We thank the reviewers for their insightful comments and suggestions. To facilitate the revision process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the reviewer comments and suggested changes are incorporated into the revised manuscript in **bold text**.

Responses to Comments from Anonymous Referee #1

R1.0, Summary: The authors present a valuable dataset for gas-particle partitioning of organic acids (<C18) measured using MOVI-HRToF-CIMS at BEAChON-RoMBAS. In my assessment, the manuscript is publishable in ACP after minor revisions discussed below:

R1.1, p.17340, line 14: I think you mean Fig. 3

Corrected as suggested.

R1.2, p.17341: The authors spend two long paragraphs here discussing the difference between measured and modeled Fp for alkanoic acids at low carbon numbers, and they provide some interesting insights, but from Fig. 3 it looks like this measurement-model discrepancy is not particularly significant and could almost be within the measurement noise. I think this lengthy discussion gives too much importance to the small discrepancy and disrupts the balance of the manuscript, considering that, later in the manuscript, some more severe measurement-model discrepancies are discussed much more briefly.

The possible reasons for discrepancies between measured and modeled F_p are the same for the alkanoic acids and for other acids shown later in the paper. We therefore prefer to keep this discussion at this point of the paper since it is the first model / measurement comparison shown.

To clarify this point, we have created a new section which contains the text from P17341, L3 (ACPD version) till P17342, L17. This section name and new starting text are:

3.2 Possible Reasons for Measurement / Model Discrepancies

This section summarizes all the possible reasons for measurement / model discrepancies. Although the discrepancies are smaller for the alkanoic acids than some of the other acids shown below, we list all the potential reasons here for clarity.

R1.3, p.17344: More information is needed for the reader regarding the decrease in oxygen containing functional groups at C12 and C15, as this is hard to understand, and the local minima in Fig. 4 look like they could just be outliers or noise in the measurement (esp. in the case of C15). Are there some especially abundant naturally occurring, low-oxidation-state acids with those carbon numbers?

We have revised this text to more explicitly recognize the uncertainty as:

"The models with hydroxyl or acid groups also capture the decrease in F_p at 12 and 15 carbons, indicating that those decreases may be a result of the decrease in oxygen-containing functional groups for acids of those carbon numbers. A possible reason for the decrease in O/C at those carbon numbers may be higher relative fractions of alkanoic acids. In fact, a larger fraction of the signal in these bins is from acids with only 2 oxygens (no excess O), which have a higher volatility compared to more functionalized acids, resulting in a decrease in the bulk average F_p. The feature is strongest at 12 carbons where ~ 60% of the gas-phase signal is contributed by the alkanoic acid (deprotonated dodecanoic acid, $C_{12}H_{23}O_2^-$) (see Fig. S6 in the supplemental material for the gas and particle phase signals for various ions in the C_{12} bin on Aug 26, 2011). Dodecanoic acid and other alkanoic acids are both naturally occurring (from plant waxes and oils) and have also been reported in wood combustion, vehicular and meat cooking emissions (Rogge et al., 1991, 1993)."

R1.4, p. 17344 line 21: I think some words are missing from this sentence.

We have reworded this sentence to:

"Above C_{15}, all the models converge indicating that the influence of the identity of the functional group becomes small compared to the decrease in C^* due to the increasing carbon number."

R1.5a, p. 17344 line 25: I suggest showing on one or more of your figures the model curve for aqueous partitioning, rather than just discussing it verbally

Regarding aqueous partitioning ($F_{p,aq}$), the figure for alkanoic acids was already included in the supplement published with the ACPD version as Figure S4 and was already discussed in P17342 L2-11 of the ACPD version. Figure A below is an updated version of this figure with additional Henry's law constants (H) data for alkanoic acids from EPA HENRYWIN program (EPA, 2013). The updated version has been included in the revised supplemental material.

We have added the following text to the supplemental material.

