

Interactive comment on “Application of positive matrix factor analysis in heterogeneous kinetics studies: an improvement to the mixed-phase relative rates technique” by Y. Liu et al.

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We appreciate the careful consideration of our manuscript by the reviewers. We have carefully responded to all of the point-by-point comments and issues raised by the reviewers and have revised the manuscript accordingly. These revisions are described in detail below.

Reviewer #1 This paper describes an approach for analyzing laboratory data on the heterogeneous oxidation of organic submicron particles. The authors point out that the use of hard ionization mass spectrometry can lead to biases in the inferred kinetics,

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since product ions may interfere with reactant ions. They thus recommend the use of positive matrix factorization (PMF) rather than spectral subtraction (which involves using the fastest-decaying ion) for deriving kinetic parameters. Applying this approach to the heterogeneous reaction between gas-phase OH and particulate citric acid, they measure an uptake coefficient that is ~ 8 times faster than what we had measured previously (Kessler et al., 2012, hereafter K2012). This is an interesting new approach, on a topic of importance to the atmospheric chemistry community. It makes a fairly strong prediction, that the reanalysis of AMS-based heterogeneous oxidation experiments will lead to faster inferred kinetics (which in turn lead to shorter inferred atmospheric lifetimes of the particulate organics). However, as described below, using this technique on our own data, we are unable to see such an enhancement. Thus the primary conclusion of the study appears not to always be the case; thus before it can be published in ACP, this paper needs to be rewritten considerably.

Response: Thank you so much for your instructive comments and suggestions. After carefully comparing our results with yours, we believe that there is a prominent difference between the mass spectra of the oxidized products in both papers which will have implications for the results of both papers and is described further in the responses below. However, we do agree that our paper perhaps has made an overly strong prediction which needs to be somewhat softened in light of the results of your reanalysis. As you correctly suggested, the differences can be explained by differences in the reaction conditions between both studies. Our experiments were performed under significantly lower OH exposures (0.7×10^{11} molecules cm^{-3} s), compared to 0.7×10^{12} molecules cm^{-3} s in K2012. This may lead to totally different product distributions. At low OH exposure, it may be more likely to produce products that are highly similar to the reactants. Slowik et al. also observed that the kinetics depends on tracer size for OH oxidation of ambient SOA using a C-ToF-AMS (Slowik et al., 2012). Therefore, in our revised manuscript, we have constrained our discussion and conclusions to be under the conditions that the structure of the products is similar to the reactant (as is the case here) and when the concentration of OA is measured with a unit mass resolu-

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tion aerosol mass spectrometer. In the revised abstract, introduction, discussion and conclusion sections, we have softened our predictions. For example, in the Abstract, we revised it as "The results suggest that heterogeneous kinetics can be significantly underestimated when the structure of the product is highly similar to the reactant and when a non-molecular tracer is measured with unit mass resolution aerosol mass spectrometer." (Page 2, lines 39-41) And in the Conclusion we revised it as "The current results suggest that the lifetime of OA estimated in models due to heterogeneous oxidation might be overestimated for a reaction system where the products are highly similar to the reactant and the kinetic data are derived by individual non-molecular m/z tracers of OA. The results also suggest that it may be necessary to revisit the kinetic data of other organic aerosol components (and OH uptake coefficients) which have been derived using the relative rates technique (George et al., 2007; Lambe et al., 2007) based on UMR-AMS." (Page 24, lines 480-486)

Major comments: (1) We ran PMF on the (UMR) mass spectrometric data of K2012, for the citric acid oxidation case. Results are shown below:

As in the present study, two factors (right panels) were found; however these factors (which represent ~99% of the variance of the data) look substantially different from one another. Fitting the decays (right panel) yields a second-order rate constant of $k=4.3 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This is in excellent agreement with our previous analysis, using the fastest-decaying ion ($\text{C}_4\text{H}_4\text{O}^+$, m/z 68.03), and is far lower the rate constant determined from PMF in the present study. Thus the difference in results in the two studies does not derive from the choice of analysis approach taken in K2012. The present manuscript needs to be rewritten to reflect this.

