We thank the two anonymous referees and Dr. Tang for their comments. We respond (in italics) to each point separately below.

Anonymous Referee #1

This paper presents a set of laboratory experiments measuring the reactive uptake of HO2 to Arizona Test Dust aerosol particles using an entrained aerosol flow reactor and conversion of HO2 to OH followed by LIF detection of the OH. The methodology has been used and described previously by the authors to study HO2 uptake to other types of aerosol particles. The paper is well written, the data are compelling, and the conclusions are careful and well supported by the data. The topic continues to be important given the typical lack of agreement between models of atmospheric photochemistry and measurements of HO2. There is a growing body of literature that concludes heterogeneous chemistry of HO2 is a significant component of HOx loss, but these conclusions are often based on indirect comparisons of measurements and photochemical models and are thus in need of fundamental parameters measured and reported in this paper. I therefore suggest publication after a few minor comments/suggestions are addressed.

1. Is there a reason Saharan dust could not be used in the dust generator? The choice of ATD instead of Saharan or Gobi, etc should be discussed in a bit more detail.

We chose to study ATD owing to its availability and smaller size distribution. There is no strong reason though why other types of dust could not be used in the future, and indeed such experiments are planned.
The following sentence was added to the introduction:
'ATD (0 – 3 μm) was chosen in this work rather than Saharan dust due to the smaller size of the ATD particles which reduces the risk of aerosol deposition along the flow tube.'

2. For the RH dependence, was the humidification timescale for the ATD particles varied to see if there were a time dependence in the humidification?

The humidification timescale for the ATD particles was not varied to see whether there was a time dependence. The particles were humidified for approximately 10 seconds in a separate conditioning flow tube before coming into contact with the HO_2 in the main flow tube. However, this could be investigated in a future study by having different conditioning flow tube sizes.

3. Has the effect of aerosol particles on the LIF detection efficiency been discussed in previous papers on the apparatus? It does not appear that particles are removed prior to the excitation volume. The critical orifice likely is an effective virtual impactor, but some particles may be transmitted, no? Have the authors ruled out that the anticorrelation between ATD number concentration and HO2 is due to reactive uptake and not detection efficiency changes? I'm guessing so, but the authors should mention the paper where this issue is discussed.

Yes, the impact of aerosols on the detection efficiency of HO_2 by LIF in our system has previously been discussed by George et al. (2013) which concerned the uptake of HO_2 onto inorganic salt aerosols. The background signal obtained when the laser wavelength was either online or offline from the OH electronic transition and with the mercury lamp switched off does not change with varying aerosol concentrations, which shows that there is no contribution to the signal from Mie scattering. In addition, for some inorganic salt aerosols, no reactive uptake of HO_2 could be measured in the

presence of aerosols, with the invariant signal in the absence or presence of aerosols showing that the efficiency towards HO_2 did not change. The following sentence was added at the end of Section 2.2. 'Mie scattering has previously been found not to contribute towards the FAGE cell signal and aerosols were found not to influence the LIF detection sensitivity towards HO_2 (George at al., 2013)'.

4. I assume rs is the surface area weighted mean radius, based on the s subscript, but the authors should state that explicitly. Also, both the number weighted and surface weighted distribution should be presented since the surface weighted distribution is more relevant to the uptake process and calculating the gas-phase diffusion limitations.

Yes, that is correct. r_s has now been defined in Section 2.4 as $r_s^2 = A_{total} / (4\pi N_{total})$. A_{total} and N_{total} have also been defined.

Figure 2 has now been changed to include both the number weighted and surface weighted distributions.

5. In the interpretation of Figure 5, there is no discussion of the time dependence of the wall loss. Is the wall loss found to be pseudo-first order? In Figure 5, presumably the effect of wall loss has been subtracted, but was that subtraction done assuming first order behaviour, and if so, is that justified? Also, it seems utilizing a smaller diameter tube might have allowed the shorter interaction times to be probed to see at what point the non-linearity in time became apparent.

Yes, the wall loss was found to be pseudo-first-order (in the sense that a plot of $ln[HO_2]$ versus distance was always found to be linear in the absence of aerosol). However, in these experiments the reduction of HO_2 signal was observed for a variety of fixed injector positions (rather than a scan of the injector). For each position along the flow-tube, corresponding to a particular reaction time, the signal was obtained as a function of aerosol number concentration, and this included a signal with no aerosol, and so for each reaction time the effect of wall-loss was directly subtracted.