"<u>Estimating H for bulk acids vs. carbon number:</u>

Since experimental data for H of functionalized acids of different carbon numbers are not available, $F_{p,aq}$ of bulk acids is estimated using two different estimates: 1) from the H of pure mono and di-acids and the average excess oxygen at each carbon number; and 2) from the values estimated by Hodzic et al. (2013) for functionalized acids using group contribution theory. Di-acid H values are from EPA HENRYWIN program and Compernolle and Müller (2013). Tables S3 in the supplemental material lists the H values used in the $F_{p,aq}$ calculation here. For calculating H of bulk-averaged acids from mono and di-acids we calculated the geometric mean of mono and di-acid H values weighed by the measured excess O for a given carbon number (shown in Fig 5 of the main manuscript), since the excess O is always on average between 0 (value for monoacids) and 2 (value for diacids). The following equation is used:

$$H_{bulk,i} = 10^\wedge([log_{10}(abs\left(\frac{[excessO_i - 2]}{2}\right) * H_{mono} + log_{10}(abs\left(\frac{[excessO_i]}{2}\right) * H_{diacid}]/2)$$

The values of H for bulk-averaged acid estimated from the group contribution theory-based estimates from Hodzic et al. (2013) are from 413 multifunctional acids. The H values are first binned into carbon number bins and further separated based on their excess O. A geometric mean is then calculated for only those acids having an excess O of 1 and 2 resulting in two H values for each carbon number, $H_{exO=1}$ and $H_{exO=2}$. This limitation of excess O = 2 is based on the fact that the measured excess O is < 2 for C_1-C_{18} carbon numbers (shown in Fig 5 of the main manuscript). Finally, a geometric mean of $H_{exO=1}$ and $H_{exO=2}$ is calculated and weighed by the measured excess O using the equation,

$$H_{bulk,i} = 10^\wedge([log_{10}(abs([excessO_i - 2]) * H_{exO=1,i} + log_{10}(abs([excessO_i - 1]) * H_{exO=2,i}]/2)$$

All values of H are at 298 K. The geometric mean H values show a spread of 1-2 orders of magnitude for a given carbon number (Figure B). $F_{p,aq}$ is estimated using the aerosol liquid water content (LWC) content calculated with the E-AIM model-II. For LWC calculation highest RH is fixed at 99% since above this the model gave un-realistically high LWC, and if such values of RH > 99% were reached in the field the particles would grow beyond the size ranges of the instrumentation. Figure C shows campaign average $F_{p,aq}$ for bulk-averaged acids as a function of carbon number using the datasets described above. The partitioning of bulk-averaged acids to the aqueous-phase is very small (below 0.5%) independent of the data source used for H. These values are lower than those calculated by partitioning to the organic fraction, and have the opposite trend with carbon number than observed experimentally.

We also calculated the time series of $F_{p,aq}$ for C_7-C_9 and C_{10}-C_{12} carbon number bulk-averaged acids (shown in figures D and E) and two terpenoic acids: pinic and MBTCA (shown in figures F and G). H values for these terpenoic acids are from the EPA HENRYWIN program. Since H value for MBTCA is not available we used the value of tricarballylic acid ($H = 1.47 \times 10^{14}$ M atm^{-1}). For bulk-averaged acids $F_{p,aq}$ is negligible even for high LWC content. For pinic acid, $F_{p,aq}$ increases to 0.3 during high LWC but is still lower than the partitioning estimated to organic fraction. For MBTCA, we calculate complete partitioning to the aqueous-phase. We added these figures to the supplement section and modified the text on P17344 line 23 as below

"As above, Henry's law partitioning to the aqueous-phase predicts F_p that is several orders of magnitude smaller than partitioning to the organic fraction. Figure 6 shows the estimated aqueous partitioning of bulk-averaged acids using H values of pure mono-and di-acids and multifunctional acids (see Fig. S7 in the supplemental material for the different H values used in this estimation)."

For C_7-C_9 and C_{10}-C_{12}, text is added on P17346 line 4:

"Aqueous partitioning estimated for C_7-C_9 and C_{10}-C_{12} bulk acids is shown in Figs. S13 and S14 and show that their estimated partitioning to the aerosol water is minimal compared to the partitioning to the organic fraction."