Response: We agree with your results above and thank you for sharing your reanalyzed data. Firstly, as shown in your results, the mass spectrum of unreacted citric acid (CA) is similar to ours. However, the factor mass spectra of the oxidized products in your study are highly different from our products, and that of unreacted CA (likely due to the drastically different OH exposure levels). Therefore, an excellent agreement between

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the PMF and tracer based kinetics in your results may be reasonably expected since the products should have little influence on the signal of the tracer. We also observed a good agreement between the PMF and $\text{M}^+(\text{m/z } 326)$ tracer based kinetics of TPhP (Table 1) because the reactant and product mass spectra are quite different (Figure R1). However, a large difference between these two methods is expected to arise for CA in our experiments as the oxidized products are highly similar to the unreacted CA under our specific reaction conditions. This also demonstrates that the PMF analysis proposed in this work is reasonable particularly when the oxidized products are highly similar to the reactant (such as in our study). We do agree that this approach may be more important for some reaction systems than others, and will dependent upon various other factors. In light of this, we have softened our stance that the PMF approach will be an improvement for all cases.

Secondly, as you suggested in the following section, the reaction conditions between our two experiments are quite different. In your experiments, OH exposure is $0.7 \times 10^{12} \text{ molecules cm}^{-3} \text{ s}$, which is one order of magnitude higher than ours. Even in the range which you derive the kinetics it is still 3 times greater than ours. This may lead to a different product distribution as described above. Similar to the oxidation of squalane by OH (Wilson et al., 2012), there may have been several generations of products forming during CA oxidation. We believe this is likely to be the main reason why we observed a different mass spectrum of products, and why the PMF approach is required in our case but not yours. We have added these points in our discussion as: "Conversely, no significant consumption of m/z 68 was observed in the current study. The lack of a m/z 68 fragment consumption here may be explained by the choice of reaction conditions. In the work of Kessler et al., OH concentration exposure ($0.7 \times 10^{12} \text{ molecule cm}^{-3} \text{ s}$) was approximately an order of magnitude higher than that reported here. Recent evidence suggests that the product distribution during OA oxidation greatly depends upon OH exposure levels (Wilson et al., 2012). Hence, it is possible that more oxidized products formed via multi-generational chemistry at high OH were formed, which may have less of an influence on the signal of the chosen tracer (m/z 68), and result

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in product AMS spectra which are significantly different than that of the reactant thus mitigating the use of PMF (which was not the case here). Secondly, a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was used in their work, while a C-ToF-AMS with unit-mass resolution was used in this study. The higher mass resolution of the HR-ToF-AMS relative to a C-ToF-AMS, may further reduce the influence of product fragments on m/z 68 (or others). Finally, differences in temperature or other reaction conditions between experiments may also have led to differences in the morphology of CA and subsequent differences in the reactivity of CA.” (Pages 17-18, lines 369-385).

Figure R1. Mass spectra of two PMF factors determined for TPhP oxidation. (2) Such differences in kinetics are perhaps not surprising given a major difference in reported results: the ion at m/z 68 was the fastest-decaying one in the K2012 but did not change appreciably in the present study. The authors attribute this difference to the 10K difference in experimental temperatures; however going from ~60% loss (K2012) to ~0% loss (present study) of a compound would require an enormous change in volatility (something like a 100x increase in vapor pressure), and is unlikely to arise from such a modest temperature difference. Instead other factors are likely to be at play, and these should be discussed in the present paper. Two possibilities include (a) the oxidation chemistry could be different. Differences in the oxidation conditions (ratios of $O_3/OH/HO_2/h\nu$) could lead to fundamental changes in the observed chemistry. (b) the physicochemical properties of the particles could be different. Citric acid is a solid at room temperature, likely to form nonspherical particles and/or glasses upon atomization. Differences in the particle phase/shape could have a dramatic influence on the chemistry/dynamics on/within the particles. These are important topics that probably deserve more investigation than they have received in the literature so far.

