<sub>2</sub>O<sub>2</sub> predictions that is associated with the sources? Does the model prediction of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH depend on NO being accurately simulated? Is it?

We like to thank the referee for her/his valuable remarks that we have addressed in the revised version of the manuscript.

The referee's main criticism is that the argument the model H<sub>2</sub>O<sub>2</sub> bias arises from dry deposition is mainly based on qualitative arguments and needs to be based on a more quantitative assessment. In particular a quantitative assessment of the mode's sources and sinks of H<sub>2</sub>O<sub>2</sub> should be provided and compared to observations.

As mentioned in our original manuscript the model tends to underestimate the H<sub>2</sub>O<sub>2</sub> observations in particular during the first days of the cruise by a factor of 2. Assuming that the photochemical source of H<sub>2</sub>O<sub>2</sub> in the remote marine boundary layer is HO<sub>2</sub> + HO<sub>2</sub> we can quantify the H<sub>2</sub>O<sub>2</sub> source from observed HO<sub>2</sub> and compare it to HO<sub>2</sub> simulations. Time series of HO<sub>2</sub> observations have been presented in Beygi et al., 2011 (Figure 10) while the model simulations are shown in Figure 11 in the same manuscript. A scatter plot (not shown) and a regressions analysis indicate that the model tends to overestimate observed HO<sub>2</sub> by approximately 30 % throughout the whole campaign ( $HO_2(\text{obs}) = 0.83 \times HO_2(\text{model}) - 0.1$ ;  $R^2 = 0.82$ ). The total uncertainty of the HO<sub>2</sub> measurements is +/- 35 % (2-sigma) (Beygi et al., 2011), indicating that HO<sub>2</sub> observations and

simulations agree within the uncertainties of the observations (a total uncertainty for the simulations is not available and not easy to derive). Thus the simulation tends to overestimate the H<sub>2</sub>O<sub>2</sub> source by about 60 %, assuming that HO<sub>2</sub> reacts only with HO<sub>2</sub> and reactions with NO are negligible, which is justified by the very low NO<sub>x</sub> levels of the order of less than 20 pptv from both observations and simulations. This is in contrast to the underestimations of the simulated H<sub>2</sub>O<sub>2</sub> with respect to the observed one. Therefore we can argue that the underestimation of the H<sub>2</sub>O<sub>2</sub> is not due to an underestimation of its sources. The referee also raises the question whether the HO<sub>2</sub> observations suffers from an interference due to larger peroxy radicals. As discussed by Reglin et al. (ACP 13, 10703-10720, 3012, doi:10.5194/acp-13-10703-2013), an interference from CH<sub>3</sub>O<sub>2</sub> is less than 5 %. Higher contributions can be expected from peroxy radicals that are derived from reactions of OH with unsaturated organic compounds (e.g. isoprene) and thus depend on the concentrations of the precursors that can be assumed to be very small in the remote marine boundary layer.

If the H<sub>2</sub>O<sub>2</sub> sources agree within the uncertainties given by the observations, the underestimation must be due to an overestimation of the H<sub>2</sub>O<sub>2</sub> sinks by the simulations. The model simulation of the photochemical H<sub>2</sub>O<sub>2</sub> sinks indicate that during noon the maximum contribution of H<sub>2</sub>O<sub>2</sub> photolysis and reaction with OH varies between 2 % (March 11) and a maximum of 12 % (March 19). So the influence of the photochemical sinks on the H<sub>2</sub>O<sub>2</sub> mixing ratio is marginal (setting both sinks to zero would increase the simulated H<sub>2</sub>O<sub>2</sub> mixing ratios by approx. 10 %).

Revised manuscript (line 273-281):

A scatter plot (not shown) and a regression analysis indicate that the model tends to overestimate observed HO<sub>2</sub> by approximately 20 % throughout the campaign ( $HO_2(\text{obs}) = (0.786 \pm 0.004) \times HO_2(\text{model}) - (0.44 \pm 0.03)$ ;  $R^2 = 0.87$ ). The total uncertainty of the HO<sub>2</sub> measurements is  $\pm 35$  % ( $2\sigma$ ) (Hosaynali Beygi et al., 2011), indicating that HO<sub>2</sub> observations and simulations agree within the uncertainties of the observations (a total uncertainty for the simulations is not available and not easy to derive). Thus the simulation tends to overestimate the H<sub>2</sub>O<sub>2</sub> source by about 40 %, assuming that HO<sub>2</sub> reacts only with HO<sub>2</sub> and reactions with NO are negligible, which is justified by the very low NO<sub>x</sub> levels of less than 20 pptv in both observations and simulations.

Are there any other HP sinks to be considered, such as uptake to aqueous aerosols, that could have an impact? What about aerosol uptake of HO<sub>2</sub>?

Other sinks of H<sub>2</sub>O<sub>2</sub> in particular H<sub>2</sub>O<sub>2</sub> uptake on aerosols are not considered in the model and thus cannot be responsible for the underestimation of the H<sub>2</sub>O<sub>2</sub> mixing ratio in the simulations. The same is true for HO<sub>2</sub> loss on aerosols, which is also not considered in the model.

Revised manuscript (line 287 – 294):

The model simulations of the photochemical H<sub>2</sub>O<sub>2</sub> sinks indicate that during noon the maximum contribution of H<sub>2</sub>O<sub>2</sub> photolysis and reaction with OH varies between 2 % (March 11) and a

maximum of 12 % (March 19). Hence the influence of the photochemical sinks on the H<sub>2</sub>O<sub>2</sub> mixing ratio is marginal (setting both sinks to zero would increase the simulated H<sub>2</sub>O<sub>2</sub> mixing ratios by approx. 10 %). Other sinks of H<sub>2</sub>O<sub>2</sub>, in particular H<sub>2</sub>O<sub>2</sub> uptake on aerosols, were not considered in the model simulation and thus cannot be responsible for the underestimation of the H<sub>2</sub>O<sub>2</sub> mixing ratio in the simulations. The same is true for HO<sub>2</sub> loss on aerosols, which was also not considered in the model simulation.

Overall, the attribution of HP model bias to dry deposition relies too much on hand-waving. The paper needs a more quantitative consideration of the other budget terms, and a propagation of those uncertainties (or envelope of sensitivity runs) to the predicted HP. If the model-measurement discrepancy is larger than can reasonably be accommodated by those other terms, then it becomes reasonable to invoke dry deposition. It may well be that this is the case, but not enough has been done to establish it.

Overall the model tends to overestimate the H<sub>2</sub>O<sub>2</sub> source by 60% and indicates a maximum overestimation of the photochemical sinks of 10 %. Since there are no other H<sub>2</sub>O<sub>2</sub> sinks in the model, an overestimation of the dry deposition sinks is the only viable explanation for the overestimation of the H<sub>2</sub>O<sub>2</sub> sink in the simulations.

It's hard to know what to make of the MHP analysis, since the authors don't seem to know how much to trust the measurements. The sampling efficiency of 60% was not measured but calculated based on a previous study, and MHP was assumed to be the dominant peroxide (the technique measures the sum). For this portion of the paper to be useful, we need a quantitative treatment of what the authors consider to be the uncertainties on the measured concentrations, and to see to what degree these are smaller than the model-measurement differences.

The referee also raises the issue of the MHP analysis. Unfortunately, the measurements for MHP are not specific and without a detailed knowledge of the composition of all organic peroxides a quantitative determination of MHP mixing ratios is impossible. A discussion of the uncertainties has thus to be based on extreme cases (all ROOH is MHP vs. no MHP at all). The model analysis on ROx radicals presented in Beygi et al., 2011 indicates that no other organic peroxy radicals other than CH<sub>3</sub>O<sub>2</sub> are to be expected in the very clean marine boundary layer, indicating that no other ROOH than MHP are expected to contribute to the ROOH signal of the analyzer. A sampling efficiency of 60 % for MHP is a reasonable assumption. The efficiency cannot be higher than that for H<sub>2</sub>O<sub>2</sub> (95 %) and is unlikely smaller than 30 %, thus yielding an uncertainty of +/- 30 %, which is much smaller than the difference between simulations and observations that are of the order of at least a factor of 2.