For pinic acid, we added the below text at the end on P17347 line 25:

"Aqueous partitioning of pinic acid (see Fig. S15) is a strong function of aerosol LWC and can contribute significantly during periods of high aerosol LWC (e.g., on August 27th), but during other times when aerosol LWC is low, aqueous partitioning is estimated to be minimal. The experimental time trends are more consistent with the modeled partitioning to the organic fraction than to LWC."

Similarly, for MBTCA, we added the below text on P17348 line 2:

"Similar to partitioning to OA, MBTCA is estimated to partition readily to aerosol water even during low aerosol LWC periods. Figure S16 shows the aqueous partitioning of MBTCA along with partitioning to OA. The discrepancy between measured F_p and modeled $F_{p,aq}$ indicates towards a possibility that either the H value used here is high or the elemental composition assigned as MBTCA is that of an isomeric compound with higher P_{vap} and lower H than that used here."

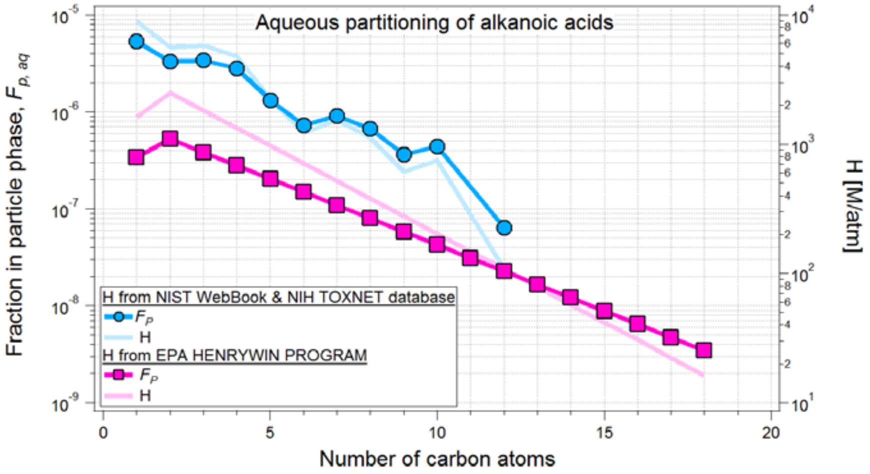


Figure A (replacing old Fig. S4)

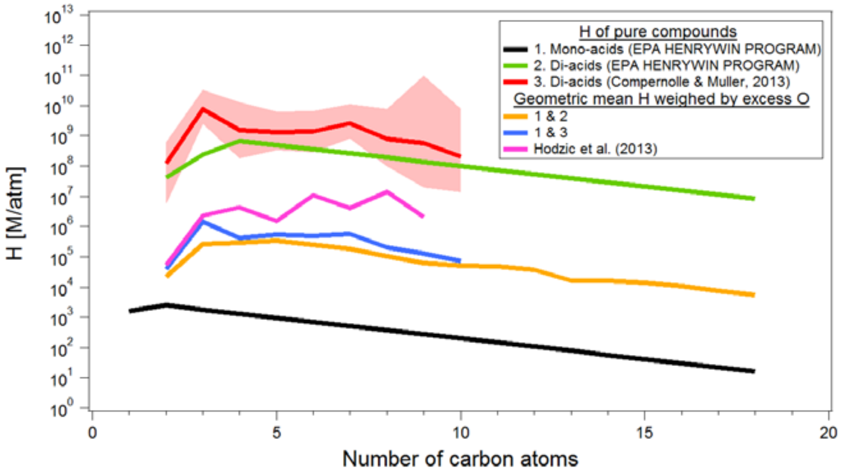


Figure B (new Fig. S7)