Response: Thank you for your suggestions. We agree that different oxidation condition (ratios of $O_3/OH/HO_2/h\nu$) is likely the main reason for this difference as we described in our response above. We believe the different decay behaviours of m/z 68 are due

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to the different OH exposure, and subsequently different product distributions. In your study (with higher OH), it is possible to produce highly oxidized products which do not give the fragment of m/z 68, thus, consumption of this fragment is observable in your work. This is well supported by its mass spectrum. On the other hand, the lower temperature in this study or other factors might lead to a different morphology of CA and subsequent differences in the reactivity of CA. We cannot probe the morphology of the particles at this time, but agree that this could be an important factor which has not received near the attention required in the literature. We have highlighted the differences between our work and yours in the revised manuscript, and provided plausible reasons for this and described above. This has been added in our revised paper (Pages 17-18, lines 369-385). Ultimately, both rate constants are quite different from each other, and this highlights an important issue in heterogeneous reactions of the atmosphere, and in the experiments trying to derive such kinetics. It implies that the particle composition and/or morphology as determined by reaction conditions in the laboratory and the ambient atmosphere will have a large effect on the OH kinetics, which in itself is an important conclusion, and has been discussed in the revised paper as: “The significant difference between the reported rate constants highlights an important issue in heterogeneous reactions of the atmosphere, and in the experiments trying to derive such kinetics. It implies that the particle composition and/or morphology as determined by the reaction conditions in the laboratory or the ambient atmosphere will have a large effect on the OH kinetics” (Page 20, Lines 418-422). As for the differences in the measured k_2 of CA, we believe this might also be a result of the different oxidation conditions. It has been previously been observed that the presence of O_3 can inhibit the rate of OH reaction, perhaps by reacting with OH radicals or by O_3 or intermediate species blocking active surface sites (Renbaum and Smith, 2011). A Langmuir-Hinshelwood mechanism has been observed for the reaction of O_3 on organic surface (Pöschl, 2005). For many heterogeneous reactions, it has also been found that a higher concentration of gas phase reactant often leads to a lower uptake coefficient due to surface saturation (Ma et al., 2010 ;Li et al., 2002). Finally,

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differences in k_2 may arise from the competition between reaction products and reactants for available OH, or via the blocking or coating of the reactant by products which would require liquid phase diffusion of OH to degrade the original CA. In experiments with higher OH exposures it is possible that significantly more product mass is mixed and/or coated onto the original particle thus decreasing the perceived k_2 . All of these are possibilities, and are discussed in the revised paper as: "A number of factors may be responsible for the discrepancy between derived rate constants. It has previously been observed that the presence of O₃ can inhibit the rate of OH reaction, perhaps by reacting with OH radicals or by O₃ or intermediate species blocking surface active sites (Renbaum and Smith, 2011). A Langmuir-Hinshelwood mechanism has been observed for the reaction of O₃ on organic surfaces (Pöschl, 2005). It has also been demonstrated that a higher concentration of gas phase reactant often leads to a lower uptake coefficient due to surface saturation (Ma et al., 2010 ;Li et al., 2002). Differences in k_2 may also arise from the competition between reaction products and reactants for available OH, or via the blocking or coating of the reactant by products which would require liquid phase diffusion of OH to degrade the original CA. In experiments with higher OH exposures (Kessler et al 2012) it is possible that significantly more product mass is mixed and/or coated onto the original particle thus decreasing the perceived k_2 . Finally, as pointed out above, the differing reaction conditions may have led to a different CA morphology and subsequent differences in the reactivity towards OH." (Pages 19-20, lines 404-418).

Other points - A distinction between unit-mass resolution (UMR) aerosol mass spectrometry and high-resolution (HR) aerosol mass spectrometry needs to be made in this paper. The present manuscript utilizes UMR mass spectra only, whereas K2012 (and others) used HR spectra. Such a difference is unlikely to affect results for citric acid – the PMF analysis presented above is for our mass spectra at UMR – but is nonetheless important, given that HR analysis provides an extra level of distinction between different chemical species. Right now the UMR-HR difference is not mentioned at all in the present manuscript.