Revised manuscript (line 134 – 140):

A discussion of uncertainties of the MHP measurements can be based on extreme cases (all ROOH is MHP vs. no MHP at all). The model analysis on ROx radicals presented in Hosaynali Beygi et al. (2011) indicates that no other organic peroxy radicals other than CH<sub>3</sub>O<sub>2</sub> are expected in the very clean marine boundary layer, indicating that MHP dominates the ROOH signal of the

analyzer. A sampling efficiency of 60 % for MHP is a reasonable assumption. The efficiency cannot be higher than that for H<sub>2</sub>O<sub>2</sub> (95 %) and is unlikely smaller than 30 %, thus yielding an uncertainty of ± 30 %.

Specific comments:

30557, 22-26: “As shown by Hosaynali Beygi et al. (2011), EMAC reproduces observed HO<sub>2</sub> levels during the whole campaign and indicates similar levels for HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>, the precursors of CH<sub>3</sub>OOH. Given that the precursor levels are simulated realistically by EMAC, it is very unlikely that an underestimation of the peroxide production is responsible for the H<sub>2</sub>O<sub>2</sub> underestimation during the first half of the campaign.” Perhaps I missed it, but I don’t see in the Hosaynali Beygi paper where they directly evaluate the EMAC simulation of HO<sub>2</sub>. Same goes for OH, which is referred to later (“the model also reproduces OH concentrations”). There is an evaluation of a constrained box model (their Fig 9), but that is not the same thing.

As mentioned above HO<sub>2</sub> observations and model simulations are shown in different figures of Beygi et al., 2011 (Figure 10 and 11, respectively).

Revised manuscript (line 271 -272):

(observations are shown in Figure 10 and model results in Figure 11 of Hosaynali Beygi et al., 2011)

Fig 4, why do the model H<sub>2</sub>O<sub>2</sub> concentrations become negative early on March 14?

The negative H<sub>2</sub>O<sub>2</sub> mixing ratios in Fig. 4 are an artifact and have been removed.

In the revised manuscript figures 3, 4 and 6 that were affected by negative model results have been revised.

Since the second channel is MHP + all other peroxides, wouldn’t it make more sense to compare with the same model quantity rather than just the model MHP?

As regarding using ROOH instead of MHP see the discussion above.

30557, 18: “hence the main problem seems to be that the model underestimates H<sub>2</sub>O<sub>2</sub> during the early phase of the campaign” not sure I follow. Isn’t the fact that CH<sub>3</sub>OOH is overestimated throughout also a problem?

We erased the phrase main problem and replaced it by “hence one problem seems to be ...” (revised manuscript line 267).

30551, 25-27: doesn’t catalase react to some degree with MHP also? Please provide some quantitative information on how specific this is.

It is true, that catalase reacts to some extent with MHP. The commercial analyzer (AERO-Laser, Model AL 2001CA) that has been used is based on the design of Lazarus et al. (Automated

fluorometric method for hydrogen peroxide in air, Anal. Chem., 58, 594-597, 1986). As discussed in this paper, the effect of catalase destruction on MHP is estimated to be off the order of 3 %, an order of magnitude less than the uncertainty due to the sampling issues discussed above.

Revised manuscript (line 140 – 144):

One should also mention that catalase reacts to some extent with MHP. The commercial analyzer (AERO-Laser, Model AL 2001CA) that has been used is based on the original design of Lazarus et al. (1986). As discussed in this paper, the effect of catalase destruction on MHP is estimated to be about 3 %, an order of magnitude less than the uncertainty due to the sampling issue discussed above.

30552, 15: does the 25 ppt detection limit apply to MHP as well as H<sub>2</sub>O<sub>2</sub>?

The detection limit is determined from the reproducibility of the zero air measurements in both channels of the analyzer and strictly applies to the H<sub>2</sub>O<sub>2</sub> channel. A rough estimate for MHP can be gained by multiplication with the sampling efficiency of 0.6, yielding a value of 40 pptv.

Revised manuscript (line 145 – 147):

The detection limit is determined from the reproducibility of the zero air measurements in both channels of the analyzer and strictly applies to the H<sub>2</sub>O<sub>2</sub> channel. A rough estimate for MHP can be gained by multiplying with the sampling efficiency of 0.6, yielding a value of 40 pptv.

30555, 18: “measured and observed H<sub>2</sub>O<sub>2</sub>” should be “measured and modeled”, I guess

We replaced “measured and observed” by measured and modeled”. (revised manuscript line 216).

30557, 13 and Fig 6: please discuss what we learn from the ratio of the two that wasn't already apparent from the plots of the species individually

Figure 6 further supports the interpretation that the problems in the H<sub>2</sub>O<sub>2</sub> simulations only occur during the first phase of the campaign at high wind speeds, and cease later in the campaign.

L. Ganzeveld (Referee)

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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 therefor would strongly recommend publication of this paper in ACP. However, 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 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),

Dear Laurens,

Thank you very much for the thorough review of our manuscript that helped us to detect a major flaw: due to a scaling error the deposition velocities for H<sub>2</sub>O<sub>2</sub> cited in the manuscript were too high by an order of magnitude. The actual deposition velocities calculated by the model varied between 0.5 cm/s at a wind speed of 5 m/s and 1.8 cm/s at 10 m/s. The sensitivity study was done limiting the maximum wind used in the deposition calculation to 5m/s (resulting in a maximum deposition velocity of H<sub>2</sub>O<sub>2</sub> of around 0.6 cm/s). These values are in good agreement with those derived from airborne measurements in the marine boundary layer over the Atlantic Ocean off the coast of South America during GABRIEL 2005 (Stickler et al., 2007). Based on H<sub>2</sub>O<sub>2</sub> observations and an assumption for the entrainment from the free troposphere Stickler et al. estimated an H<sub>2</sub>O<sub>2</sub> deposition velocity of 1.3 cm/s (range <0.1 to >1.8 cm/s, depending on the assumptions for the entrainment rate) at a wind speed of 6 m/s. The single column model used in the study of Stickler et al (2007) gave a maximum deposition velocity of 0.5 cm/s at that wind speed, which is in good agreement with the EMAC results.

Revised manuscript (307 -318):

On the other hand, the H<sub>2</sub>O<sub>2</sub> deposition velocity is a strong function of wind speed, linearly increasing from ~ 0.5 cm/s at a wind speed of 5 m/s to about 1.8 cm/s at 10 m/s. This indicates that the deposition loss for this highly soluble species is limited by the transfer velocity to the ocean surface. These values are in good agreement with those derived from airborne measurements in the marine boundary layer over the Atlantic Ocean off the coast of South America during GABRIEL 2005 (Stickler et al., 2007). Based on H<sub>2</sub>O<sub>2</sub> observations and an assumed rate of entrainment from the free troposphere Stickler et al. estimated an H<sub>2</sub>O<sub>2</sub> deposition velocity of 1.3 cm/s (range <0.1 to >1.8 cm/s, depending on the assumptions for the entrainment rate) at a wind speed of 6 m/s. The single column model used in the study of Stickler

et al. (2007) yielded a maximum deposition velocity of 0.5 cm/s at that wind speed, which is in good agreement with the EMAC results.

And revised manuscript (line 326 – 328):

performed a sensitivity study (SR1) with EMAC, limiting the maximum wind used in the deposition calculation to 5m/s, resulting in a maximum deposition velocity of H<sub>2</sub>O<sub>2</sub> of around 0.6 cm/s.

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

Abstract: The transport of free tropospheric air into the MBL was indeed observed only a one particular time.

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.

Introduction: The purpose of the comparison of the observation to the EMAC simulations is indeed to test our understanding of the chemical and physical processes that affect the mixing ratio of those species in the MBL.