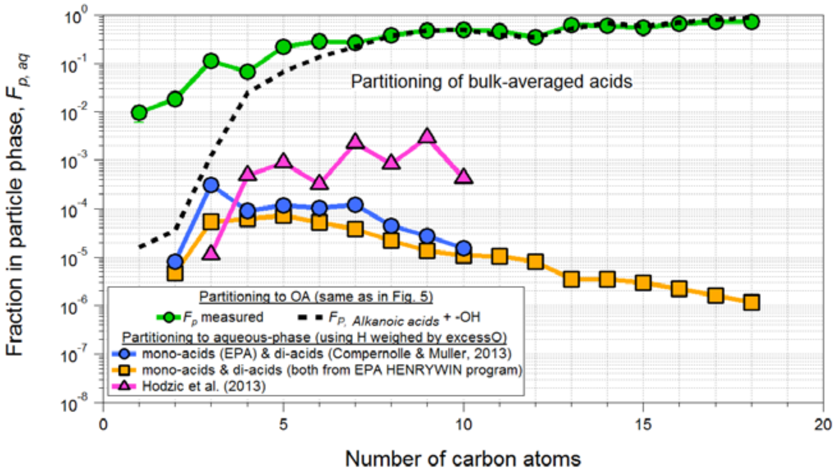


Figure C (new Fig. 6)

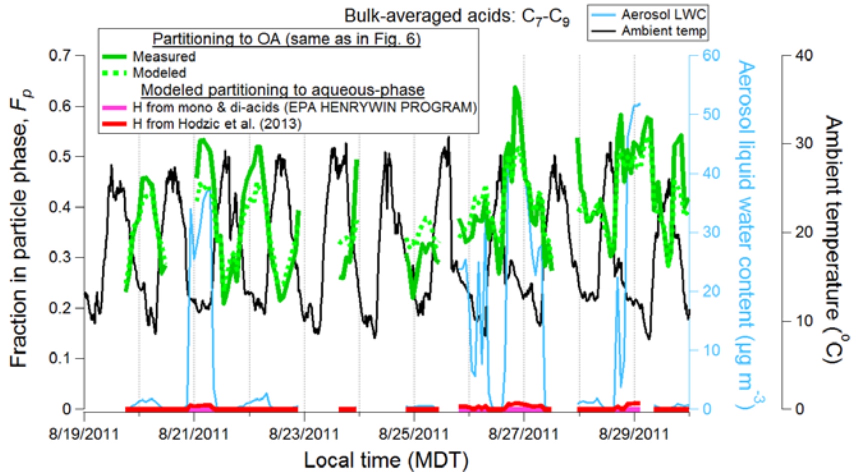


Figure D (new Fig. S13)

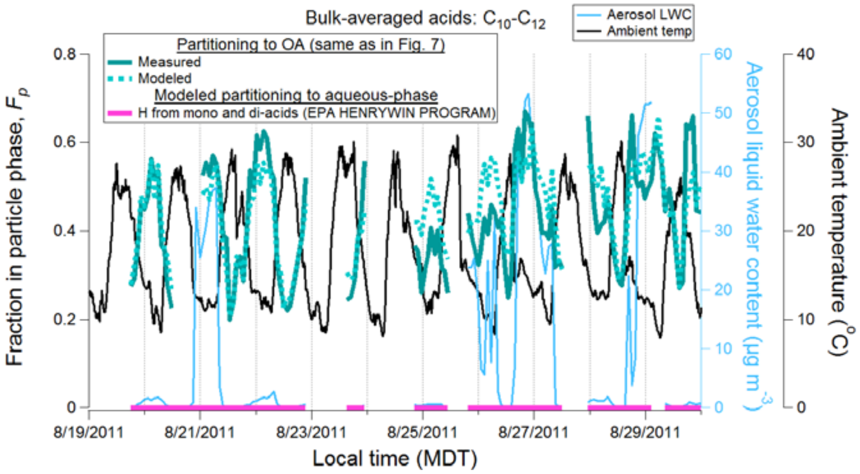


Figure E (new Fig. S14)