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Response: Yes, unit-mass resolution (UMR) AMS was used in our study, while HR-AMS was used in K2012. HR-AMS is more specific when monitoring a compound via a tracer. Thus, the fragment from products might have less influence on the signal of the tracer. We have pointed this out in the revised paper: "Secondly, a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was used in their work, while a C-ToF-AMS with unit-mass resolution was used in this study. The higher mass resolution of the HR-ToF-AMS relative to a C-ToF-AMS, may further reduce the influence of product fragments on m/z 68 (or others)." (Page 18, lines 379-382).

- The authors make the important distinction between soft and hard ionization for tracking decay of individual particulate organic species (p. 8698, line 17-25). Soft ionization is clearly preferable; however for one system we have made a direct comparison between results from the two (Figure 5 of Smith et al. 2009). For that system (squalane+OH) the two compare extremely favorably (at least when high-resolution EI peaks are used). Of course the agreement may not be as good for other chemical systems, but this result shows that the use of EI peaks may not be as fundamentally problematic as suggested in the present manuscript.

Response: As mentioned in the above response, we think our assumption might be more reasonable when a low resolution (UMR) aerosol mass spectrometer was used to measure OA concentration. We have pointed it out in the revised paper: "The results suggest that heterogeneous kinetics can be significantly underestimated when the structure of the products is highly similar to the reactant and when a non-molecular tracer is measured with a unit mass resolution aerosol mass spectrometer." (Page 2, lines 39-41) and other places in the revised paper (Page 7, lines 140-142; Page 23, lines 465,472; Page 24, line 486).

- P. 8707, line 11-12: the argument that the use of larger fragments results in larger derived values of k may be true in the present study, but is not always the case; for example the ion used in K2012 (C₄H₄O⁺ for citric acid) was chosen because it decayed away faster than all the other major peaks, including higher-mass ones.

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Response: Thanks for the input. We revised this sentence to be more specific to our study only: "This suggests that the derived rate constant greatly depends upon the size of the tracer fragment, with larger fragments resulting in larger values of k_2 in this study. (Page 18, line 393)"

- Mathematically, the only way that a PMF-factor-derived rate constant can be faster than the decay constant of any constituent ion is if the two PMF factors (assigned to products and reactants) are very similar. The authors argue that this is indeed the case in the present system, as shown in Figures 3-4 (and justify this in Schemes 1-2). However, this requires a very high degree of confidence in the PMF results. Here, the two factors account for only ~85% of the variance in the mass spectrometric data, which is extremely low – there is a good deal of residual mass spectrometric signal that is unaccounted for. This remaining 15% variability is on the order of the change in the intensity of the individual ions (see fig. 5c), making it extremely difficult to make any solid conclusions about the chemistry based on these PMF results alone.

Response: Thank you for your comment. Given your above comment we have rechecked our PMF analysis. Indeed we have made an error in reporting the value of accounted variance. The correct value is 99.98 %. It has been corrected in our revised paper (Page 12, line 257). The variances and an example of PMF analysis results are shown in Figure R2. Our results have also been verified by the mass spectrum of pure CA. Thus, we believe the kinetics calculated based upon the PMF results are indeed credible enough to justify our conclusions.

Figure R2. The variance of the data for a two factor PMF analysis.

Reviewer #2 Liu et al. report the use of a modified relative rates technique to calculate heterogeneous oxidation kinetics of organic aerosols from mass spectrometer data. Positive Matrix Factorization (PMF) is used to separate the mass spectral contributions of unoxidized and oxidized aerosol, then kinetic rate constants are calculated from the decay of the "unoxidized" factor relative to the decay of methanol. The authors suggest that rate constants derived from the decay of mass spectral tracers are underestimated