Results; page 30555. So it is mainly a one time event that H<sub>2</sub>O<sub>2</sub> significantly increased associated with changes in BL dynamics

Results, page 30555: As pointed out above, it was indeed a onetime event.

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 O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>.

Page 30556: Indeed we are referring to the overall trace gas trends that are reproduced by the model.

Page 30557: Given the fact that model underestimates both O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> during the first part of the cruise, for the southern Atlantic and that the chemical precursors seem 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 O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>.

Page 30557: As suggested, an underestimation of entrainment from the troposphere would also explain the underestimation of the H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> mixing ratios during the first phase of the campaign. But this leads to a contradiction with the MHP data, which would be affected by the same transport. Similar to H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, MHP mixing ratios increase with altitude and show a maximum above the boundary layer (Stickler et al., 2007, Klippel et al. 2011). Thus one would expect that a too small transport from the free troposphere in the simulations would also produce an underestimation of the simulated MHP concentrations in the MBL, but the opposite is the case: the model overestimates MHP significantly. Therefore we conclude that different processes are responsible for the temporal underestimation of H<sub>2</sub>O<sub>2</sub> (during the first part of the campaign) and the time independent overestimation of MHP, as most clearly expressed in the time series of the ratio of these two species in Figure 6.

Revised manuscript (line 415 – 425):

Note that an underestimation of entrainment from the free troposphere would also explain the underestimation of the H<sub>2</sub>O<sub>2</sub> (and O<sub>3</sub>) mixing ratios during the first phase of the campaign. However, this leads to an inconsistency with the MHP data, which would be affected by the same transport. Similar to H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, MHP mixing ratios increase with altitude and show a maximum above the boundary layer (Stickler et al., 2007, Klippel et al. 2011). Thus one would expect that a transport limitation from the free troposphere in the simulations would also produce an underestimation of the simulated MHP concentrations in the MBL, but the opposite is the case; actually the model significantly overestimates MHP. Therefore, we conclude that different processes are responsible for the temporal underestimation of H<sub>2</sub>O<sub>2</sub> (during the first part of the campaign) and the time independent overestimation of MHP, as most clearly corroborated in the time series of the ratio of these two species in Figure 6.

Page 30558: “Kerkweg et al. (2006) according to an implementation of the dry depo-

sition 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 H<sub>2</sub>O<sub>2</sub>; For H<sub>2</sub>O<sub>2</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> does not depend on the wind speed and is about 0.5 cm s<sup>-1</sup>, indicating that the deposition loss is limited by the solubility of O<sub>3</sub>". This statement should also be changed. Ozone solubility might be in between those two (didn't check that) but the oceanic ozone deposition velocity should be <0.05 cm s<sup>-1</sup> (and not 0.5!). This is also based on a selected oceanic surface uptake resistance of 2000 s m<sup>-1</sup> (also included in EMAC) based on the Ganzeveld et al. 1995 review of observed O<sub>3</sub> dry deposition velocities over water surfaces. Actually, the O<sub>3</sub> oceanic dry deposition velocity based on its solubility is 40 times smaller than the typically observed V<sub>d</sub>O<sub>3</sub> implying that there is a significant chemical enhancement of oceanic O<sub>3</sub> deposition due its reaction with Iodide and DOM (Ganzeveld et al. GBC 2009).

Reading further through the discussion about the issues of too high H<sub>2</sub>O<sub>2</sub> dry deposition with simulated values large at 18 cm s<sup>-1</sup>, 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 V<sub>d</sub> that would only be limited by turbulent transport and that gives a maximum V<sub>d</sub> of ~ 5 cm s<sup>-1</sup> for wind speeds large as 25 m s<sup>-1</sup>. For a wind speed of 5 cm s<sup>-1</sup>, this is about 1 cm<sup>-1</sup>. 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 30558: The error in the deposition velocities for H<sub>2</sub>O<sub>2</sub> was already addressed above. In the revised manuscript we will follow your suggestion to clarify the discussion of deposition processes and their dependency on transfer velocities and solubility for individual species.

Revised manuscript (line 299 307):

The dry deposition in EMAC (Kerkweg et al., 2006) is based on the dry deposition scheme of Ganzeveld et al. (Ganzeveld and Lelieveld, 1995, Ganzeveld et al., 1998) partly following Wesley (1989). For highly soluble species like  $\text{H}_2\text{O}_2$  the ocean surface resistance is assumed to be negligible and the deposition velocity strongly depends on the wind speed, which determines the transfer velocity to the ocean surface. For less soluble species like  $\text{O}_3$  and MHP the dry deposition velocity is dominated by a non-zero ocean uptake resistance (Ganzeveld and Lelieveld, 1995). The deposition velocity calculated by the model for  $\text{O}_3$  does not depend on the wind speed and is about 0.05 cm/s, indicating that the deposition loss is limited by the ocean uptake resistance.

And added references:

Ganzeveld and Leliveld (line 471 – 473)

And Ganzeveld et al. (line 474 – 475)

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

Page 30560: We will follow your suggestion and discuss the reasons for the boundary layer height variations following the introduction of Figure 7. (revised manuscript line 360 -364).

Summary: “Quantitatively, the model tends to UNDERestimate  $\text{H}_2\text{O}_2$  mixing ratios during the first part of the cruise

Summary: We replaced “overestimation” by” underestimation”. (revised manuscript line 432)

# Hydrogen peroxide in the marine boundary layer over the southern Atlantic during the OOMPH cruise in March 2007

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## Abstract

In the OOMPH (Ocean Organics Modifying Particles in both Hemispheres) project a ship measurement cruise took place in the late austral summer from 1<sup>st</sup> to 23<sup>rd</sup> March, 2007. The French research vessel Marion Dufresne sailed from Punta Arenas, Chile (70.85°W, 53.12°S) to La Reunion island (55.36°E, 21.06°S) across the southern Atlantic Ocean. In-situ measurements of hydrogen peroxide, methylhydroperoxide and ozone were performed and are compared to simulations with the atmospheric chemistry global circulation model EMAC. The model generally reproduces the measured trace gas levels, but underestimates hydrogen peroxide mixing ratios at high wind speeds, indicating too strong dry deposition to the ocean surface. 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, which is realistically reproduced by the model.

## 1 Introduction

The oxidizing power of the lower atmosphere in the gas phase is defined by the concentrations of the hydroxyl radical (OH), ozone (O<sub>3</sub>), the nitrate radical (NO<sub>3</sub>), halogen radicals (e.g. ClO, BrO, IO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), an important oxidizer in the liquid phase (Thompson, 1992). The dominant oxidizing agent is OH, whose primary source is the photolysis of O<sub>3</sub> and subsequent reaction of the formed O<sup>1</sup>D-atom with water vapor (Levy, 1971). The major sinks of OH are reactions with carbon monoxide (CO), methane (CH<sub>4</sub>), and volatile organic compounds

(VOC) yielding peroxy radicals ( $\text{HO}_2$  and  $\text{RO}_2$ ). The fate of these peroxy radicals strongly depends on the concentrations of nitrogen oxides ( $\text{NO}_x$ ,  $\text{NO}$  plus  $\text{NO}_2$ ). In semi-polluted and polluted regions with  $\text{NO}_x$  levels in excess of several tens of pptv, the peroxy radicals predominantly react with  $\text{NO}$ , yielding  $\text{NO}_2$  and recycling  $\text{OH}$ . In these environments the subsequent photolysis of  $\text{NO}_2$  yields ozone, with  $\text{NO}_x$  acting as a catalyst. In low  $\text{NO}_x$  environments, such as the marine boundary layer, the peroxy radicals undergo self-reactions ( $\text{HO}_2 + \text{HO}_2$  and  $\text{RO}_2 + \text{HO}_2$ ) yielding  $\text{H}_2\text{O}_2$  and organic peroxides (e.g.  $\text{CH}_3\text{OOH}$  from methane oxidation), and also destroying ozone ( $\text{HO}_2 + \text{O}_3$  and  $\text{OH} + \text{O}_3$ ). The peroxides serve as reservoir species for the  $\text{HO}_x$  ( $\text{OH}$  plus  $\text{HO}_2$ ) radicals, which can be recycled by photolysis or reaction with  $\text{OH}$ . Hydrogen peroxide is also an important oxidizing agent in the liquid phase, notably of sulfur dioxide. Since many peroxides are water soluble, physical removal processes (deposition to surfaces and washout in rain events) strongly influence the oxidizing power of the lower atmosphere.