In the revised MS Equation 3 has been corrected to include the wall loss term. The following sentence has also been added:
'For each position along the flow-tube, corresponding to a particular reaction time, the signal was obtained as a function of aerosol number concentration, and this included a signal with no aerosol, and so for each reaction time the effect of wall-loss was directly subtracted'.

Using a smaller diameter flow tube to probe different interaction times is a good idea as it becomes prohibitive to employ considerably larger volumetric flow rates, and could be done in a future study in order to probe shorter reaction times as a further probe of the mechanism for reactive uptake, although smaller diameter flow tubes will have the problem of larges wall losses.

6. It seems from the exponential fit in Figure 8 giving non-zero limiting values that R7 as written can't be an explanation and that there would need to be a regeneration of the reactant at the very least - i.e. a catalytic loss but where the catalyst steady state concentration is somewhat determined by the concentration of HO_2.

Yes, that is true. If the uptake was solely determined by Reaction 7 then it would be expected that over time the uptake coefficient would fall to zero. However, it is possible that Reaction 7 is responsible for the time dependent part of Figure 8, but that there is also another reaction or reactions occurring which would result in a constant uptake at longer times once all of the trace component X had been used up.

7. In the model description, products of the HO_2 uptake are ignored - i.e. a complete loss of HOx is assumed for HO_2 uptake to dust. How sensitive was the model to that assumption? That is, if HO_2 uptake produced H_2O_2 that was released to the gas phase would there have been a noticeable change in the steady state HOx abundance due to H_2O_2 photolysis under these conditions.

Yes, it is assumed that uptake of HO2 onto the dust aerosol is an irreversible sink for HO2. The products of reactive uptake would indeed generate H2O2, some of which could then partition into the gas phase (although we note the recent work of Mao et al., (2013) which suggests in the presence of Cu/Fe in the aerosol the products may be H2O rather than H2O2). In this environment, the photolysis of H2O2 is only a minor source of OH (< 3%) (Whalley et al., Atmos. Chem. Phys., 10, 1555–1576, 2010). There were no measurements of H2O2 at Cape Verde, but in a similar remote marine environment at Cape Grim, Tasmania, where H2O2 levels might be expected to be fairly similar, the photolysis of H2O2 only constituted 2% of the total rate of production of OH (Sommariva et al., Atmos. Chem. Phys., 4, 839–856, 2004). Thus if aerosols did release H2O2, which contributed towards the concentration present at Cape Verde, the likely concentration of H2O2 would only be a minor source of OH, which in turn would represent a minor source of HO2 following oxidation of CO and VOCs by OH.

Anonymous Referee #2

The authors describe laboratory experiments to determine uptake coefficient of HO_2 onto Arizona Test Dust particles using an aerosol flow tube coupled to an instrument based on laser-induced fluorescence (LIF). Although generation of the particles was unstable, the uptake coefficient was determined successfully as functions of initial HO_2 concentrations, relative humidity, and exposure time. The determined uptake coefficient (0.031) was used to assess the impact of the heterogeneous process on the ambient HO_2 concentration levels at Cape Verde when dust was present at high concentrations. Many of recent observational studies on the atmospheric HOx radicals reported lower-than-expected HO_2 (or HO_2*) concentrations and thus any possible heterogeneous loss of HO_2 onto various types of particles must be studied. The result here is valuable, because the heterogeneous loss experiment on dust particles was made for the first time with an aerosol flow tube coupled to a sensitive LIF instrument, realizing loss measurements of HO_2 at realistic ambient concentration levels. However, there are several points need to be clarified. One is on the mechanism. The authors should explain if 1st order loss (implicitly assumed in equation (3) for the determination of uptake coefficient) is still effective with the proposed mechanism (R3-R7) involving recombination of HO_2, and if the observed lower uptake coefficient with higher HO_2 initial concentration is in line with the proposed mechanism. Another is on the box model assessment of the impact. The assumption that the gas diffusion limitation is avoided (equation (9)) should be justified, even if the dust particles present in the atmosphere were coarse. The paper is publishable after the authors successfully address to the issues raised above and the following specific points.

There are two general points made here to which we respond to within the specific points that are raised below.

Specific comments:

1. Page 4229, Title. The paper title is very similar to that of Bedjanian et al. 2013. I may add "measured with an aerosol flow tube method" at the end of the title. Maybe "Arizona Test Dust particles" is better.

