**Atmospheric
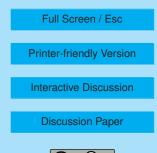Chemistry
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Discussions**

Interactive
Comment

# *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.

**Anonymous Referee #1**

Received and published: 5 May 2010

**General**:

This work addresses the reaction of H2O2 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 H2O2 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 H2O2 to a desert dust

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Interactive Discussion

Discussion Paper

"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 African 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 H2O2 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 ?

**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 ?

**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.

**P11088 L18** Figure 3 shows that the H2O2 concentration barely changes when there is contact with the dust. The order of the reaction is thus undetermined. Single measurements of time dependent H2O2 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 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?

**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.

**P11089 L23** The concentration of H2O2 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. In this regard it would have been useful to read something about the (expected) products of the reaction of H2O2 on dust. 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? 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 H2O2? Please comment!

**P11091 L3** The authors rationalise the enhanced uptake of H2O2 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. What is the uptake coefficient for H2O2 to an aqueous surface? Also, the authors do not mention the fact that in their previous publication on H2O2 with TiO2, they observed the opposite trend. Why?

**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 ?

**P11094** The contributions to H2O2 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 ?

**Typos** P 11082 L23 Meteorological P11095 L12 typically very dusty ? (delete typically)

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