Review of "Heterogeneous reaction of peroxyacetic acid and hydrogen peroxide on ambient aerosol particles under dry and humid conditions: kinetics, mechanism and implications", by Q. Q. Wu, L. B. Huang, H. Liang, Y. Zhao, D. Huang, and Z. M. Chen (ACP-2015-70).

This study presents the results of an investigation of H_2O_2 and peroxyacetic acid (PAA) uptake to $PM_{2.5}$ and mineral dust samples over a wide range of relative humidities. Differences in the RH-dependent uptake of H_2O_2 and PAA to $PM_{2.5}$ are used to draw conclusions regarding the factors driving uptake of these species under humid conditions.

Interestingly, the RH dependence of H_2O_2/PAA uptake to Arizona Test Dust, a commonly used model dust, is opposite to that observed for Asian dust samples collected in the field. These results add to a growing body of evidence that the reactivity of "processed" dust is often markedly different from freshly emitted dust (and individual dust components, *e.g.* metal oxides and carbonates).

The paper is timely and interesting, and I recommend its publication in *Atmospheric Chemistry and Physics* after revisions addressing one major concern, a number of technical/scientific questions, and a thorough edit for language/clarity.

Concerns regarding estimation of effective particle surface area (A_{es})

Estimation of available surface area (A_{es}, in this manuscript) for heterogeneous reactions is an ongoing challenge in the field. However, I have two broad issues related to the method (described in Section 2.4) used to estimate A_{es}.

The first is related to the use of the filter geometric surface area to approximate A_{es} at high particle loadings (P5721L10–13). From what I understand, the assumption here is that, in the "plateau regime", where Lf no longer changes with particle mass, the effective surface area can be approximated by the geometric surface area. However, in the Bedjanian *et al.* (ACP 2013) paper that's cited, it is explicitly acknowledged that the geometric surface area is a lower limit for the available surface area, and that uptake coefficients calculated using this value are thus upper limits. I don't think that it's reasonable to simply assume that, in cases where Lf > Lf_c, A_{gs} = A_{es}.

The second issue concerns differences between the experiments reported here and those reported in the Bedjanian paper (and in other papers looking at gas–dust interactions using flow tube techniques, Knudsen cells, etc.), and the appropriateness of applying the conceptual framework from these latter papers in this study.

In these other types of experiments, a linear increase in γ implies that the addition of more substrate results in a proportional increase in surface area available for uptake (whether the "entire" surface area is available for uptake is another issue entirely; see the Interactive Comment from Anonymous Referee #2 for the Bedjanian *et al.* paper), and a levelling off of γ at high sample masses implies that the gas-phase species can't access all of the sample over the timescale of the uptake experiment (*i.e.* that uptake is limited by diffusion into the lower layers of the "thick" sample).

In the present work, however, PAA and H_2O_2 are passing directly through the filters, and thus theoretically should be passing through, or "accessing", all of the sample, even if it is "thick". So, the plateau regime in these experiments means something else entirely: to me, it implies an issue with particle agglomeration, which is becoming more prominent as more $PM_{2.5}$ is collected on the filter, *i.e.* that PAA/H_2O_2 aren't accessing the "interior" of the agglomerations. In my mind, this agglomeration should also be an issue, albeit a lesser one, at lower particle masses.

In short, I think that the "low-mass regime = linear", "high-mass regime = plateau" is too simplistic a conceptual framework to employ here. Indeed, the linear fit to the left-most data points in Figure 2 is questionable at best.

On a more specific note, it isn't clear to me how Equations 10 and 11 (P5722L56) were derived, since Lf wasn't measured for ADS and ATD as a function of particle mass (from what I understand, only two masses were used). This requires explanation, especially if these A_{es} values were used to calculate γ for these samples.

In summary, I think that the paper would be greatly strengthened by a reevaluation of the approach used to estimate A_{es}. It might be useful to provide estimates of higher and lower bounds for this quantity, and then to calculate the range of associated γ values. In the end, all γ values should be accompanied by a description of the surface area used in their calculation.