We thank you for the suggestion. The title of the paper has been changed from 'Uptake of HO_2 radicals onto Arizona Test Dust aerosols' to 'Uptake of HO_2 radicals onto Arizona Test Dust particles using an aerosol flow tube'.

2. Page 4231, lines 23-26. It seems from the sentences that Bedjanian et al. (2013) used an aerosol flow tube, which is not the case.

The word 'surfaces' has been added to the end of the sentence to make this clear.

3. Page 4232, line 17. How do the authors define the length? From the point where mixing of HO2 with particles takes place to the aperture of the HO2 detection cell?

The following sentence has been added:
"The distances were measured from the end of the flow tube to the injector position (a length of 0 cm would have represented the injector being at the end of the flow tube attached to the FAGE cell)."

4. Page 4234, lines 9-14, Figure 1. Did the FAGE instrument sample almost all the gas flowed into the flow tube? Or additional overflow line is present?

The following sentence was added to the text:
'The FAGE instrument sampled 4.3 lpm and the CPC sampled 0.3 lpm with the remainder of the flow (0.6 – 1 lpm) exiting via an exhaust line.'

5. Page 4234, line 15. Were the dust particles sieved before put into the disperser, to obtain relatively narrow size distribution shown in Figure 2?

No the particles were not sieved. The ATD that was bought had a size range already of 0 – 3 μm which resulted in the narrow size range shown in Figure 2, with the impactor taking away the larger particles. The size range of the ATD used in this work has been added into the introduction.

6. Page 4235, lines 5-12. Did the raw SMPS measurement provide Stoke's diameter?

Yes. The words 'measured by the SMPS' have been added to the text after Stokes diameter.

7. Page 4236, line 20. Define r_s.

r_s has now been defined in Section 2.4 as $r_s^2 = A_{total} / (4\pi N_{total})$. A_{total} and N_{total} have also been defined.

8. Page 4236, line 21, Page 4242, lines 8-14. Clearly mention that the uptake coefficient is determined assuming spherical particle shape in this study.

The words 'assuming a spherical shape' has been added to the definition of the aerosol surface area (A_d).

9. Page 4237, line 9, equation (7). 0.283

This has been changed.

10. Page 4237, line 15. The title of the subsection can be simply "Time dependence of the uptake coefficient"

This wasn't changed as this would mean that Sections 2.5 and 3.2 would have the same title.

11. Page 4239, equations (R3)-(R7). The authors should explain if 1st order loss (implicitly assumed in equation (3) for the determination of uptake coefficient) is still effective with the proposed mechanism (R3-R7) involving recombination of HO2.

If the mechanism involved reactions 3 to 7 the decays could still appear first order. In the paper the decays have been described as pseudo-first order. For HO_2 uptake into aqueous aerosols the mechanism is known to involve the recombination of HO_2 and the decays still appear to be first order (e.g George et al. 2013). George et al. also observed similar trends in time and initial HO_2 concentration dependence as seen in this work and a model is currently being developed to explain the results shown by George et al. The model will then be altered to try and explain the trends observed on dust aerosols. The following sentence has been added to the paper at the end of Section 3.1.
'However, a model is currently being developed to further interpret the trends that have been observed.'

12. Page 4239 line 13. How fast can the surface be saturated? Rough estimation is possible.

This is very difficult to estimate because the actual surface area of the aerosols is unknown. In this work an assumption was made that the aerosols were spherical. However, in reality the aerosols are not spherical and the actual 'real' surface area that is exposed to the HO_2 is unknown. There is also an uncertainty in the rate of adsorption and desorption of HO_2 to the surface, the area that HO_2 would fill on the surface of the aerosol and the rate of reaction at the surface of the aerosol. Changes in all of these parameters (especially the actual surface area) could have a large impact on how fast the surface could be saturated. The BET surface area was not measured in this work. However, by assuming a BET surface area of 85 m^2g^{-1} (measured by Bedjanian et al. (2013)) and an aerosol density of 2.7 g cm^{-3} the true surface area could be up to approximately 20 times larger than the spherical assumption.

However, it is not expected that the surface would become fully saturated, rather it would become partially saturated. By assuming a diameter of 4×10^{-8} cm for the diameter of HO_2, an aerosol radius of 273 nm, an aerosol number concentration of 20,000 cm^{-3}, a desorption lifetime of HO_2 of 0.2 seconds and a sticking probability of 0.001 when the surface coverage is zero the equilibrated surface

coverage (ignoring reactions) can be estimated at 30 % when the HO_2 concentration is 3×10^8 molecule cm^{-3} and 59 % when the HO_2 concentration is 1×10^9 molecule cm^{-3} which would affect the uptake coefficient. This was estimated using the methodology described by Pöschl et al. (2001). However, this calculation assumed spherical particles whilst in reality the surface area would be larger.

