

Interactive comment on* “Heterogeneous uptake of gaseous hydrogen peroxide by Gobi and Saharan dust aerosols: a potential missing sink for H₂O₂ 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 response and manuscript amendments are indicated below by italicised text.

This study reports the first measurement of the uptake coefficient of hydrogen peroxide on authentic mineral dust surfaces. The experiments were performed in an aerosol flow tube under nearly realistic atmospheric conditions. The observed uptake

C5409

coefficient scaled with the relative humidity during the reaction. The authors further applied a photochemical box model to evaluate the potential effects of this reaction as a potential sink for hydrogen peroxide in the atmosphere. Given the widespread abundance of hydrogen peroxide in the atmosphere and its importance in HO_x cycling, this study is of substantial novelty. While the data set is relatively limited with respect to the range of concentration and reaction time, it includes a variation of relative humidity, which is appreciated. The paper is overall well written and structured. It could profit from a more in depth discussion of the data, the potential mechanism and a few critical caveats. A few specific aspects should be considered before final publication in ACP.

Section 2.1: since XPS provides the surface composition, it would be interesting to note any differences to bulk composition, which might be known for these samples.

Point well taken. The same issue was raised by Reviewer 1 and has been dealt with at some length as described above.

MANUSCRIPT AMENDED

Is suspension in water and nebulizing and drying considered deleting any memory of previous exposure of the dust samples to ambient air?

This is an interesting point raised also by reviewer 1. Please see our response to referee 1.

MANUSCRIPT AMENDED

C5410

The differences in size distribution of the two samples (apart from one being sand and one being transported dust, a point to note and discuss on its own) indicates that they do not respond to the production method the same way. To what degree are the results affected?

The results should be relatively unaffected by the different size distribution of the two dust samples. The uptake coefficients are determined from the total aerosol surface areas available for reaction irrespectively of the production method. The total surface areas are calculated by summing over the entire measured size distribution, regardless of the shape of the distribution.

NO ACTION

Section 3.1 Kinetic analysis: The discussion of the diffusion correction to correctly account for the wall loss is confusing. The method of Brown allows retrieving a true wall loss rate from the measured loss rate in absence of aerosol. Since rather the effective (measured) wall loss rate determines its contribution to equation (1), it is not clear why the Brown method is being used at all.

We have now described the Brown correction more clearly by appropriately amending the revised manuscript, see respective comment for reviewer 1.

MANUSCRIPT AMENDED

Section 3.3: P11091, top lines: it is mentioned that some surface sites may have dissociatively adsorbed H_2O_2 on them. What is the mechanism the authors have in mind?

C5411

We have now dealt with this issue at some length in responding to Reviewer 1 who raised the same point.

MANUSCRIPT AMENDED

What fraction of the surface sites has been reacted with H_2O_2 during the residence time in the flow reactor?

Good point, which we have now addressed by adding the following text. We thank the reviewer for raising this issue. We have added the following text:

P11091 L12: "Knowing the aerosol particle density and specific area and the number of molecules consumed at any given time, one may estimate the fraction of the surface sites that have reacted with H_2O_2 . Thus we may use the results of a particular kinetic run to estimate the coverage of H_2O_2 at (say) 15 sec reaction time. Taking the number density of available surface sites to lie in the range 10^{18} – $10^{19} m^{-2}$, yields a coverage value of between 5 and 50 percent of a monolayer, which is physically plausible and consistent with our overall view of the system."

MANUSCRIPT AMENDED

While the data are consistent with 1st order conditions over the time scale of the experiments, separate experiments over longer reaction times might have been helpful to see whether deactivation occurs or whether the process appears catalytic.

We agree with the reviewer that it would be interesting to observe effects over

C5412

longer reaction times. This was not possible due to experimental limitations as noted above in response to Reviewer 1. We have now added the following text in the revised manuscript.