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relative to rate constants derived using PMF to isolate the unoxidized component. The magnitude of this discrepancy increases with decreasing mass-to-charge ratio because of mass spectral interferences from oxidation products. In my opinion, this manuscript presents a useful method for constraining the oxidation kinetics of organic aerosols. However, given that citric acid was the only compound studied, I am uncertain how representative the results are for other species. For example, the PMF/tracer discrepancies for tris-1,3-dichloro-2-propylphosphate (~1.5) and tris-2-ethylhexyl phosphate (~1.6) are relatively low compared to citric acid (~4-8). As the authors state, one reason could be that the molecular ion was available as a tracer for those phosphate species. But isn't it also possible that the mass spectral method works poorly for citric acid, especially given that representative CA tracers ($C_3H_3O_3^+$, $C_5H_5O_4^+$, $C_5H_7O_5^+$) are highly oxygenated to begin with?

Response: Thank you for your positive comments. Strictly speaking, the need for the PMF approach will depend on the differences in structure between reactants and products, and so you are correct that the oxidized nature of CA may make it more difficult to use a tracer approach. As summarized in Table 1, the PMF/tracer discrepancies depend on the molecular structure of the reactant and the product and the size of the tracer selected. CA contains three –COOH groups and one –OH group. In terms of the general oxidation mechanism of organic compounds by OH radicals, the OH oxidation products should be highly similar to CA as shown in Scheme R1. The products are likely to give the same fragments as CA (highlighted in red). This has been pointed out in the Scheme 2 in the original paper. For these organophosphate esters, the structure discrepancies between the reactant and the products are more prominent compared to the CA system. Regardless, there is no reason to extend the PMF/Tracer discrepancy of ~4-8 to other compounds. The discrepancy for other compounds will depend upon a number of factors including: structure of products, OH exposure level, particle morphology, and organic species competing OH reactions. We have discussed these points in the revised manuscript (Page 22-23, lines 448-468) and a new sentence has also been added as "The discrepancy between the tracer and PMF based methods for

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other compounds will depend upon a number of factors including: structure of products, OH exposure level, particle morphology, and organic species competing OH reactions.” (Page 23, lines 466-468). We are not attempting to state that the PMF/Tracer discrepancy is representative of other compounds, only that it may be an issue to consider.

Scheme R1. Possible degradation path of CA by OH.

Because this method was not applied to a range of other representative species, the general applicability of the results seems inconclusive. Therefore in my opinion the manuscript is not appropriate for publication as a research article in ACP. I think that consideration as a technical note in ACP or as a research article in a more methods oriented journal (e.g. AMT) should be considered instead. Regardless, I think the manuscript would be strengthened significantly through application of the PMF method to species with different mass spectral characteristics that are already referenced in the manuscript, such as linear/branched alkanes, bis(2-ethylhexyl)sebacate, monocarboxylic acids, either by obtaining literature data from the relevant studies or by conducting additional experiments with the setup discussed here. Other specific comments are listed below.

Response: Thank you for your instructive comments and suggestions. Although further experiments on a large range of compounds would be useful, we believe that the number of compounds chosen here is sufficient to warrant publication in ACP. Since we are not attempting to formulate an empirical relationship between molecular structure (or other parameter) and the PMF/Tracer discrepancy we believe the current set of experiments should be sufficient, as we are only highlighting an issue which needs further attention. We do agree that more work in this field in general is required in the future. Nonetheless, the results are useful to the atmospheric risk assessment community for organophosphate flame retardants, which were also reported this study and are an area of concern with respect to long range transport. We have added the line: “Future work is thus required to elucidate the chemical and physical parameters which control the OH heterogeneous reaction kinetics and the associated need to apply PMF

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for a variety of chemical systems. This may be best accomplished through systematic application of the PMF approach to species with differing mass spectral characteristics, such as linear/branched alkanes, monocarboxylic acids and other oxygenates.” in the conclusion (Page 24, 489-494).

1. P8697, L10: Donahue et al. (2005) should be cited here. Additionally, Donahue et al. (2005) present a mixed phase relative rates formulation (Equation 6) that accounts for possible concentration gradients in the condensed phase due to reagent-limited diffusion. Figure 6 in this work suggests that this does not develop in oxidized citric acid particles; a sentence or two describing this observation and implications would be worth adding.