13. Page 4239. Can the saturation be delayed if using larger amount of particles, while fixing HO_2 concentrations?

It would be expected that the surface coverage would be less if there were more particles and that therefore the uptake coefficient would be slightly higher. This could be investigated in a further study by systematically changing the maximum aerosol number used.

14. Page 4240, line 25. Aerosol particle surfaces used in this study can also be regarded as solid surface. Use "coated surface."

This has been changed as suggested.

15. Page 4241, lines 11-13. I did not understand why high humidity resulted in lower HO_2 concentrations. Did the author mean partition into HO2-H2O?

The lower HO_2 concentrations at higher humidities was due to the higher wall losses along the flow tube (which are a function of humidity). This was mentioned in Section 3.1 and the words 'due to the higher wall losses' has been added to clarify the reason for the lower HO_2 concentrations at higher humidities.

16. Page 4244, line 2. Mention that the gamma value used here is in the higher side of the observed range.

The following sentence has been added:
'The value of $\gamma = 0.031 \pm 0.008$ was on the higher side of the observed range of HO_2 uptake coefficients measured in this work.'

17. Page 4244, lines 3-7. What is the size distribution of the ambient dust particles? Can they be represented by 1 um? The assumption that gas-phase diffusion does not limit the loss process is made with equation (9). Is it still valid?

Yes, ambient dust particles can be represented by a diameter of 1 μm. During the field campaigns mentioned in the text the aerosol diameters were approximately 1 μm as shown in the papers that have been referenced. It might be expected that gas-phase diffusion would decrease the HO_2 uptake coefficient slightly due to the large size of the aerosols and a slight depletion of HO_2 near the surface of the dust. However, as the observed uptake is likely to be much smaller than the mass accommodation it seems likely that the limiting step would not be gas-phase diffusion. However, as a small decrease might be expected the following sentence has been added:
'It should be noted that diffusive limitations due to the larger aerosol diameters were disregarded in these calculations.'

18. Page 4245, lines 23-24. The discussion on the rate determining step should have appeared earlier.

The following sentence has been added to Section 3.2:
'The reaction of the HO_2 at the surface of the aerosol would become the rate determining step once the aerosol surface was saturated.'

19. Page 4246, line 16. Kumar et al. (2014) did not appear in the reference list. Also include references Dentener et al., 1996; Seinfeld et al., 2004; Tang et al. 2014; Read et al. 2008; and Whalley et al. 2008, found in text.

These references have either been added or changed.

Short comment (Mingjin Tang)

Matthews et al. (2014) reported the first measurement of the uptake coefficient of HO_2 radicals onto airborne mineral dust particles (ATD particles), which can be of significant importance in the troposphere. The experimental work has been nicely carried out, and its atmospheric implication has been properly discussed. I have a few comments for the authors to consider:

1) Surface area of dust particles:
If I understand it correctly, the average surface area per particle, *Ad*, is calculated from the average diameter, *i.e.* Eq. (5) (P4236, line 20-21). The particles used in this study are poly-dispersed and on per particle base, and larger particles contribute more to the overall surface. Therefore, using Eq. (5) to calculate the average surface area per particle would underestimate *Ad* and therefore overestimate γ(HO2).

The average surface area per particle can be calculated by dividing the total surface area concentration of the aerosol by its total number concentration (*e.g.*, Tang et al., 2014), both of which can be derived from its size distribution (*e.g.*, Figure 2). The true average surface area could be 50% larger than that calculated by Eq. (5).

The method for calculating Ad has been clarified. r_s has now been defined in Section 2.4 as $r_s^2 = A_{total} / (4\pi N_{total})$. A_{total} and N_{total} have also been defined.

2) Time-dependent uptake
I find that what is present in Figure 8 is somehow contradiction with Figure 6. Figure 6 (together with Figure 5) confirms that within the experimental uncertainties the decay of HO_2 appears to be of pseudo first order; however, Figure 8 suggests that for the same time regime as in Figure 6, the uptake coefficient is time-dependent, *i.e.* the first-order decay rate is not constant over time. This may need to be further discussed and clarified.

