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Interactive comment on "Observations and model calculations of trace gas scavenging in a dense Saharan dust plume during MINATROC" *by* M. de Reus et al.

M. de Reus et al.

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We would like to thank the referee for his/her comments on the paper. The constructive comments helped to improve the paper. In the following text we will answer the questions raised by the referee. These answers are also incorporated in the revised version of our manuscript. Since several questions to the same topic are raised at different positions in the referee report, we organised the answers by subject. After this the specific questions of the referee are answered separately.

Why boxmodel?

The reason why we did not only present the data in this paper but also included box-

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model calculations, is that from the measurement it is obvious that the concentration of O3, HNO3, ROx and H2O2 are strongly reduced during the dust period. However, the reason why cannot be deduced from the measurements directly. For the reduction of the ozone mixing ratio there are several possibilities mentioned in the text: transport of ozone poor air, heterogeneous loss on mineral dust aerosol and a decrease of the net ozone production rate. The reduction of the ROx and H2O2 mixing ratios during the dust event might have been caused by the reduction of the photolyses rates due to the optical thick dust layer or through heterogeneous loss on mineral dust aerosol. The reduction of HNO3 in dust plumes, however, is generally assumed to be caused by heterogeneous reactions on mineral dust aerosol. To investigate the causes of the reduction in O3, H2O2 and ROx in the dust plume (box)model calculations are very important.

Why 10 days simulations?

We did run the boxmodel for 10 days to be sure that steady state is reached for the different compounds. I agree with the referee that this is very long and that a shorter time would have been enough for the short lived gases which we investigated in this paper. In the text we indicated that at noon a steady state HCHO and ROx mixing ratio is reached within 6 and 1 hours, respectively. In the revised version of the paper we defined the time to reach a steady state concentration as the time the boxmodel needs to reach a mixing ratio which did not change more than 1 promile in the last 30 minutes and calculated the steady state time for one day during the campaign. When no isoprene is included in the model calculations, steady state concentrations are reached after 9 and 6 hours for HCHO and ROx, respectively, at local noon. Including isoprene in the calculations increases the time in which steady state is reached to 25 and 24 hours for HCHO and ROx, respectively. For H2O2 a steady state time of 20 hours was found at local noon. For the highest analysed zenith angle (70 degrees), steady state is reached within 22, 15, and 64 hours for HCHO, ROx and H2O2, respectively. These times are added to the text in the revised version of the paper.

We also checked the temporal evolution of the HCHO, ROx and H2O2 mixing ratio at different solar zenith angles. These examples show that all gases show a gradual in- or decrease until a steady state mixing ratio is reached. The fact that the HCHO, H2O2 and ROx reach a steady state mixing ratio, implies that O3 does not provide an infinite pool of oxidants for a simulation of 10 days.
Running the model for 10 days in stead of the above defined steady state time will not lead to significantly different results, since the mixing ratios of HCHO, ROx and H2O2 do not change much after this point. For ROx and HCHO the difference between the above defined steady state concentrations and the concentration after 10 days of simulation is smaller than 2 %. For H2O2 differences up to 10 % at high solar zenith angles can be found.

After this paper was submitted the boxmodel has been developed further and a diurnal cycle of the photolysis rate has been implemented. With this setup of the model the NO mixing ratio cannot be fixed but a diurnal emission pattern had to be included so that the resulting NO concentration was similar to the measured concentration. Hence, it is not without a lot of effort to use the new setup and repeat the simulations of this paper. First tests with the new setup of the model for another measurement campaign, however, did not show large differences between the two approaches (fixed photolysis rates or a diurnal cycle in the photolysis rates).

The model is used to calculate steady state concentrations and not to simulate the history of the airmass. By keeping the concentrations of the long lived trace gases and the photolysis rates constant we tried to simulate the concentrations of the gases when the airmass would have been in photochemical steady state. So we do NOT intend to perform a lagrangian simulation. A discussion point remains if the airmass really reached steady state at the measurement site.

Only for the simulation of the effect of dust on the trace gas mixing ratio we included dust uptake during the last three days of simulation, since the uptake of trace gases is not only important at the measurement site, but already happens from the moment that the airmass travels over the Saharan desert. To calculate a realistic uptake coefficient we have to use a realistic time for dust uptake. We realise that here we mix up the steady state and lagrangian approach of the boxmodel.

H2O2 simulations:

We discussed the boxmodel simulations of HCHO extensively, because we wanted to show the capabilities and limitations of the boxmodel. We did choose the simulation of HCHO because it is a relatively short lived trace gas, its concentration is determined by photochemistry and does not seem to be influenced by dust. After that we performed boxmodel simulations for ROx, since the observations show that the ROx mixing ratios were influenced by dust aerosols. However, we had to conclude that the boxmodel was not able to simulate a reduction in the ROx mixing ratio. For the simulations of H2O2 we had to include dry deposition to simulate the observed mixing ratios outside the dust event, which includes another assumption. Therefore, we first try to convince the reader that the boxmodel can do a good job for components which are not effected significantly by dry deposition and the dust plume.

