

## ***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.***

**H. Fischer et al.**

horst.fischer@mpic.de

Received and published: 24 March 2015

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 our argument that the model H<sub>2</sub>O<sub>2</sub> bias relates to 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 model 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 ob-

C12744

served H<sub>2</sub>O<sub>2</sub> 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 regressions analysis indicate that the model tends to overestimate observed HO<sub>2</sub> by approximately 30 % throughout the campaign ( $\text{HO}_2(\text{obs}) = 0.83 \times \text{HO}_2(\text{model}) - 0.1$ ;  $R^2 = 0.82$ ). The total uncertainty of the HO<sub>2</sub> measurements is  $\pm 35$  % (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 higher concentrations of peroxy radicals. As discussed by Regelin et al. (ACP 13, 10.703-10720, 3012, doi:10.5194/acp-13-10703-2013), the 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, which 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

C12745

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 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.

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.

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 not possible. 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 RO<sub>x</sub> 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  $\pm$  30 %, which is much smaller than the difference between simulations and observations that are of the order of at least a factor of 2.

Specific comments:

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).

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

C12746

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

We deleted the phrase main problem and replaced it by "hence one problem seems to be ..."

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 of the order of 3 %, an order of magnitude less than the uncertainty due to the sampling issues 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. An estimate for MHP can be gained by multiplication with the sampling efficiency of 0.6, yielding a value of 40 pptv.

We replaced "measured and observed" by measured and modeled".

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.

---

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

C12747