Figure 6 (and 5) were created using the data analysis methodology described in Section 2.5 and assuming pseudo first order kinetics. These show pseudo first order behaviour and produce an average uptake coefficient between ~ 7 and 23 seconds. However, Figure 8 was created using the data analysis methodology described in Section 2.5 as mentioned in the caption of Figure 8. The uptake coefficients for Figure 8 are the average uptake coefficients between time zero and a given

reaction time assuming first order kinetics. Therefore, these uptake coefficients are different to those in Figure 6 and are not in disagreement with Figure 5.

3) Intercept in Figure 5

Due to the time required to fully mix the injector flow with the main flow in the flow tube, the y-axis intercept of Figure 5 is usually negative. However, it appears to be positive in this work, and this is attributed to a faster uptake at the initial stage (P4238, line 1-5). Could this be due to the self-reaction of HO2 radicals? The HO2 concentration is very low in the flow tube so that its self-reaction is not important after the flow is well mixed, but this reaction can be important before complete mixing because the HO2 concentration in the injector flow is higher.

At every injector position at which an uptake coefficient was measured a new initial HO_2 concentration was present. By placing the injector at different positions (and therefore having different initial HO_2 concentrations) the wall loss (or the signal in the absence of aerosols) was automatically removed from the data and would similarly have removed a gas phase self-reaction term which will be present in the absence of aerosols. Therefore, the plot in Figure 5 does not include a wall loss term or a gas phase self-reaction term and the intercept cannot be explained by a fast initial HO_2 self-reaction in the gas phase. The HO_2 exiting the injector would have been diluted by about a factor of 5. Therefore, it is expected that for the lower HO_2 concentration measured in this work, the initial HO_2 concentration exiting the injector would have been approximately 1.5×10^9 molecule cm^{-3} At this concentration the HO_2 self-reaction would still have been extremely slow, for example, assuming a rate coefficient of $2x10^{-12} cm^3 molecule^{-1} s^{-1}$, the product $k[HO_2]$ is only $3x10^{-3} s^{-1}$ which gives a lifetime for loss of HO_2 which is much longer than the timescales of the experiment.

4) Discussion on surface saturation

The uptake coefficient was found to depend on $[HO_2]$, and two explanations are provided (Page 4239). I think the degree to which the surface is saturated (or surface coverage by HO_2 radicals) can be calculated, assuming a certain area of each HO_2 uptaken by the surface will occupy, given the measured HO_2 concentrations in the AFT and $\gamma(HO_2)$.

By assuming a diameter of 4×10^{-8} cm for the diameter of HO_2, an aerosol radius of 273 nm, an aerosol number concentration of 20,000 cm^{-3}, a desorption lifetime of HO_2 of 0.2 seconds and a sticking probability of 0.001 when the surface coverage is zero the equilibrated surface coverage can be estimated at 30 % (ignoring reactions) when the HO_2 concentration is 3×10^8 molecule cm^{-3} and 59 % when the HO_2 concentration is 1×10^9 molecule cm^{-3}. This was estimated using the methodology described by Pöschl et al. (2001). However, this calculation assumed spherical particles whereas in reality the aerosol surface area would be much larger and the surface coverage would be lower. The actual surface area is unknown and very difficult to estimate. There are also large uncertainties in the diameter of HO_2, the desorption lifetime of HO_2 and the sticking probability when the surface coverage is zero. Therefore, although a very rough estimate has been calculated for the degree to which the surface is saturated the uncertainty in this calculation is large.

5) Other minor comments:

5.1 Page 4232, line 10: Though the flow tube was detailed in a previous study, it may be helpful to provide its basis information here (e.g., ID, length, linear flow velocity, and Reynolds number etc.).

The following sentence was added:
'The total flow through the flow tube (107 cm length, 5.9 cm I.D) was 5.4 ± 0.2 lpm which resulted in a Reynolds number of ~ 130.'

5.2 Page 4236, line 4-9: I believe the methodology to operate an aerosol flow tube with changing aerosol concentrations, including data analysis, was first described by Wagner et al. (2008).

This reference has been added into the paper in Section 2.4.

5.3: Reference: I assume (Tang et al., 2013) and (Tang et al., 2014) are actually the same paper. The authors may want to go through the citations and the reference list in the revised version. References: Tang, M. J., Schuster, G., and Crowley, J. N.: Heterogeneous reaction of N2O5 with illite and Arizona test dust particles, Atmos. Chem. Phys., 14, 245-254, 10.5194/acp-14-245-2014, 2014.

This reference has been added and Tang et al., 2013 has been replaced by Tang et al., 2014.