In the marine boundary layer at low  $\text{NO}_x$  concentrations the concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{ROOH}$  and  $\text{O}_3$  are strongly coupled, since their formation and destruction compete for the  $\text{HO}_x$  radicals. In order to model oxidation processes in this environment, formation and destruction of peroxides have to be accurately described, including the physical removal processes.

Previous measurements of peroxides ( $\text{H}_2\text{O}_2$  and  $\text{ROOH}$ ) in the marine boundary layer in the 1980s and 1990s have been summarized in the review article by Lee et al. (2000). Since this review additional observations in the marine boundary layer have been reported in the literature (Junkermann and Stockwell, 1999; Weller et al., 2000; Kieber et al., 2001; O'Sullivan et al., 2004; Chang et al., 2004; Stickler et al., 2007). These observations indicate highest mixing ratios (> 500 pptv) of  $\text{H}_2\text{O}_2$  in the tropics (Slemr and Tremmel, 1994; Heikes et al., 1996; O'Sullivan et al., 1999; Junkermann and Stockwell, 1999; Weller et al., 2000; O'Sullivan et al., 2004) and decreasing concentrations toward higher latitudes in both hemispheres, reaching 200 – 300 pptv south of  $40^\circ$  in the southern hemisphere (Slemr and Tremmel, 1994; O'Sullivan et al., 1999; Junkermann and Stockwell, 1999; Weller et al., 2000; O'Sullivan et al., 2004). In general mixing ratios are about a factor of two higher in the northern hemisphere than at corresponding latitudes in the south (O'Sullivan et al., 1999). A significant dissimilarity between the different ocean basins has not been observed, while higher  $\text{H}_2\text{O}_2$  mixing ratios have been observed in continental outflow (e.g. Heikes et al., 1996).

The mixing ratios of the most abundant organic peroxide  $\text{CH}_3\text{OOH}$  show similar behavior as  $\text{H}_2\text{O}_2$  in the marine boundary layer, with highest levels in the tropics and decreasing towards the poles. Also the absolute mixing ratios are comparable, yielding  $\text{H}_2\text{O}_2/\text{CH}_3\text{OOH}$  ratios close to 1 in air masses not affected by recent rainout (Lee et al., 2000).

Here we describe in-situ ship-based observations of  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and a proxy for  $\text{CH}_3\text{OOH}$  in the marine boundary layer of the southern Atlantic Ocean in the austral late summer of 2007. These measurements are compared to the atmospheric chemistry global circulation model EMAC (Jöckel et al., 2006, Jöckel et al., 2010). Section 2 describes the methods (measurement principles and model) used, while the observations and model comparisons are described and discussed in section 3. The final section summarizes the findings of this study.

## **2 Methods**

### **2.1 OOMPH cruise MD160**

As part of the OOMPH (Ocean Organics Modifying Particles in both Hemispheres) project a measurement cruise took place in the late austral summer from 1<sup>st</sup> to 23<sup>rd</sup> March, 2007. The French research vessel Marion Dufresne sailed from Punta Arenas, Chile ( $70.85^\circ\text{W}$ ,  $53.12^\circ\text{S}$ ) to La Reunion island ( $55.36^\circ\text{E}$ ,  $21.06^\circ\text{S}$ ) crossing the southern Atlantic between the east coast of South America to the southern Indian Ocean east of South Africa between  $20^\circ\text{W}$ ,  $60^\circ\text{S}$  and  $35^\circ\text{E}$ ,  $35^\circ\text{S}$  (Figure 1). During the first part of the cruise at high southern latitudes, cold air was encountered from the Antarctic continent. During this part of the cruise, cloud cover was extensive. Further north, temperatures increased together with solar radiation intensity and photolysis frequencies. The wind was generally from the west, with wind speeds varying between calm conditions and gale force winds up to  $33 \text{ ms}^{-1}$ . The average wind varied between more than  $10 \text{ ms}^{-1}$  during the first part and  $8 \text{ ms}^{-1}$  during the second part of the campaign (Figure 2). Details of the cruise can be found in Williams et al. (2010) and Hosaynali Beygi et al. (2011).

### **2.2 Trace gas measurements**

Data used in this study were obtained by two in-situ instruments mounted in a temperature controlled container placed on the foredeck of the ship (see Fig. 3 in Hosaynali Beygi et al., 2011). Air was sampled from the top of an atmospheric mast (10 m above the deck, 20-25 m above the sea surface) through 17.1 m  $\frac{1}{2}$ " Teflon tubes, shielded from sunlight by a black cover.

The inlet was designed as a bypass with a total flow of 24 slm (retention time 3.4 s) sustained by a membrane pump. From the bypass inlet small flows were directed to the in-situ instruments inside the container via short ¼" Teflon lines.

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was measured with a commercial analyzer (AL2001 CA, Aero Laser, Garmisch Partenkirchen, Germany) based on wet chemical dual enzyme detection scheme described by Lazarus et al. (1985, 1986). Gaseous peroxides are sampled in a buffered (potassium hydrogen phthalate/NaOH) sampling solution (pH 5.8) in a glass stripping coil at a flow of 3 slm. The sampling efficiency for  $\text{H}_2\text{O}_2$  was determined several times in the field and was always higher than 0.8. After passing the sampling coil the degassed liquid peroxide solution is divided into two channels and subsequently reacts with p-hydroxyphenyl acetic acid (POPHA) and horseradish peroxidase. The reaction with hydrogen peroxide, organic hydroperoxides and organic peroxides yields a fluorescent dye (6,6'-dihydroxy-3,3'-biphenyldiacetic acid) in stoichiometric quantities that is subsequently detected via fluorescence spectroscopy at 400-420 nm after excitation at 326 nm with a Cd ray lamp in a detection cell. Since the detection scheme is unspecific, the  $\text{H}_2\text{O}_2$  concentration is determined from the difference of the two channels, with channel A measuring all peroxides (ROOH), while channel B measures ROOH –  $\text{H}_2\text{O}_2$  after selective destruction of  $\text{H}_2\text{O}_2$  via addition of catalase (efficiency > 95% as determined in the field) prior to the reaction with POPHA. Thus the difference between both channels provides the  $\text{H}_2\text{O}_2$  concentration, while channel B provides an unspecific measurement of all organic hydroperoxides and organic peroxides. Nevertheless, assuming that methylhydroperoxide (MHP;  $\text{CH}_3\text{OOH}$ ) is the most abundant organic peroxide in the remote marine boundary layer, as shown by previous measurements (e.g. Heikes et al., 1996), we obtain an upper limit assuming that ROOH consists of MHP only. The organic peroxide data is subsequently corrected for the lower sampling efficiency of  $\text{CH}_3\text{OOH}$  compared to  $\text{H}_2\text{O}_2$ . The time resolution (10–90%) of the instrument is 30 sec.

