



Hydrogen peroxide in the marine boundary layer

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

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ysis of NO_2 yields ozone, with NO_x acting as a catalyst. In low 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 H_2O_2 and organic peroxides (e.g. CH_3OOH 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 HO_x (OH plus HO_2) radicals, which can be recycled by photolysis or reaction with 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 NO_x concentrations the concentrations of H_2O_2 , ROOH and O_3 are strongly coupled, since their formation and destruction compete for the 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 (H_2O_2 and 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 H_2O_2 in the tropics (Slemr and Tremmel, 1994; Heikes et al., 1996; O'Sullivan et al., 1999, 2004; Junkermann and Stockwell, 1999; Weller et al., 2000) and decreasing concentrations toward higher latitudes in both hemispheres, reaching 200–300 pptv south of 40° in the Southern Hemisphere (Slemr and Tremmel, 1994; O'Sullivan et al., 1999, 2004; Junkermann and Stockwell, 1999; Weller et al., 2000). 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 H_2O_2 mixing ratios have been observed in continental outflow (e.g. Heikes et al., 1996).

during the first part and 8 ms^{-1} during the second part of the campaign (Fig. 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 $1/2''$ 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 $1/4''$ Teflon lines.

Hydrogen peroxide (H_2O_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 H_2O_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 H_2O_2 concentration is determined from the difference of the two channels, with channel A measuring all peroxides (ROOH), while channel B measures ROOH – H_2O_2 after selective destruction of H_2O_2 via addition of catalase (efficiency > 95 % as determined in the field) prior to the reaction with POPHA.

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3 Results and discussion

3.1 Data processing

For the present analysis the original observations were averaged over 12 min 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° W) of the ship track to 140 min for the most easterly (35° 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 and 275° . This stack air contained very high concentrations of NO (up to 200 ppbv in individual plumes), leading to complete titration of O_3 , while H_2O_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 O_x ($O_3 + NO_2$) for the experimental data, to deduce the original O_3 concentration that would have occurred without NO-titration to NO_2 . In general, the difference between O_x and O_3 is marginal due to the very low NO_x 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_3 using O_x in all cases is smaller than 2% . From the model only the original O_3 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_3 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_3 mixing ratios during the first part of the cruise (10 – 14 March) and a slight overestimation between 15 and 17 March. During the last part of the cruise after 17 March both model and observations agree quite well. Overall, the mean observed and simulated O_3 are 20.3 ± 1.8 ppbv and 19.7 ± 2 ppbv, re-

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spectively. A least-square fit between simulated (y axis) and observed (x axis) ozone yields a slope of 0.98 ± 0.01 and an offset of -0.43 ± 0.21 ppbv. The regression coefficient R^2 is rather low (0.2). Taking into account that observed O_x measurements are affected by background NO_2 , 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_3 mixing ratio of 18.3 ppbv. Similar O_3 mixing ratios of the order of 20 ppbv were also observed in the southern Atlantic south of 40° S during two *Polarstern* cruises in November 1990 (Slemr and Tremmel, 1994) and October/November 1994 (Junker-mann and Stockwell, 1999). As discussed in Lelieveld et al. (2004) seasonal variations of O_3 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_3 trend for this latitude band is 0.17 ± 0.08 ppbv year $^{-1}$ (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 confirmation of the continuation of this trend is not possible.

Time series of measured and observed H_2O_2 are shown in Fig. 4. During the first part of the cruise (10 to 14 March) observed H_2O_2 mixing ratios indicate small variability at levels between 200 and 300 pptv. During this period the model significantly underestimates observed H_2O_2 , by more than a factor of two. After 14 March in the eastern part of the South Atlantic H_2O_2 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 15 March, while later on measurements and model results agree quite well. A period of relatively high H_2O_2 (in excess of 1 ppbv) was observed and simulated after midnight on 16 March, southwest of the African coast (see Fig. 1). On average observed and simulated H_2O_2 were 350 ± 220 pptv and 310 ± 240 pptv, respectively. Slope and intercept of a least-square regression analysis are 2.04 ± 0.04 and -0.27 ± 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 O_3 . As can be deduced from the time series (Fig. 4) the model tends to reproduce trace gas levels over the Southern Atlantic. The measured H_2O_2 mixing ratios are comparable to previously reported observations south of $35^\circ S$ in the Atlantic lower troposphere, being approximately 200–300 pptv (Slemr and Tremmel, 1994; Junkerman and Stockwell, 1999; Weller et al., 2000).

