**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Heterogeneous uptake of gaseous hydrogen peroxide by Gobi and Saharan dust aerosols: a potential missing sink for H_2O_2 in the troposphere" *by* M. Pradhan et al.

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We thank the reviewer for the constructive comments and questions. In response to these comments, we have amended our paper as summarized below. Our responce and manuscript amendments are indicated below by italised text.

General:
This work addresses the reaction of H_2O_2 with dispersed samples of Saharan dust and Gobi sand. Uptake coefficients are derived, which increase with relative humidity

and which are sufficiently large (up to 1e-3) for Saharan dust to impact on H_2O_2 lifetimes in regions heavily affected by dust emissions. The technique employed, aerosol flow tube coupled to DMA and CIMS detectors should give reasonably reliable results. The experiments do not cover sufficient parameter space to make very reliable extrapolations to the atmosphere and there are a number of issues that should be considered (see below). However, as this is the first study of the uptake of H_2O_2 to a desert dust "type" aerosol it should be published once some improvements have been made.

Specific:

P11085 L9 The Gobi sample appears to be ground sand. This will not have the same mineralogical composition as Asian dust from this region. Transportable dust samples comprise mainly of the clay mineral fraction and not the quartz-rich sand fraction and are (probably) more reactive. The Saharan dust samples originates from the Cape Verde islands off the West Afcan coast where they were either deposited at some time in the past or collected on filters. This is not clear from the manuscript. Is it conceivable that very old dust deposits (which have been exposed to the atmosphere for a (very) long time) will display a different reactivity toward H_2O_2 to freshly generated dust ? More information about the origin of the Saharan dust (and collection method) would be useful. Are there any descriptions of this Saharan dust sample (mineralogy, source region) in the literature ?

We agree that these issues deserve clarification. We have now added the following text in the revised manuscript.
*P11085 L11: "... by high resolution X-ray photoelectron spectroscopy (XPS) (Fig. 1) a technique that provides information about **surface** as opposed to bulk chemical composition, the property that actually matters in regard to surface chemical behaviour."*

AND

P11085 L18: *"It is evident that the surface composition of the two samples is broadly similar, though certain minor components show large differences in relative concentrations. Silica and alumina are the most abundant constituents in both samples, as would be expected; interestingly, the Saharan dust contains a small amount of Ti present as TiO_2 whereas this material is undetectable in the Gobi sample. Moreover, both samples contain Fe as Fe_2O_3: the significance of these findings will be discussed below. In passing we note that similar Saharan dust samples, also collected from the Cape Verde islands, were used by Hanisch and Crowley (2003): their bulk composition, determined by energy dispersive X-ray spectroscopy, was similar to the surface composition we observed by XPS."*
<u>**MANUSCRIPT AMENDED**</u>

P11086 L1 The dust aerosol samples were generated from an aqueous suspension. What tests did the authors perform to make sure that generation in this manner does not change the chemical characteristics of the dust ?

The presence of water is not expected to change significantly the chemical characteristics of the mineral dust particles which our XPS measurements show to consist of insoluble inorganic compounds. This is stated in the revised manuscript:
P11086 L3: *"In view of the XPS results which show that the surfaces of the dust particles consist of insoluble inorganic compounds, this procedure is not expected to change significantly the chemical characteristics of the dusts."*
<u>**MANUSCRIPT AMENDED**</u>

P11086 L6 Dust size distribution and number density were determined using a DMA. This will give you a mobility diameter of a non-spherical particle. What errors are associated with assuming that the particles are spherical. ? This propagates directly to the calculation of the uptake coefficient. The authors allude to this problem on page 111088 (L21) but make no attempt to assess the associated uncertainty. The errors quoted are less than 5 percent, which is unrealistic. I would estimate that a factor 2 is closer to the truth. In this regard, it also makes no sense to talk about "significant differences" in the uptake coefficient between the Gobi and Saharan samples.

The shape of mineral dust particles is indeed not spherical as assumed by the DMA measurements. However, it is difficult to assess this uncertainty. Assuming both dusts have about the same non-spherical shapes this error cancels out. Although the shape is not determined in detail in this study we continue to use the assumption of spherical particles throughout the manuscript but clearly state now that the uncertainty of the data is possibly as large as a factor of 1.5 - 2. However, relative differences observed between the two types of dust should not be affected significantly by this uncertainty.
This is now made clear in the revised manuscript:
P11086 L23: *"The non-spherical shape of mineral dust particles induces a systematic error when the electrical mobility diameters of the DMA are used to estimate the particle surface areas, which can be as high as a factor of 1.5 to 2 (Wagner et al., 2008; Hinds, 1982). However, the geometric shape of the mineral dust particles used in this study was not determined and the values reported here are based on mobility equivalent diameters throughout the manuscript. It is assumed that the two types of dust particles have roughly the same non-spherical shapes and thus relative differences observed between the two types of dust should not be affected significantly by this uncertainty."*
P11088 L18: *"It should be noted that the aerosol surface areas reported here are*

based on mobility equivalent diameters as measured by the DMA and that non-spherical properties are not taken into account (see section 2.2)."