The in-field calibration of the instrument involves regular zero gas measurements (scrubbed ambient air after passage through cartridges filled with silica gel and hopcalite (Infiltec, Speyer, Germany)), liquid calibrations (liquid  $\text{H}_2\text{O}_2$  standard of  $35.5 \mu\text{g l}^{-1}$ ) and gas phase calibrations with a  $\text{H}_2\text{O}_2$  permeation tube (30%  $\text{H}_2\text{O}_2$  in a glass flask temperature controlled to  $40^\circ\text{C}$  providing a calibration gas concentration of 6.38 ppbv). The detection limit of the instrument was determined from the  $1\sigma$  variability of the in-field zero measurements performed every 2.5 h, estimated at 25 pptv. The total uncertainty determined from the precision ( $1\sigma$  variability of 9 in-

field gas phase and liquid calibrations), the uncertainty of the standard, the inlet transmission and an ozone interference correction was about 12-13 %. During the campaign the inlet transmission was determined twice by adding the gas phase standard at the top of the inlet line. Comparison of two calibrations directly in front of the analyzer yielded a transmission that decreased from 67% at the beginning of the campaign to 57% towards the end. The instrument has also been used (in combination with a constant pressure inlet) for airborne measurement of H<sub>2</sub>O<sub>2</sub> in the free troposphere over the rainforest in South America (Stickler et al., 2007) and over Europe (Klippel et al., 2011).

A discussion of uncertainties of the MHP measurements can be based on extreme cases (all ROOH is MHP vs. no MHP at all). The model analysis on ROx radicals presented in Hosaynali Beygi et al. (2011) indicates that no other organic peroxy radicals other than CH<sub>3</sub>O<sub>2</sub> are expected in the very clean marine boundary layer, indicating that MHP dominates the ROOH signal of the analyzer. A sampling efficiency of 60 % for MHP is a reasonable assumption. The efficiency cannot be higher than that for H<sub>2</sub>O<sub>2</sub> (95 %) and is unlikely smaller than 30 %, thus yielding an uncertainty of ± 30 %. One should also mention that catalase reacts to some extent with MHP. The commercial analyzer (AERO-Laser, Model AL 2001CA) that has been used is based on the original design of Lazarus et al. (1986). As discussed in this paper, the effect of catalase destruction on MHP is estimated to be about 3 %, an order of magnitude less than the uncertainty due to the sampling issue discussed above.

The detection limit is determined from the reproducibility of the zero air measurements in both channels of the analyzer and strictly applies to the H<sub>2</sub>O<sub>2</sub> channel. A rough estimate for MHP can be gained by multiplying with the sampling efficiency of 0.6, yielding a value of 40 pptv.

The instrument used to measure ozone (together with NO and NO<sub>2</sub>) is a high resolution (1 s) and highly sensitive 3-channel chemiluminescence detector (CLD, ECO-Physics CLD 790 SR, Duernten, Switzerland). The instrument and its performance characteristics during this campaign have been described in detail in a previous publication on the NO<sub>x</sub>/O<sub>3</sub> photostationary state by Hosaynali Beygi et al. (2011). The total uncertainty for the O<sub>3</sub> channel was determined from the 2σ deviation of the in-field calibrations (ozone calibrator model TE49C, Thermo Instruments, Germany) and the accuracy of the standard, estimated at 1% (Hosaynali Beygi et al., 2011).

### **2.3 Atmospheric chemistry model EMAC**

Simulations of trace gas mixing ratios along the ship cruise were performed using the EMAC (ECHAM/MESSy Atmospheric Chemistry) global circulation model (Jöckel et al., 2010). EMAC uses the Modular Earth Submodel System (MESSy; Jöckel et al., 2005) to link multi-institutional sub models describing atmospheric processes interacting with oceans, land and human influences. For this study EMAC was applied in the T42L90MA-resolution ( $2.8^\circ \times 2.8^\circ$  resolution in latitude and longitude, 90 vertical levels up to 0.01 hPa), using results from the lowest model level ( $\sim 30\text{m}$ ) for comparison with measurements. The model was sampled (spatial bilinearly interpolated) along the ship track at every time step (i.e. 12 minutes) using the SD4 submodel (Jöckel et al., 2010), without any temporal interpolation. The meteorology was nudged to the operational ECMWF analysis. Tropospheric gas-phase and heterogeneous chemistry was calculated with the sub-model MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere; Sander et al., 2005), aqueous-phase chemistry in cloud droplets and wet scavenging with the sub-model SCAV (Tost et al., 2006) and primary emissions and dry deposition of trace gases and aerosols with the sub-models ONLEM, OFFLEM, TNUDGE and DRYDEP (Kerkweg et al., 2006a and 2006b). Previous results of a model comparison with airborne  $\text{H}_2\text{O}_2$  measurements in the free troposphere have been discussed in Klippel et al. (2011).

### **3 Results and discussion**

#### **3.1 Data processing**

For the present analysis the original observations were averaged over 12 minute time intervals to be coherent with the model output time stepping. The time scale used is UTC, thus leading to deviations from solar noon of  $-80$  min for the most westerly point ( $20^\circ\text{W}$ ) of the ship track to  $140$  min for the most easterly ( $35^\circ\text{E}$ ). Unfortunately due to the prevailing westerly winds the instruments often measured air polluted by the ship exhausts, notably when the wind was from the sector between  $55^\circ$  and  $275^\circ$ . This stack air contained very high concentrations of NO (up to  $200$  ppbv in individual plumes), leading to complete titration of  $\text{O}_3$ , while  $\text{H}_2\text{O}_2$  was not affected at all on the short time scales involved, as has been observed previously (Weller et al., 2000). In total 53% of the observations were effected by stack emissions. Therefore we used Ox ( $\text{O}_3 + \text{NO}_2$ ) for the experimental data, to deduce the original  $\text{O}_3$  concentration that would have occurred without NO-titration to  $\text{NO}_2$ . In general, the difference between Ox and  $\text{O}_3$  is marginal due to the very low NOx mixing ratios of less than  $20$  pptv in the remote marine boundary layer over the

southern Atlantic and less than 200 pptv east of South Africa (Hosaynali Beygi et al., 2011). Thus the error in O<sub>3</sub> using Ox in all cases is smaller than 2 %. From the model only the original O<sub>3</sub> data are used.

### 3.2 Distribution of measured and simulated trace gases

Figure 3 shows the time series for measured and simulated ozone mixing ratios. Observed O<sub>3</sub> varies between 17 and 25 ppbv, with lower values in the south-western Atlantic and higher values closer to Africa. The model qualitatively reproduces this gradient with a slight tendency to underestimate O<sub>3</sub> mixing ratios during the first part of the cruise (March 10 – March 14) and a slight overestimation between March 15 and 17. During the last part of the cruise after March 17 both model and observations agree quite well. Overall, the mean observed and simulated O<sub>3</sub> are  $20.3 \pm 1.8$  ppbv and  $19.7 \pm 2$  ppbv, respectively. A least-square fit between simulated (y-axis) and observed (x-axis) ozone yields a slope of  $0.98 \pm 0.01$  and an offset of  $-0.43 \pm 0.21$  ppbv. The regression coefficient R<sup>2</sup> is rather low (0.2). Taking into account that observed Ox measurements are affected by background NO<sub>2</sub>, the agreement between observations and model results is quite satisfactorily. Observations and model results are in good agreement with observations by Helmig et al. (2012) during the GasEx 2008 cruise in the southern Atlantic at 50° S between 65°W and 35°W in March 2008, who reported an average O<sub>3</sub> mixing ratio of 18.3 ppbv. **Similar O<sub>3</sub> mixing ratios of the order of 20 ppbv were also observed over the southern Atlantic, south of 40° S, during three Polarstern cruises in November 1990 (Slemr and Tremmel, 1994), October/November 1994 (Junkermann and Stockwell, 1999) and March 1999 (Jacobi and Schrems, 1999).** As discussed in Lelieveld et al. (2004) seasonal variations of O<sub>3</sub> in the latitude band between 40° and 60° S are rather small, with slightly lower values in austral summer. For the period between 1977 and 2002 the calculated O<sub>3</sub> trend for this latitude band is  $0.17 \pm 0.08$  ppbv/year (Lelieveld et al., 2004), indicating a moderate increase of approximately 1 ppbv between 2002 and 2007. Based on the limited number of observations during OOMPH a conclusion about the continuation of this trend is not possible.