Response: The Doanhue work has been cited in the revised paper (Page 4, line 80). As the reviewer points out, diffusion of the oxidant in particle phase might have an influence on the reaction kinetics. From Figure 6, we found this influence is not prominent under our conditions. First-order decay curves have also been observed in a wide ranges of OH exposure for oxidation of BES (c/c_0 : 1-0.4) (Hearn and Smith, 2006), palmitic acid (c/c_0 : 1-0.5) (McNeill et al., 2008), squalane (c/c_0 : 1-0.3) (Smith et al., 2009), erythritol and levoglucosan (c/c_0 : 1-0.2) (Kessler et al., 2010). Based on the c/c_0 and the initial diameter of CA particles, the maximal probe depth of OH is ~ 25 nm (Figure R3). The residence time is 52 s in this study. This requires that the diffusion coefficient of OH (DOH) in CA particles to be smaller than $1.2 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ ($D = l^2/2t$) to sustain a non-equilibrium concentration gradient (Donahue et al., 2005). At present time, the DOH in CA particles is unavailable. However, Price et al. (Price et al., 2014) have measured the diffusion of D2O in several organics (sucrose and levoglucosan) to be larger than $\sim 1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ even under dry conditions. This implies that the concentration gradient of OH in CA particles might be negligible under our conditions. We have added this discussion with respect to this issue in our revised paper: “It should be pointed out that oxidant diffusion in the particle phase should lead to a concentration gradient of oxidant and a negative impact on reaction kinetics (Donahue et al., 2005).

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However, as shown in Figure 6, this effect is negligible under the current experimental conditions. Based upon the measured c/c_0 and the initial diameter of the CA particles, the maximum OH diffusion depth is approximately 25 nm. Given the residence time (t) in this study (52 s), a significant OH concentration gradient will exist in particle phase if the DOH in CA particles is smaller than $1.2 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ ($D=l^2/t$) (Donahue et al., 2005). At the present time, the DOH in CA particles is unavailable. However, Price et al. (Price et al., 2014) have reported the diffusion of D₂O in several organics (sucrose and levoglucosan) to be larger than $\sim 1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ even under dry condition. This implies that a gradient in OH concentration in the CA particles is negligible under the current conditions." (Pages 16-17, lines 351-362).

Figure R3. Relationship between probe depth of OH in CA particle and OH exposure.

2. P8698, L15: There are several condensed phase relative rate studies (e.g. Huff Hartz et al., 2007; Weitkamp et al., 2008; Lambe et al., 2009; Isaacman et al., 2012) using techniques that are less affected by mass spectral interferences (e.g. GC-MS). In addition, the development of high resolution, soft-ionization mass spectrometers capable of exact mass measurements with minimal fragmentation would seem to minimize "contamination" issues. I think these studies and developments should be discussed briefly so the current work can be placed in better context.

Response: We have summarized the work using GC-MS in the revised paper (Page 6, lines 112-118). The issue of high resolution instruments was also pointed out as "Although gas chromatograph mass spectrometry (GC-MS) was widely used in the kinetics studies (Weitkamp et al., 2008a; Weitkamp et al., 2008b; Lambe et al., 2009; Isaacman et al., 2012), quantifying the particle phase loss of an organic compound in such studies often relies upon aerosol mass spectrometry techniques to monitor specific particle phase reactant ions of interest in semi-real time. Aerosol mass spectrometry instruments utilizing high resolution detector and soft ionization techniques,..." We also pointed out that the "contamination" issue should be important when a unit mass ratio (UMR) resolution aerosol mass spectrometer was used to measure the OA

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concentration as "The results suggest that heterogeneous kinetics can be significantly underestimated when the structure of the products is highly similar to the reactant and when a non-molecular tracer is measured with a unit mass resolution aerosol mass spectrometer." (Page 2, lines 39-41) and other places (Page 7, lines 140-142; Page 23, lines 465,472; Page 24, line 486).