Scientific/technical comments and questions

P5716L23
Were these aqueous solutions?

P5717L10
How were the concentrations of PAA/H_2O_2 determined? Reference should be made here to Section 2.3.

P5718L6
How were the ADS particles collected?

P5718L8
A brief description of the resuspension apparatus (rotating brush generator?) should be provided.

P5718L25
Some information regarding the timescale/resolution of an uptake measurement should be provided here. If the RH was "continuously" increasing, then presumably the uptake values shown in Figure 3 were obtained over a range of RH? Or, was the RH stepped to the values shown in Figure 3, and then held at those values for long enough to achieve (and measure) a steady-state peroxide concentration (and thus steady-state uptake coefficient)? How often were measurements of peroxide concentrations made?

P5722L18–20
If the uptake coefficient is scaled to A_{es}, why would there be a dependence on $PM_{2.5}$ mass?

P5722L21

I would suggest plotting this empirical fit in Figure 4 rather than just connecting the mean uptake values (and would suggest the same for Figure 5).

P5723L13–16

The El Zein *et al.* (JPC A) paper cited here reported an inverse dependence of the initial γ value, rather than the steady-state value, on relative humidity. In addition, the steady-state uptake coefficients reported in this study were calculated using BET surface areas, so I'm not sure how appropriate this comparison is from both a qualitative/quantitative perspective.

On this note, I would suggest including a summary table showing how the uptake coefficients/RH dependencies obtained in this study fit into those obtained previously.

P5723L17

To me, it looks as though the samples obtained on haze days were much more variable than those obtained on non-haze days ...

P5723L17–22

Were uptake measurements of both PAA and H_2O_2 made on the same samples? Is it possible that previous exposure of samples to PAA could have influenced H_2O_2 uptake? If not, which samples were used for H_2O_2 uptake measurements? Or, were PAA/H_2O_2 uptake measurements made simultaneously? This needs to be clarified in the text.

P5724L4–6

I don't see how the larger value of γ for H_2O_2 at lower RH implies a physical process.

P5724L9–10

What do the error bars in Figure 3 represent, exactly? If there are only two data points (ascending and descending RH values), I think that the spread in data would be better represented using different symbols for the ascending/descending γ values.

P5725L1

Again, what do these errors represent? In addition, these values appear to be for ADS_l. The PAA uptake coefficient for ADS_h at 3% RH is higher than that for ADS_l, while the opposite is true for ATD (*i.e.* the uptake coefficient for ATD_l is higher than that for ATD_h). If these uptake coefficients are scaled to A_{es} (or some proxy for it), then why are the values for high/low loadings so different?

P5725L18

"The value of γ H_2O_2 on ADS changed from $(1.25 \pm 0.5) \times 10^{-4}$ at 3 % RH to $(4.54 \pm 0.12) \times 10^{-4}$ at 90 % RH"

I don't see this trace on Fig. 7 at all! In addition, the presentation of values for both "high" and "low" dust loadings is confusing in the absence of explanation of differences/ similarities between results obtained at the surface of these samples.

P5727L7

Does this value represent a bulk pH? It may be possible that some individual particles are basic, and that measured uptake to $PM_{2.5}$ is an average value that includes contributions from both unreactive and reactive particle types.

P5728L1–2
Is there a reference for this?

P5728L14
The Rubasinghege *et al.* paper looks at the acid-induced dissolution of α-FeOOH in solutions (pH 2) of HNO_3, HCl, and H_2SO_4, and investigates the effect of the anion on dissolution. Would these effects still be valid at the pH values in the aerosol samples used in these experiments?

P5729L8–10
I think that this statement is too definitive, and should be qualified somewhat, since no specific direct evidence for each of these pathways exists.

P5731L16–20
I am not sure that I understand the purpose of this passage. Presumably these larger particles are of crustal origin and contribute to PAA uptake?

There are a number of minor typos/usage errors and clarity issues throughout the manuscript. A non-exhaustive list follows.

P5714L6
"the aerosols" should perhaps read "aerosol-phase processes"?