Time series of measured and **simulated** H<sub>2</sub>O<sub>2</sub> are shown in Figure 4. During the first part of the cruise (March 10 to 14) observed H<sub>2</sub>O<sub>2</sub> mixing ratios indicate small variability at levels between 200 and 300 pptv. During this period the model significantly underestimates observed H<sub>2</sub>O<sub>2</sub>, by more than a factor of two. After March 14 in the eastern part of the South Atlantic H<sub>2</sub>O<sub>2</sub> mixing ratios tend to increase both in the observations and the model simulations, with the model

overestimating observations during the first part, in particular on March 15, while later on measurements and model results agree quite well. A period of relatively high  $\text{H}_2\text{O}_2$  (in excess of 1 ppbv) was observed and simulated after midnight on March 16, southwest of the African coast (see Figure 1). On average observed and simulated  $\text{H}_2\text{O}_2$  were  $350 \pm 220$  pptv and  $310 \pm 240$  pptv, respectively. Slope and intercept of a least-square regression analysis are  $2.04 \pm 0.04$  and  $-0.27 \pm 0.04$  ppbv, respectively. The regression coefficient  $R^2$  is 0.46. The imperfect agreement here between model results and observations is due to the rather limited dynamical range of mixing ratios and the strong offset during the first part of the cruise. This is also the case for  $\text{O}_3$ . As can be deduced from the time series (Figure 4) the model tends to reproduce trace gas levels over the Southern Atlantic. The measured  $\text{H}_2\text{O}_2$  mixing ratios are comparable to previously reported observations south of  $35^\circ\text{S}$  in the Atlantic lower troposphere, being approximately 200 – 300 pptv (Slemr and Tremmel, 1994; Junkerman and Stockwell, 1999; Weller et al., 2000). Observations of  $\text{CH}_3\text{OOH}$  mixing ratios are shown in the time series in Figure 5 along with EMAC simulations. The temporal evolution is similar to  $\text{H}_2\text{O}_2$ , with low values (less than 200 pptv) during the first part of the cruise, a strong mixing ratio increase starting on midnight of March 16 and lower concentrations afterwards. The relative change is reproduced by the model, with a general tendency to overestimate  $\text{CH}_3\text{OOH}$  mixing ratios except during the period when the high peak was encountered on March 16. Average measured  $\text{CH}_3\text{OOH}$  mixing ratios are  $280 \pm 250$  pptv, while the model calculates a mean value of  $450 \pm 190$  pptv. The offset between model and observations is clearly shown in the least-square regression analysis that yields an intercept at  $0.18 \pm 0.05$  ppbv and a slope of  $0.37 \pm 0.12$  at an  $R^2$  of 0.6. In general the observed mixing ratios are in good agreement with reported levels in the literature (Slemr and Tremmel, 1994; Junkerman and Stockwell, 1999; Weller et al., 2000).

With the exception of the mixing ratio peaks on March 16, the variability of  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  is small across the South Atlantic basin between South America and South Africa. The slightly northward orientation of the ship track results in a steady increase in temperature and photolysis rates (Hosaynali Beygi et al., 2011) leading to increasing photochemical activity that is likely responsible for the slight increase of the mixing ratios of the three species from the southwestern to the north-eastern part of the South Atlantic. As shown in a backward trajectory analysis presented in Hosaynali Beygi et al. (2011) the air mass origin did not change throughout the cruise. All air masses encountered during the cruise originated in the western Antarctic

Peninsula during the preceding week and had not been in contact with land surfaces for at least 5 days.

### 3.3 Discussion

Based on  $\text{H}_2\text{O}_2$  mixing ratios and the comparison between observations and model results, one can differentiate three different periods in Fig. 4: From March 10 to 14 the model significantly underestimates the  $\text{H}_2\text{O}_2$  mixing ratios, while the agreement is much better during the final phase of the campaign (after March 17). In between these two periods  $\text{H}_2\text{O}_2$  mixing ratios show a strong increase to well above 1 ppbv that is well reproduced by the model.

Similar behavior is also observed for ozone (Figure 3). The model also tends to underestimate  $\text{O}_3$  mixing ratios during the early phase of the campaign, while the agreement is much better in the second half of the campaign. On the other hand, the  $\text{CH}_3\text{OOH}$  mixing ratios are almost always overestimated by the model (Figure 5). Considering the ratio between  $\text{CH}_3\text{OOH}$  and  $\text{H}_2\text{O}_2$  there is an even stronger discrepancy (Figure 6). Over the whole campaign, the observed ratio varies between 0.5 and 1 with a mean value and standard deviation of  $0.8 \pm 1.1$ , while the model predicts a time dependent ratio between 2 and 4 during the first half of the campaign and lower values, in good agreement with the observations, during the second half of the campaign. Hence **one** problem seems to be that the model underestimates  $\text{H}_2\text{O}_2$  during the early phase of the campaign, due to either an underestimation of the  $\text{H}_2\text{O}_2$  production or an overestimation of the sinks. Gas phase  $\text{H}_2\text{O}_2$  in the marine boundary layers stems from the recombination of two  $\text{HO}_2$  radicals. As shown by Hosaynali Beygi et al. (2011), EMAC reproduces observed  $\text{HO}_2$  levels (**observations are shown in Figure 10 and model results in Figure 11 of Hosaynali Beygi et al., 2011**) during the whole campaign and indicates similar levels for  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$ , the precursors of  $\text{CH}_3\text{OOH}$ . **A scatter plot (not shown) and a regression analysis indicate that the model tends to overestimate observed  $\text{HO}_2$  by approximately 20 % throughout the campaign ( $\text{HO}_2(\text{obs}) = (0.786 \pm 0.004) \times \text{HO}_2(\text{model}) - (0.44 \pm 0.03)$ ;  $R^2 = 0.87$ ). The total uncertainty of the  $\text{HO}_2$  measurements is  $\pm 35\%$  ( $2\sigma$ ) (Hosaynali Beygi et al., 2011), indicating that  $\text{HO}_2$  observations and simulations agree within the uncertainties of the observations (a total uncertainty for the simulations is not available and not easy to derive). Thus the simulation tends to overestimate the  $\text{H}_2\text{O}_2$  source by about 40 %, assuming that  $\text{HO}_2$  reacts only with  $\text{HO}_2$  and reactions with  $\text{NO}$  are negligible, which is justified by the very low  $\text{NO}_x$  levels of less than 20 pptv in both observations and simulations. Given that the precursor levels are **slightly overestimated** by EMAC, it is very unlikely that an**

underestimation of the peroxide production is responsible for the  $\text{H}_2\text{O}_2$  underestimation during the first half of the campaign. This indicates that the discrepancies are due to an overestimation of the  $\text{H}_2\text{O}_2$  sinks in the model during this period. Photochemical sinks (reaction with OH and  $\text{H}_2\text{O}_2$  photolysis) are also unlikely causes, since the model also reproduces OH concentrations (Beygi et al., 2011) and radiation intensities (not shown). The model simulations of the photochemical  $\text{H}_2\text{O}_2$  sinks indicate that during noon the maximum contribution of  $\text{H}_2\text{O}_2$  photolysis and reaction with OH varies between 2 % (March 11) and a maximum of 12 % (March 19). Hence the influence of the photochemical sinks on the  $\text{H}_2\text{O}_2$  mixing ratio is marginal (setting both sinks to zero would increase the simulated  $\text{H}_2\text{O}_2$  mixing ratios by approx. 10 %). Other sinks of  $\text{H}_2\text{O}_2$ , in particular  $\text{H}_2\text{O}_2$  uptake on aerosols, were not considered in the model simulation and thus cannot be responsible for the underestimation of the  $\text{H}_2\text{O}_2$  mixing ratio in the simulations. The same is true for  $\text{HO}_2$  loss on aerosols, which was also not considered in the model simulation.