Other parameters which could have influenced the H2O2 mixing ratios during the dust event are reduced photolysis rates and precursor gas mixing ratios. The boxmodel explicitly includes the change in precursor gas mixing ratios and photolysis rates during the dust event, since the model is constrained with the observed mixing ratios of long lived trace gases and photolysis rates. Since the mixing factor during the dust event is low compared to the dust-poor days, it is possible that the dry deposition rate during the dust event has changed compared to the dust-poor days. A reduced mixing factor would cause a lower dry deposition rate, because the contribution of local boundary layer air is reduced, resulting in less physical contact with the ground. This would cause even higher simulated H2O2 mixing ratios during the dust event and increase the discrepancy between observations and model calculations. With the current dataset there is no possibility to prove this hypothesis.

Specific questions:

p658/line 12: changed to “for all models the comparison with observations is a main limitation”

p658/17: changed in the text

p660/15: changed to “destroyed by the enzyme catalase”

p660/26: changed to “AERO laser detectors”

p661/6: Laboratory calibrations show that 7.4% of the H_2O_2 is lost in the inlet line, while no reduction of the HCHO mixing ratio was observed due to the long inlet line.

p663/17-19: changed in the text

p664/5-6: specifications about the number of averaged values has been added to the text and for the dust event the three values for the mixing ratio have been given directly.

p664/18-20: VOC and NMHC data are only available from July 29, and hence, have been averaged only for this period. For all other parameters data from the entire campaign have been used to determine the average concentrations. This has been added to Table 2. For the ratio of different VOC and NMHC to for example CO it would give a slightly different result when the average CO mixing ratio would have been determined using the data after July 28 only. We decided, however, to use the most complete data set to determine the average mixing ratios for this campaign.

p664/27: the aerosol optical depth was measured with a lidar, which was stationed at Izana. Hence, the measured optical thickness is only valid for the part of the dust plume above the altitude of the measurement station. An aerosol optical thickness of 0.5 was reached during a period when a dust plume was present above the altitude of the measurement station, but no dust was measured at the station itself. Added to the text.

p665/22: the way we use the boxmodel implies that steady state mixing ratios have been reached. We added this note once more at the beginning of section 6. In section 5 we added the following remark “Note that biogenic emissions from vegetation at the slopes of the mountain close to the measurement site influence the observed trace gas mixing ratios at the measurement site in a different manner than anthropogenic emissions, which are transported over a much larger distance from the marine boundary layer. Hence, the calculated mixing factor is a good indicator for the influence of antropogenic pollution from the marine boundary layer, but not for the influence of more local biogenic emissions”. Moreover a plot of the diurnal cycle of acetone and isoprene have been added to Figure 2 and have been discussed in the text.

p665/27: the relatively high NOy mixing ratios (compared to the HNO3 mixing ratios observed by Umann et al. [manuscript submitted to JGR]) in the dust plume indicate that aerosol nitrate is converted. Since the converter is at the same time the tip of the NOy inlet no losses are expected in the inlet line. However, the converter is not characterised towards the evaporation and conversion efficiency of aerosol nitrate which makes it impossible to quantitatively determine the aerosol nitrate concentration from this measurement. The model results are not sensitive to a changing initial HNO3 mixing ratio (see Table 4). Hence, a possible overestimation of the HNO3 mixing ratio due to the evaporation of aerosol nitrate does not change the results presented in this paper.

p667/20: The concentrations of a large set of trace gases is kept constant during the model simulations. The same is true for the temperature, pressure and relative humidity. Which trace gases are kept constant is described in section 6.1. We added an extra reference to this section in section 6. Variations in the dust concentration are included in the calculation of the heterogeneous uptake coefficient for the different trace gases. Also the photolysis rates are directly influenced by the dust concentration and are used as input parameter for the model.

p668/10: Since both HNO3 and NO are kept constant during the model simulations there is little room for a change in the NOy partitioning. The model results are not sensitive to a changing initial HNO3 mixing ratio, but very sensitive to a change in the NO mixing ratio. This has been shown in section 6.2.2 and summarised in Table 4. Note again that we do not intend to perform a lagrangian simulation.

p669/10: see general comments above. A discussion about the time it takes for the different components to reach steady state has been added to section 6.2.

p669/13: a zenith angle below 70 degrees is achieved between 08:15 and 18:15 UTC. Added to the text.

p674/24: the boundary layer calculations refer to the above mentioned model simulations of Ayers et al., 1997 and Weller et al., 2000 for the remote marine boundary layer. The marine boundary calculations of Wagner et al. 2002 and Zhou et al., 1996 are performed for a polluted marine boundary layer. Changed in the text.

p675/7: The local air circulation patterns at the measurement site cause the sampling of free tropospheric air masses during the night and anthropogenically influenced airmasses during the day. Dry deposition only occurs in airmasses which have had physical contact with the ground. Since it is assumed that the influence of the anthropogenically influenced local boundary layer increases with increasing solar radiation, we assumed that dry deposition of H2O2 is most important around noon, and less important with increasing solar zenith angle. Therefore we included a sinusoidal dry deposition rate for H2O2, with a maximum at local noon. A discussion about the dry deposition rate during the dust event can be found above.

p676/20: We do not fully understand this comment of the referee. Peroxy radicals are included in the model simulations. All parameters which are important for the production and loss of H2O2 besides dry deposition (temperature, pressure, relative humidity, photolysis rates, O3, NO, CO, NMHC) are included in the model and are constrained to the measured values.

P680/4: See general comment above.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 655, 2005.