Also, it's not entirely clear to me from this sentence what the field observations suggest: that PAA is important? That the PAA budget is potentially influenced by aerosol processes? I'm assuming you mean the latter, but the sentence should be revised to make this more clear.

P5714L7
"onto the ambient" should read "onto ambient"

P5714L9
"at the uptake coefficient" should read "with an uptake coefficient"

P5714L14
I would specify that mineral dust is one of the main components of PM2.5 "in this region"

P5715L10–15
To my understanding, the Mao *et al.* and Liang *et al.* articles cited here focus primarily on the influence of HO_2 uptake (and, specifically, on HO_2 uptake mechanisms that don't produce H_2O_2). I think that inclusion of these papers—and, by extension, the transition metal-catalyzed HO_2 uptake story—here is somewhat of a distraction.

P5715L15–20
With reference to the previous comment, what do these studies show regarding the relative contribution of direct H_2O_2 uptake to H_2O_2 concentrations (*i.e.* vs. HO_2-mediated H_2O_2 loss)? I think that it would make sense here to more clearly describe the conclusions of the studies that have "ascertained the importance" of this process.

P5715L16
"on the model" should read "on model"

P5715L28
This is too broad: which temperate areas?

P5716L1
"that the heterogeneous" should read "that heterogeneous", *i.e.* "the" is not necessary

P5716L3–4
This sentence is awkwardly phrased, and should perhaps be revised to more clearly indicate that PAA is used as a representative organic peroxide.

P5716L9
Should read "kinetics of H_2O_2 uptake on $PM_{2.5}$"

P5716L10
"to ensure the constant" should read "to ensure a constant"

P5717L15
"particle loaded" should read "particle-loaded" — there are also a number of other instances in the manuscript where hyphens are missing from compound adjectives

P5717L17
"PKU located" should read "PKU is located"

P5718L9
"sampled in" should read "sampled on"

P5718L14
"gaseous peroxide" should read "gaseous peroxides"

P5718L19–22
I think it would be clearer if this were placed after equation 4, since, from what I understand, $[C]_{in}$ in this equation was approximated by $[C]_{out, blank}$.

P5720L7
"at the flow rate" should read "at a flow rate"

P5720L14
"challenge for the γ determination" should read "challenge for the determination of γ"

P5721L22
Should this be 4.89×10^{-1}?

P5722L15–17
This sentence is unclear and should be rephrased.

P5723L14
"on the ATD" should read "on ATD"

P5726L5
"to the physical processes" should read "to physical processes"

P5728L12
"for the aqueous reaction" should read "for aqueous reactions"

P5728L15
"by the Fe catalysis" should read "by Fe catalysis"

P5728L16
The Mishra reference is missing ... but I don't necessarily think that its conclusions are valid for application here, since PAA/H_2O_2 are weak acids.

P5730L5
"The field observations" should read "Field observations"

P5731L15
What value was used for the mean diameter of the total particles?

P5732L16
"the urban area" should read "urban areas"

P5732L21
"from the urban area" should read "from urban areas"; "affecting the oxidants" should read "affecting oxidant"

Figure 5
The y-axis should be expanded (*i.e.* it should start at zero).

References

Anonymous Referee #2: Interactive comment on Atmos. Chem. Phys. Discuss., 13, 8873, 2013, Atmos. Chem. Phys. Discuss., 13, C2563–C2565, 2013.

Bedjanian, Y., Romanias, M. N., and El Zein, A.: Uptake of HO_2 radicals on Arizona Test Dust, Atmos. Chem. Phys., 13, 6461–6471, doi:10.5194/acp-13-6461-2013, 2013.

El Zein, A., Romanias, M. N., and Bedjanian, Y.: Heterogeneous interaction of H_2O_2 with Arizona Test Dust, J. Phys. Chem. A, 118, 441–448, doi:10.1021/jp409946j, 2014.

Rubasinghege, G.; Lentz, R. W.; Scherer, M. M.; Grassian, V. H.: Simulated atmospheric processing of iron oxyhydroxide minerals at low pH: Roles of particle size and acid anion in iron dissolution, PNAS 2010 107 (15) 6628–6633.