This leaves physical removal processes, such as rainout and dry deposition to the surface, as most likely causes. Although the model predicts some rain events, they are not particularly extensive during the first phase, when the problems occur. A striking observation is that the wind speeds are significantly higher during the first part of the campaign, being well above 10 m/s up to March 15 (Figure 1), while they are generally lower in the second half of the campaign. The dry deposition in EMAC (Kerkweg et al., 2006) is based on the dry deposition scheme of Ganzeveld et al. (Ganzeveld and Lelieveld, 1995, Ganzeveld et al., 1998) partly following Wesley (1989). For highly soluble species like  $\text{H}_2\text{O}_2$  the ocean surface resistance is assumed to be negligible and the deposition velocity strongly depends on the wind speed, which determines the transfer velocity to the ocean surface. For less soluble species like  $\text{O}_3$  and MHP the dry deposition velocity is dominated by a non-zero ocean uptake resistance (Ganzeveld and Lelieveld, 1995). The deposition velocity calculated by the model for  $\text{O}_3$  does not depend on the wind speed and is about 0.05 cm/s, indicating that the deposition loss is limited by the ocean uptake resistance. On the other hand, the  $\text{H}_2\text{O}_2$  deposition velocity is a strong function of wind speed, linearly increasing from ~ 0.5 cm/s at a wind speed of 5 m/s to about 1.8 cm/s at 10 m/s. This indicates that the deposition loss for this highly soluble species is limited by the transfer velocity to the ocean surface. These values are in good agreement with those derived from airborne measurements in the marine boundary layer over the Atlantic Ocean off the coast of South America during GABRIEL 2005 (Stickler et al., 2007). Based on  $\text{H}_2\text{O}_2$  observations and an assumed rate of entrainment from the free troposphere Stickler et al. estimated an  $\text{H}_2\text{O}_2$

deposition velocity of 1.3 cm/s (range <0.1 to >1.8 cm/s, depending on the assumptions for the entrainment rate) at a wind speed of 6 m/s. The single column model used in the study of Stickler et al. (2007) yielded a maximum deposition velocity of 0.5 cm/s at that wind speed, which is in good agreement with the EMAC results. Accordingly, due to the absence of low clouds and precipitation during the campaign (for the considered period) dry deposition is the dominant loss process for H<sub>2</sub>O<sub>2</sub> in the model, even during the day. During the night dry deposition is the only loss mechanism, as photochemical destruction ceases. The model indicates that during daytime the contribution of dry deposition to total H<sub>2</sub>O<sub>2</sub> loss varies between 98 % (noon values) during the first part of the campaign (March 11<sup>th</sup> to 14<sup>th</sup>) and about 90 % during the second half (after March 15), due to a combination of decreasing dry deposition loss due to decreasing wind speeds and a simultaneous increase by enhanced photochemical activity at lower latitudes. We performed a sensitivity study (SR1) with EMAC, limiting the maximum wind used in the deposition calculation to 5m/s, resulting in a maximum deposition velocity of H<sub>2</sub>O<sub>2</sub> of around 0.6 cm/s. The green line in Figure 4 shows that this leads to an increase in simulated H<sub>2</sub>O<sub>2</sub> mixing ratios by approximately 50 % (mean calculated mixing ratio: 460 ± 350 pptv). It should be mentioned that globally this effect is strongest in the marine boundary layer in regions of high wind speed, notably in the latitude band between 40° and 60° of the storm tracks in both hemispheres. Outside of these regions the effect is much smaller and leads to increases in the H<sub>2</sub>O<sub>2</sub> mixing of less than 20%. Thus it appears that the differences between model simulations and H<sub>2</sub>O<sub>2</sub> observations are due to a model overestimation of dry deposition to the ocean at high wind speed. This hardly affects CH<sub>3</sub>OOH and O<sub>3</sub> whose deposition loss is limited by their solubility and thus independent of wind speed, while H<sub>2</sub>O<sub>2</sub> is much more strongly affected. The importance of the deposition parameterization, being a critical process in the simulation of H<sub>2</sub>O<sub>2</sub> in the lower troposphere was also emphasized by Chang et al. (2004), who performed sensitivity studies with a single column model to simulate observations from PEM-Tropics B.

Another interesting feature of the H<sub>2</sub>O<sub>2</sub> time series in Fig. 4 is the strong increase of H<sub>2</sub>O<sub>2</sub> in the night from March 15 to 16. Shortly before midnight the H<sub>2</sub>O<sub>2</sub> mixing ratio increases strongly from ~ 0.7 ppbv up to about 1.5 ppbv, and decreasing to the previous mixing ratios before noon on March 16. The sudden increase occurs together with a similar increase in CH<sub>3</sub>OOH (Figure 5), which is well reproduced by EMAC. Since the sudden increase in H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH occurs during nighttime a photochemical source can be excluded. During this phase of the campaign the ship was south of the southern tip of Africa. One explanation for the sudden increase could be a

change in air mass origin. Heikes et al. (1996) observed a significant increase of marine boundary layer  $\text{H}_2\text{O}_2$  mixing ratios north of  $20^\circ\text{N}$  in continental outflow. Trajectory calculations for the OOMPH campaign were presented in the supplements to the paper by Hosaynali Beygi et al. (2011). They indicate, however, no change in air mass origin during the period between March 15 and 17, so that this option can be dismissed.

Due to the dry deposition close to the ocean surface, both  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  are expected to exhibit an increase in mixing ratios with height. Aircraft observations over the ocean indeed show maxima of both species above the marine boundary layer (Heikes et al., 1996; O'Sullivan et al., 1999; O'Sullivan et al., 2004; Stickler et al., 2007). Thus transport from above the boundary layer can be a source of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  for the marine boundary layer. Observations of the boundary layer height were not made during the OOMPH campaign, thus we have to rely on model results. The curtain plot in Figure 7 shows a time series of the vertical profiles for  $\text{O}_3$  (upper panel) and  $\text{H}_2\text{O}_2$  (lower panel). Superimposed is the temporal evolution of the boundary layer height calculated by EMAC. **Note that the diurnal variation of the boundary layer height during March 17<sup>th</sup> – 19<sup>th</sup> is related to the proximity to the African continent. Due to the limited resolution of the model the data points here are interpolated between an oceanic and a continental grid 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.** Shortly before the event the simulation indicates a very shallow boundary layer ( $\sim 200$  m), that starts to increase around midnight on March 16<sup>th</sup>. Hence the increase in  $\text{H}_2\text{O}_2$  is related to an increase in boundary layer height, and downward mixing of air masses that have not been affected by deposition and thus having higher mixing ratios of peroxides. Thus it seems that nighttime transport of free tropospheric air into the marine boundary layer is responsible for the concentration increase during the period from March 15<sup>th</sup> to 16<sup>th</sup>. This vertical redistribution process should also affect other species with a positive altitude gradient, in particular ozone. Model profiles indicate that the mixing ratio gradient for  $\text{O}_3$  is much smaller than for  $\text{H}_2\text{O}_2$  (upper panel in Fig. 7). This is consistent with the moderate change in  $\text{O}_3$  mixing ratios during this event.

Finally, the difference in simulated and observed absolute mixing ratios of  $\text{CH}_3\text{OOH}$  needs to be addressed. Figure 5 indicates that although the model reproduces the relative changes quite well, the absolute values are off by a factor of about 2, with the model being consistently higher. The relative difference is higher in the beginning and lower towards the end of the campaign, but the absolute difference remains about 200 pptv. There are several potential explanations for this

discrepancy. First, as mentioned in section 2.2  $\text{CH}_3\text{OOH}$  was not directly measured, but inferred from the  $\text{ROOH}$  signal, assuming that  $\text{CH}_3\text{OOH}$  is the only organic hydroperoxide and that the sampling efficiency can be calculated according to Lee et al. (2000). An experimental verification of the sampling efficiency was not performed (contrary to  $\text{H}_2\text{O}_2$ ) since no  $\text{CH}_3\text{OOH}$  gas phase source was available. If the actual sampling efficiency was lower than the calculated 60%, this could close the gap between observations and model results. Additionally, the sampling efficiency would have to be lower at the beginning of the campaign and higher later on, since a simple multiplication by a factor cannot account for the rather constant absolute difference over the campaign. Therefore, although an error in the sampling efficiency cannot be excluded, it is unlikely the only source of the discrepancy between model and observations.