P11090 L12: "Measurements at longer contact times could yield information regarding deviation from first order kinetics and insight into whether or not the overall process was catalytic. However such observations were precluded by experimental constraints."

MANUSCRIPT AMENDED

The authors should at least discuss in some depth the difference to their own observations on TiO₂ aerosol published recently.

Fair point. We have already dealt with this in some detail in response to Reviewer 1.

MANUSCRIPT AMENDED

Since H₂O₂ is miscible with water, can a solution form on the surface based on the thermodynamic properties at the concentration of the experiments?

Hydrogen peroxide is extremely soluble in water. We cannot understand what lies behind this question.

NO ACTION

Last paragraph in this section: what are the specific photocatalytic effects the

C5413

authors would expect for H₂O₂? Photocatalysts are often a source of H₂O₂ in aqueous systems.

Interesting question. We added the following in the revised manuscript.

P11091 L19: "The degree of hydration of certain photocatalytic materials can change dramatically upon illumination with UV light. For example TiO₂ switches from hydrophobic to superhydrophilic behaviour under UV illumination. In the present case, such effects could strongly alter the distribution of liquid-like water on the mineral surface and hence the uptake of H₂O₂ and indeed those of other trace gases."

MANUSCRIPT AMENDED

Section 3.4: P11093: may the heterogeneous self reaction of HO₂ on dust particles be of any significance as a source of H₂O₂?

The referee makes an interesting point about the potential for a reaction on dust particles of HO₂ radicals acting as an additional source of H₂O₂. We are unclear about whether the referee presumes that the dust should act to enhance the self reaction of HO₂ to produce H₂O₂ (similar to the water enhancement in the gas phase)? In any case no one (to our knowledge) has looked into this experimentally. In our system we are currently unable to monitor HO₂ radicals. Previous modelling studies (i.e. de Reus et al., Atmos. Chem. Phys., 5, 1787-1803, 2005) have suggested that this process is a possible source of H₂O₂. We conclude that this is a further step in the experimental work.

NO ACTION

C5414

Since the box model does not keep track of the dust composition: what is the integrated loss of H_2O_2 per dust surface area over the period the simulations were run, and is this number comparable to the exposure in the experiments? This question relates to the one above about the potential time dependence.

We thank the referee for raising this point. In the box model we calculated the integrated loss through each of the H_2O_2 loss processes (dry deposition, reaction with OH, photolysis and heterogeneous uptake on to dust). At the end of the four day run the integrated loss of H_2O_2 to dust was on the order of $\sim 4.0e10$ molecules cm^{-3} for the case of high S_a dust ($200 \mu m^2 cm^{-3}$). Using this flux and given the available number of surface sites on dust being $\leq 10^{19} m^{-2}$ yields a surface coverage of ~ 20 monolayers of H_2O_2 . Thus there is a much greater coverage in the model than in the experiment, and in any case this is an unphysical result. However, if we make the reasonable assumption that the H_2O_2 removed by the dust does not permanently fill the surface sites due to subsequent loss processes (decomposition), then this result should not have a large impact on the model results. As we don't know the fate of the adsorbed H_2O_2 (and hence the validity of our model's assumption) we now state in the revised manuscript that the results we calculate are at an upper limit.

In the revised manuscript we have added the statement:

P11093 L28: *"It should be noted that representing dust in this way may have some effect on the results as the model does not take into account the possibility that as dust is aged, and in the absence of decomposition of adsorbed hydrogen peroxide, multilayers of H_2O_2 could in principle form, this affecting the kinetics. However, peroxide multilayers would appear to be an unphysical condition examination of which is beyond the scope of our experiments. Accordingly, the results calculated here represent an upper limit."*

MANUSCRIPT AMENDED

C5415

Technical:

P11088, line 18: from a kinetic run P11089, line 17: Knudsen

P11095, line 23: for collecting the Gobi sample.

Thank you. Typos corrected.

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

C5416