Observations of CH_3OOH mixing ratios are shown in the time series in Fig. 5 along with EMAC simulations. The temporal evolution is similar to H_2O_2 , with low values (less than 200 pptv) during the first part of the cruise, a strong mixing ratio increase starting on midnight of 16 March and lower concentrations afterwards. The relative change is reproduced by the model, with a general tendency to overestimate CH_3OOH mixing ratios except during the period when the high peak was encountered on 16 March. Average measured CH_3OOH mixing ratios are 280 ± 250 pptv, while the model calculates a mean value of 450 ± 190 pptv. The offset between model and observations is clearly shown in the least-square regression analysis that yields an intercept at 0.18 ± 0.05 ppbv and a slope of 0.37 ± 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 16 March, the variability of O_3 , H_2O_2 and CH_3OOH 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 south-western 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

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signal, assuming that CH_3OOH 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 H_2O_2) since no CH_3OOH 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 HO_2 measurements made during the OOMPH cruise. Since the precursor for H_2O_2 is simulated correctly by the model, one can assume that the source strength for H_2O_2 is correctly simulated. The model predicts CH_3O_2 concentrations that are similar to HO_2 , but unfortunately measurements of CH_3O_2 were not made. Thus it is not possible to validate the model predicted precursor concentrations for CH_3OOH . But as discussed in Hosaynali Beygi et al. (2011) the simulated CH_3O_2 levels are quite realistic. Recently Fittschen et al. (2014) posed that the reaction of CH_3O_2 with OH radicals at low NO_x concentrations can be a significant sink of methylperoxy radicals and thus could reduce CH_3OOH 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 CH_3OOH the reaction of CH_3O_2 with HO_2 also produces HCHO to some extent (Ayers et al., 1997). The green line in Fig. 6 indicates that including these additional reaction pathways reduces the mixing ratio of CH_3O_2 in the marine boundary layer of the South Atlantic by about 30 %, yielding an average mixing ratio of 300 ± 110 pptv compared to the observed 180 ± 50 pptv. It seems that the missing reaction between CH_3O_2 and OH is responsible for a largest part of the CH_3OOH 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 CH_3O_2 with 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 CH_3OOH simulation vs. observations remains ambiguous.

By combining both the reduced H_2O_2 deposition velocity and the reduced CH_3OOH source due to the competing reaction of CH_3O_2 with 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 ± 1.06 (green line in Fig. 6), much closer to the observed value (0.8 ± 1.1).

4 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 H_2O_2 and CH_3OOH during a nighttime increase in boundary layer height south of the African continent. Quantitatively, the model tends to overestimate H_2O_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^{-1} . Later on during the cruise much lower wind speeds were encountered for which the model accurately reproduces observed H_2O_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 H_2O_2 at high wind speeds. This was confirmed by a model sensitivity study with limited (at 5 cm s^{-1}) deposition velocity. MHP, which is less soluble and reactive, is not as much of affected by dry deposition, although EMAC significantly overestimates its mixing ra-

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5 tio. 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 H_2O_2 . MHP was estimated from a total ROOH signal, assuming MHP being the only ROOH component and a sampling efficiency of 60 % compared to H_2O_2 . Fittschen et al. (2014) recently suggested that a competing reaction of the CH_3O_2 radicals with OH can significantly diminish the source of MHP in the marine boundary layer, in particular at the low NO_x concentrations observed during OOMPH. A sensitivity study with EMAC indicates that this reaction reduces the CH_3O_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 CH_3OOH closer to observations, it appears to be insufficient to fully remove the discrepancy between simulated and observed CH_3OOH mixing ratios during OOMPH.

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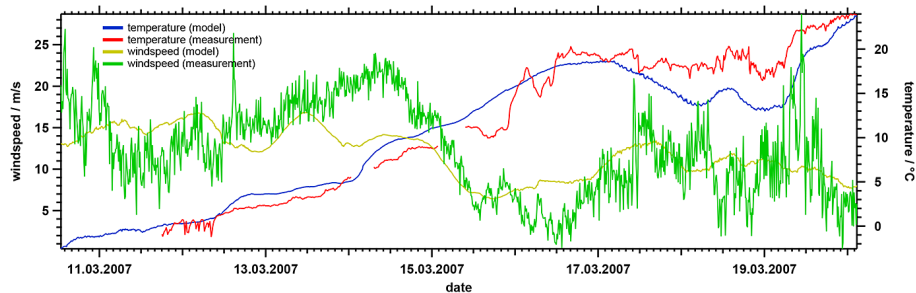


Figure 2. Time series of observed and simulated temperature and wind speed.

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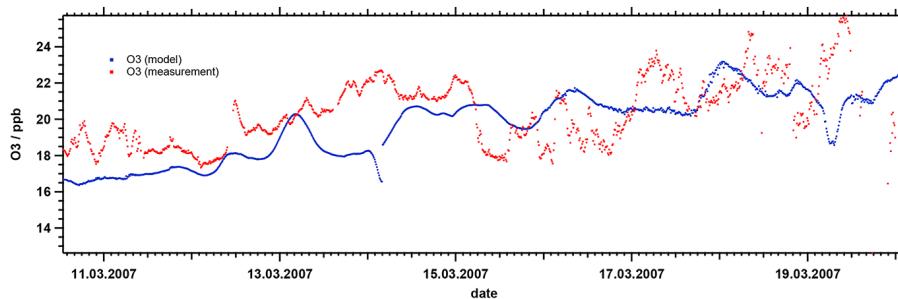


Figure 3. Time series of observed (red) and simulated (blue) ozone mixing ratios.