As discussed above, Hosaynali Beygi et al. (2011) demonstrated that EMAC very well reproduces the  $\text{HO}_2$  measurements made during the OOMPH cruise. Since the precursor for  $\text{H}_2\text{O}_2$  is simulated correctly by the model, one can assume that the source strength for  $\text{H}_2\text{O}_2$  is correctly simulated. The model predicts  $\text{CH}_3\text{O}_2$  concentrations that are similar to  $\text{HO}_2$ , but unfortunately measurements of  $\text{CH}_3\text{O}_2$  were not made. Thus it is not possible to validate the model predicted precursor concentrations for  $\text{CH}_3\text{OOH}$ . But as discussed in Hosaynali Beygi et al. (2011) the simulated  $\text{CH}_3\text{O}_2$  levels are quite realistic. Recently Fittschen et al. (2014) posed that the reaction of  $\text{CH}_3\text{O}_2$  with OH radicals at low  $\text{NO}_x$  concentrations can be a significant sink of methylperoxy radicals and thus could reduce  $\text{CH}_3\text{OOH}$  formation. In a sensitivity study (SR2) this reaction was included in the chemistry code of EMAC (Bossolasco et al., 2014). Additionally, we considered that in addition to  $\text{CH}_3\text{OOH}$  the reaction of  $\text{CH}_3\text{O}_2$  with  $\text{HO}_2$  also produces HCHO to some extent (Ayers et al., 1997). The green line in Figure 6 indicates that including these additional reaction pathways reduces the mixing ratio of  $\text{CH}_3\text{O}_2$  in the marine boundary layer of the South Atlantic by about 30%, yielding an average mixing ratio of  $300 \pm 110$  pptv compared to the observed  $180 \pm 50$  pptv. It seems that the missing reaction between  $\text{CH}_3\text{O}_2$  and OH is responsible for a largest part of the  $\text{CH}_3\text{OOH}$  overestimation by the model, in particular during the second half of the cruise when OH concentrations are high. In general, the contribution of this reaction increases with increasing OH concentration, which leads globally to a maximum impact in the tropical lower troposphere over the Pacific and Indian Oceans. The contribution of the HCHO channel in the reaction of  $\text{CH}_3\text{O}_2$  with  $\text{HO}_2$  is rather constant with a branching ratio of about 10%. Nevertheless, due to the uncertainties in both measurements and modeling the explanation for the difference in  $\text{CH}_3\text{OOH}$  simulation vs. observations remains ambiguous.

By combining both the reduced  $\text{H}_2\text{O}_2$  deposition velocity and the reduced  $\text{CH}_3\text{OOH}$  source due to the competing reaction of  $\text{CH}_3\text{O}_2$  with  $\text{OH}$  in an additional sensitivity simulation (SR3) the simulated  $\text{CH}_3\text{OOH}/\text{H}_2\text{O}_2$  ratio is reduced to a mean value of  $1.01 \pm 1.06$  (green line in Figure 6), much closer to the observed value ( $0.8 \pm 1.1$ ).

Note that an underestimation of entrainment from the free troposphere would also explain the underestimation of the  $\text{H}_2\text{O}_2$  (and  $\text{O}_3$ ) mixing ratios during the first phase of the campaign. However, this leads to an inconsistency with the MHP data, which would be affected by the same transport. Similar to  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , MHP mixing ratios increase with altitude and show a maximum above the boundary layer (Stickler et al., 2007, Klippel et al. 2011). Thus one would expect that a transport limitation from the free troposphere in the simulations would also produce an underestimation of the simulated MHP concentrations in the MBL, but the opposite is the case; actually the model significantly overestimates MHP. Therefore, we conclude that different processes are responsible for the temporal underestimation of  $\text{H}_2\text{O}_2$  (during the first part of the campaign) and the time independent overestimation of MHP, as most clearly corroborated in the time series of the ratio of these two species in Figure 6.

## Summary and conclusions

Hydrogen peroxide, MHP and ozone have been measured in the marine boundary layer over the South Atlantic Ocean during the austral summer in 2007. Observed mixing ratios are consistent with values reported in the literature. Simulations with the atmospheric chemistry model EMAC indicate that it qualitatively reproduces the observations very well. It also captures the downward mixing of high concentrations of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  during a nighttime increase in boundary layer height south of the African continent. Quantitatively, the model tends to **underestimate**  $\text{H}_2\text{O}_2$  mixing ratios during the first part of the cruise. During this part we experienced very high wind speeds, in excess of 15 m/s. Later on during the cruise much lower wind speeds were encountered for which the model accurately reproduces observed  $\text{H}_2\text{O}_2$  mixing ratios. A similar tendency has been observed for ozone. The most likely reason for the discrepancy is that the model parameterization of trace gas deposition to the ocean surface tends to overestimate the dry deposition loss of the soluble and reactive  $\text{H}_2\text{O}_2$  at high wind speeds. This was confirmed by a model sensitivity study with limited (at 5 cm/s) deposition velocity. MHP, which is less soluble and reactive, is not as much affected by dry deposition, although EMAC significantly overestimates its mixing ratio. This overestimation is rather constant over the campaign and

indicates an offset of approximately 200 pptv. The reasons for this discrepancy are not easy to identify, since the measurements provide less stringent constraints than for  $\text{H}_2\text{O}_2$ . MHP was estimated from a total ROOH signal, assuming MHP being the only ROOH component and a sampling efficiency of 60 % compared to  $\text{H}_2\text{O}_2$ . Fittschen et al. (2014) recently suggested that a competing reaction of the  $\text{CH}_3\text{O}_2$  radicals with OH can significantly diminish the source of MHP in the marine boundary layer, in particular at the low  $\text{NO}_x$  concentrations observed during OOMPH. A sensitivity study with EMAC indicates that this reaction reduces the  $\text{CH}_3\text{O}_2$  mixing ratio by about 30 %, increasing with decreasing latitude due to the meridional gradient in OH radical concentrations. Although this is a significant change, bringing  $\text{CH}_3\text{OOH}$  closer to observations, it appears to be insufficient to fully remove the discrepancy between simulated and observed  $\text{CH}_3\text{OOH}$  mixing ratios during OOMPH.

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Figure captions:

Figure 1: Ship track of the Marion Dufresne over the southern Atlantic. The track is color coded with time.

Figure 2: Time series of observed and simulated temperature and wind speed.

Figure 3: Time series of observed (red) and simulated (blue) ozone mixing ratios.

Figure 4: Time series of observed (red) and simulated (blue) hydrogen peroxide mixing ratios. In green a sensitivity simulation (SR 1) of the model is shown with reduced dry deposition velocity (see text for details).

Figure 5: Time series of observed (red) and simulated (blue) methyl hydroperoxide mixing ratios. The green line shows a sensitivity simulation (SR2) including the reaction of  $\text{CH}_3\text{O}_2$  with OH (see text for details).

Figure 6: Simulated (blue) and observed (red)  $\text{CH}_3\text{OOH}$  to  $\text{H}_2\text{O}_2$  ratio. The green line shows a sensitivity simulation (SR3) including reduced  $\text{H}_2\text{O}_2$  dry deposition velocity and the reaction of  $\text{CH}_3\text{O}_2$  with OH (see text for details).

Figure 7: EMAC simulation of  $\text{O}_3$  (top) and  $\text{H}_2\text{O}_2$  (bottom) vertical profiles versus time. Superimposed is the height of the planetary boundary layer. The increase in boundary layer height in the night from March 15 to 16 is associated with an increase in peroxide mixing ratios.