P11097 L12: New reference:
Hinds, W. C. Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, John Wiley Sons, New York, 1982.
MANUSCRIPT AMENDED

P11088 L18 Figure 3 shows that the H_2O_2 concentration barely changes when there is contact with the dust. The order of the reaction is thus undetermined. Single measurements of time dependent H_2O_2 loss are not the best way to derive the uptake coefficient (errors in contact time due to mixing etc). The authors also report some data in which the surface area was varied (Fig 4), though I have the impression that only a small l fraction of the uptake coefficients reported were measured this way. What fraction of the data in Figure 5 was derived by varying the surface area of the sample ?

We have to assume that this comment is due to a misunderstanding. The effect of H_2O_2 uptake on aerosol particles in the flow tube is clearly visible (triangle symbols in Figure 3) compared to the wall losses measured before (squares) and after (circles) aerosol particles were present in the flow tube. The wall loss data before and after the aerosol addition are almost equal, showing that there are no memory effects in the flow tube after turning off the particle flow and confirming the quality of the data presented here.
All data points shown in Figures 3 and 4 are derived from individual flow tube experiments as indicated.
As indicated in the caption of Figure 5, the data point at 35% is derived from the

measurements where we varied the surface area (Figure 4) and fit very well into the RH data set of Figure 5 confirming the robustness of our measurements.
NO ACTION

P11089 L4 The "Brown" procedure was used to correct the data for diffusion effects. It's not quite clear to me how this was done. I have the impression that Kwall was first corrected using Brown (why ?), then Ktotal was similarly corrected, then the difference was computed ?? Normally, the Brown algorithm takes care of gradients in the flow tube due to axial and radical diffusion, interaction with walls and reactants simultaneously.

The text describing the procedure to account for axial diffusion ("Brown correction") was re-phrased as it caused confusion. We hope that the respective part in the text is now clear as we explicitly mention that the Brown correction was applied to the observed reaction rate (k_{total}). The Brown correction procedure is frequently used to correct for possible diffusion gradients, see e.g., Wagner et al., 2008. This is now incorporated in the revised manuscript:
P11089 L2: "The first-order rate constant (k_{total}) was then corrected for axial diffusion using the iterative method of Brown (1978) (see e.g., Wagner et al., 2008)."
MANUSCRIPT AMENDED

P11089 L23 The concentration of H_2O_2 was always rather high in these experiments and was not varied over a sufficiently large range to test the dependence of the uptake coefficient on this parameter. This would give some insight into the reaction mechanism and also rates of saturation (if any) of surface sites. A good example is O3, for which the uptake coefficient to dust varies greatly with mixing ratio.

Agreed. However, technical difficulty of handling H_2O_2 vapour limited the accessible concentration range. We have now added the following statement in the revised manuscript:
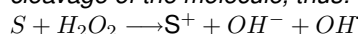***P11089 L24:*** *"Experimental constraints imposed by the difficulty of handling hydrogen peroxide vapour prevented investigation of a wider range of H_2O_2 concentrations, which might have given additional insight into the reaction mechanism."*
MANUSCRIPT AMENDED

In this regard it would have been useful to read something about the (expected) products of the reaction of H_2O_2 on dust.

Fair point. We have now added the following text in the revised manuscript.
P11091 L4: *"The generally accepted mechanism (Lin and Gurol, 1998) for this process when taking place on oxide surfaces corresponds formally to a heterolytic cleavage of the molecule, thus:*
$$S + H_2O_2 \longrightarrow S^+ + OH^- + OH$$
followed, under conditions where catalytic decomposition occurs, by a sequence of steps leading ultimately to the formation of water and oxygen. Whether or not the uptake we observe involves subsequent catalytic decomposition under our conditions, it cannot be determined from the present measurements."
MANUSCRIPT AMENDED

This would help us to assess if the reaction is catalytic or if surface sites are consumed during exposure. This has repercussions for modelling the reaction. Is an

uptake coefficient which is invariant with time really suitable ?

As stated above the uptake mechanism is not known. This could have an impact on the modelling if the uptake coefficient were to vary with time (as the aerosol is aged) - but this remains an unknown, now explicitly acknowledged. This point has now been addressed in detail in responding to Reviewer 2, below.
MANUSCRIPT AMENDED

A related issue is the effect of exposure to other trace gases with may interact with dust particles such as O3 or inorganic acids. Would this be expected to modify (increase or reduce) the uptake coefficient of H_2O_2 ? Please comment !