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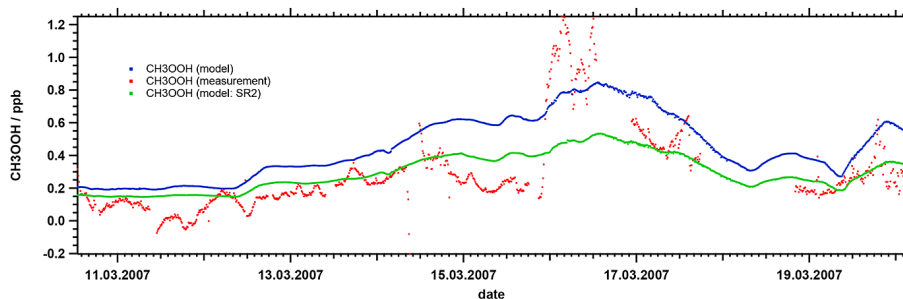


Figure 5. Time series of observed (red) and simulated (blue) methyl hydroperoxide mixing ratios. The green line shows a sensitivity simulation (SR2) including the reaction of CH_3O_2 with OH (see text for details).

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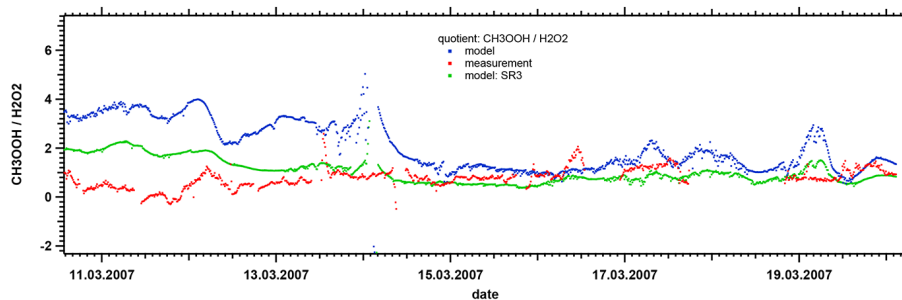


Figure 6. Simulated (blue) and observed (red) CH_3OOH to H_2O_2 ratio. The green line shows a sensitivity simulation (SR3) including reduced H_2O_2 dry deposition velocity and the reaction of CH_3O_2 with OH (see text for details).

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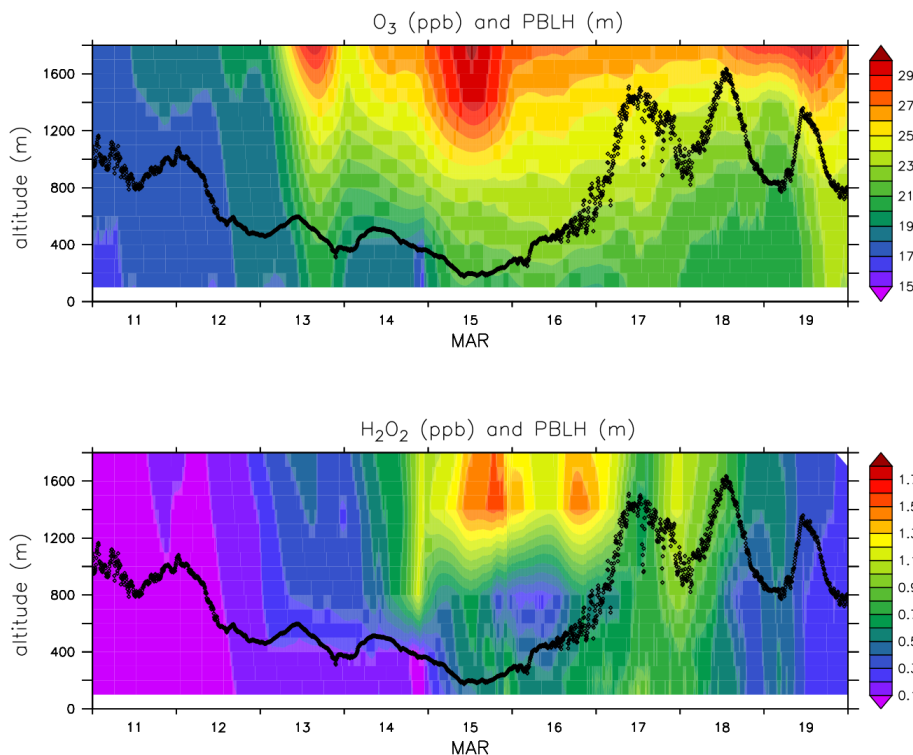


Figure 7. EMAC simulation of O₃ (top) and H₂O₂ (bottom) vertical profiles vs. time. Superimposed is the height of the planetary boundary layer. The increase in boundary layer height in the night from 15 to 16 March is associated with an increase in peroxide mixing ratios.