3. P. 8699, L27 and P8701, L20: Slowik et al. (2012) used PMF in a very similar application to isolate factors following the heterogeneous oxidation of ambient biogenic SOA. Their work should be cited. Their results showing an m/z -dependence of kOH (Table 1) are directly relevant to the implications of this study and should be discussed later in the manuscript.

Response: Slowik's work has been cited and discussed in the revised paper (Page 7, lines 147-149; Page 8, lines 158-159; Page 10, lines 211-213; Page 18, line 395).

4. P8700, Section 2.1: What is the residence time in the reactor?

Response: It is 52 s and has been pointed out in the revised paper (Page 9, line 177).

5. P8703, L13: I am confused by this statement, which suggests residual OA mass of $\sim 15\%$ (if I am reading it correctly), because L25-L26 suggest a negligible residual. Which is the case here? If the residual is significant, presumably it contains a mix of multigeneration oxidation products that should be discussed to facilitate interpretation of factors 1 and 2, and the mass spectrum and temporal pattern of the residual should be presented.

Response: In response to this and the 1st reviewer's comments we have re-checked our PMF data results (see response to Reviewer 1). We have made an error in the value of the variance. The correct value is 99.98 %. It has been corrected in our revised paper (Page 12, line 257). The variances and an example for PMF analysis result are shown in Figure R2.

6. P8709, L7: The two studies cited here (George et al., 2007; Lambe et al., 2007)

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measured uptake coefficients ~ 1 . Are the authors suggesting that these previously measured values – along with other studies measuring uptake ~ 1) are also a factor of 4-8 too low? Response: We believe this will depend upon the reaction system, although a value of greater than 1 is unlikely. The results for CA or an OPE compound cannot be directly extrapolated to other reaction systems. For example, as shown in Table 1, the ratio of the PMF to tracer based kinetics varies with reactant. The need for this approach will also depend upon a number of other factors, such as particle morphology, and oxidant levels and product distributions. We have highlighted these points at various points in the revised manuscript: “The discrepancy between the tracer and PMF based methods for other compounds will depend upon a number of factors including: structure of products, OH exposure level, particle morphology, and organic species competing OH reactions.”(Page 22, lines 466-468) and in response of the 1st question to reviewer #2.

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<http://www.atmos-chem-phys-discuss.net/14/C3329/2014/acpd-14-C3329-2014-supplement.zip>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 8695, 2014.

C3345

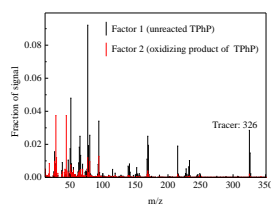


Figure R1. Mass spectra of two PMF factors determined for TPhP oxidation.

1

Fig. 1. Mass spectra of two PMF factors determined for TPhP oxidation

C3346

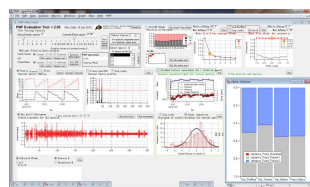
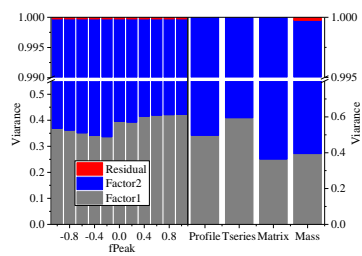


Figure R2. The variance of the data for a two factor PMF analysis.

2

Fig. 2. The variance of the data for a two factor PMF analysis

C3347

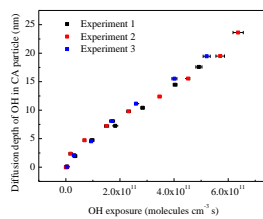


Figure R3. Relationship between probe depth of OH in CA particle and OH exposure.

4

Fig. 3. Relationship between probe depth of OH in CA particle and OH exposure

C3348

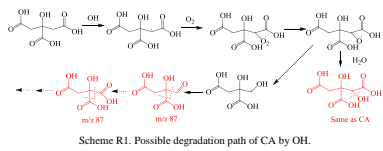


Fig. 4. Scheme R1. Possible degradation path of CA by OH

C3349