The presence of a second trace gas is in principle bound to have some effect on the uptake of H_2O_2 or indeed that of any other trace gas. Such studies are beyond the scope of the present paper. Moreover, as far as we are aware, reported experimental studies of trace gas uptake do not explore the effects of exposure to other trace gases, a far from trivial task. Our methodology is therefore in line with accepted practice.
NO ACTION

P11091 L3 The authors rationalise the enhanced uptake of H_2O_2 at larger RH as being due to uptake to surface sites with "liquid-like" water. Why should this enhance the uptake compared to the so called "dissociative adsorption" on "bare" surface sites.

Dissociative adsorption by cleavage of the O-O bond in hydrogen peroxide (see above) will be more or less activated, depending on the chemical nature of the bare oxide surface. Uptake of hydrogen peroxide into a water island will have a different activation barrier. Which of these is the greater will determine whether RH acts to increase or decrease the uptake coefficient. We have addressed this point in our response below where the reviewer raises a closely related issue involving the difference between the present results and our earlier results for TiO_2.
MANUSCRIPT AMENDED

What is the uptake coefficient for H_2O_2 to an aqueous surface ?

Not known.

Also, the authors do not mention the fact that in their previous publication on H_2O_2 with TiO2, they observed the opposite trend. Why ?

Good point. We have added the following text in the revised manuscript:
P11091 L15 *"Related to this, we recall our earlier work on H_2O_2 uptake by TiO_2 aerosols (Pradhan et al., 2010) where it was found that $\gamma_{H_2O_2}$ initially decreased with increasing RH, opposite to what is found here. This likely reflects the higher intrinsic chemical reactivity of the pristine bare TiO_2 surface relative to the lower reactivity of the (mainly silica and alumina) bare dust surfaces. Thus in the case of reactive TiO_2 increasing surface hydration acts to retard H_2O_2 uptake whereas with relatively inactive silica/alumina growing islands of water promote H_2O_2 uptake. Consistent with*

this view, at high RH when both types of surface are extensively hydrated, the γ values converge."
MANUSCRIPT AMENDED

P11092 L15 The model was allowed to run for 4 days, with data taken from the 2nd day (P 11094 L14). Is a one day run-up really sufficient for the box-model to achieve steady state ?

We feel that one day spin up is appropriate. The model is not constrained to fixed concentrations, in which case no spin-up would be needed. Instead we have opted for a model set-up which mimics the decay of an air parcel. Such analyses at longer times are less realistic as gas phase species concentrations tend to decay with time due to lack of emissions.
NO ACTION

P11094 The contributions to H_2O_2 loss from OH reaction photolysis were stated to be about equal. This seems surprising as a (typical) diurnal average OH of 0.05 ppt would result in a lifetime of about 14 hours. With a J-value of about 7e-6 /s, the photolytic lifetime would be about a factor of three longer. The authors should provide additional model output (profiles of OH etc) as supplementary information. In addition, as the authors state, deposition will be an important term in the boundary layer. Did the model take into account the diel variation in height of the BL when calculating the deposition rate ?

Our statement concerning the effects of photolysis and OH being nearly equal

in terms of loss process of H_2O_2 can be rationalised as follows. The e-folding lifetime is calculated as the inverse of the first order loss rate of H_2O_2 to either process. For photolysis the referee states that the J-value is about 7e-6 s^{-1}. This is similar to our model's midday maximum. As a rough estimate if we divide this value by 4 to get a diurnal average J-value of 1.75e-6 s^{-1} and take the inverse of this number we get a photolysis lifetime of $\sim$ 6.5 days. Converting the average OH in ppt in to a concentration in molecules cm^{-3} and multiplying by the rate constant for the reaction OH + H_2O_2 (k = 2.9e-12*exp(-160/T)) and inverting this product gives a lifetime of $\sim$ 6 days. Thus based on these figures, which are very similar to those in our model, we feel that our original statement was correct. The referee makes a valid point that the diel variation of the planetary boundary layer will cause the flux through deposition to change. In our model set-up we have adopted a fixed boundary layer height which as we mention in the revised manuscript is not entirely realistic but we feel still suitable.

We have added the following statements in the revised manuscript:
P11092 L26: *"No diurnal dependence on the height of the boundary layer was included which we note may not be entirely realistic."*

P11094 L4: *"(see supplementary information for profiles of H_2O_2 and other trace gases as a function of time for the model runs)".*
<u>**MANUSCRIPT AND SUPPLEMENTARY INFORMATION AMENDED**</u>

Typos: P11082 L23 Meteorological P11095 L12 typically very dusty ? (delete typically)

Thanks! Typos corrected and word typically deleted.

C5407

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C5397/2010/acpd-10-C5397-2010-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11081, 2010.