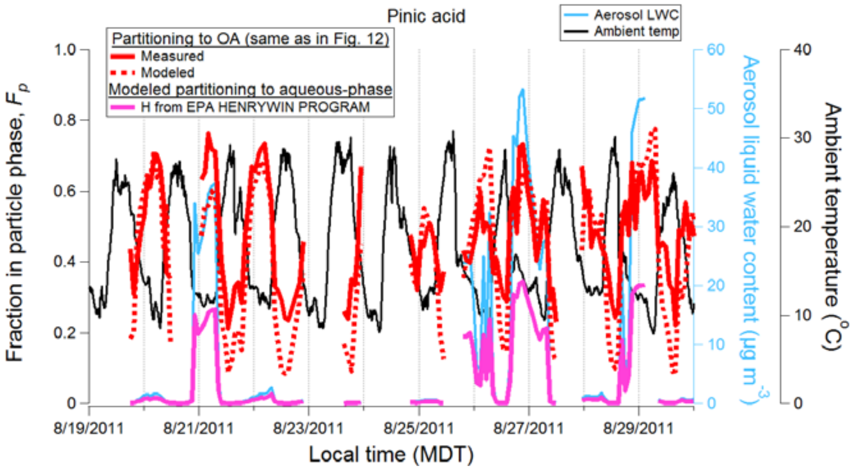


Figure F (new Fig. S15)

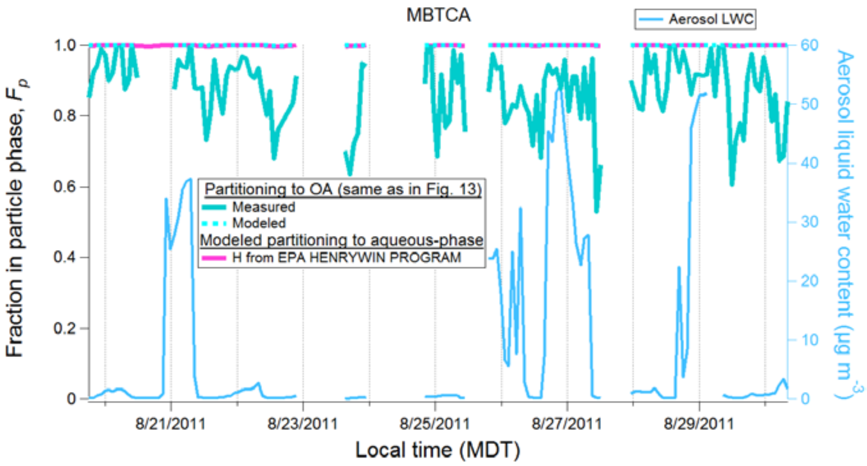


Figure G (new Fig. S16)

R1.5b: Section 3: There are far too many figures in this section. I think that just one figure can get the point of Section 3.3.1 across. Similar reductions in the other subsections may be possible. Also, is the 'excess oxygen' model used in these bulk acid figures? If not, why not, and what errors might this introduce?

We disagree with the reviewer that there are too many figures in Section 3. We feel that showing a good and a bad case, rather than just showing one or the other, provides balance to the paper and also shows the readers that the model-measurement discrepancy varies as a function of carbon number.

Yes, the excess oxygen model was used to calculate F_p. The sentence describing this was already on Pg. 17345 and lines 18-20 of the ACPD version: "In the model, C^* for each carbon number is calculated using the C^* for the alkanoic acid with a decrease calculated using the measured average excess oxygen added as hydroxyl functionality (per Fig. 5)."

R1.6, p. 17346 line 16: ". . .factors other than ambient temperatures. . ." This statement needs some followup discussion. This is an example of the lack of balance in the discussion that I mentioned above.

This refers precisely to the list of possible explanations for measurement / model discrepancies discussed in response to comment R1.2 above. The statement has been modified as shown below to make it clearer.

"Despite a diurnal cycle, low correlation between measured and modeled F_p indicates factors other than ambient temperature (e.g. some of the factors discussed in section 3.2) are affecting the phase partitioning or the F_p measurement of alkanoic acids."

R1.7, p. 17346 line 23: ". . .there should be very little. . ." Since you're talking about your measurements, don't you mean there *is*?

We have reworded this statement for clarity as:

"The measured values are several orders of magnitude higher than those predicted by the absorptive partitioning model for the same carbon number range, and the latter suggest that there should be very little particle-phase concentration of these acids."

R1.8, p. 17347 line 4: Why does more OA matter?

Because of partitioning theory, e.g. equation (2) in the ACPD manuscript: more OA increases the amount of absorbing organic phase thus increasing the particle-phase fraction of each acid.

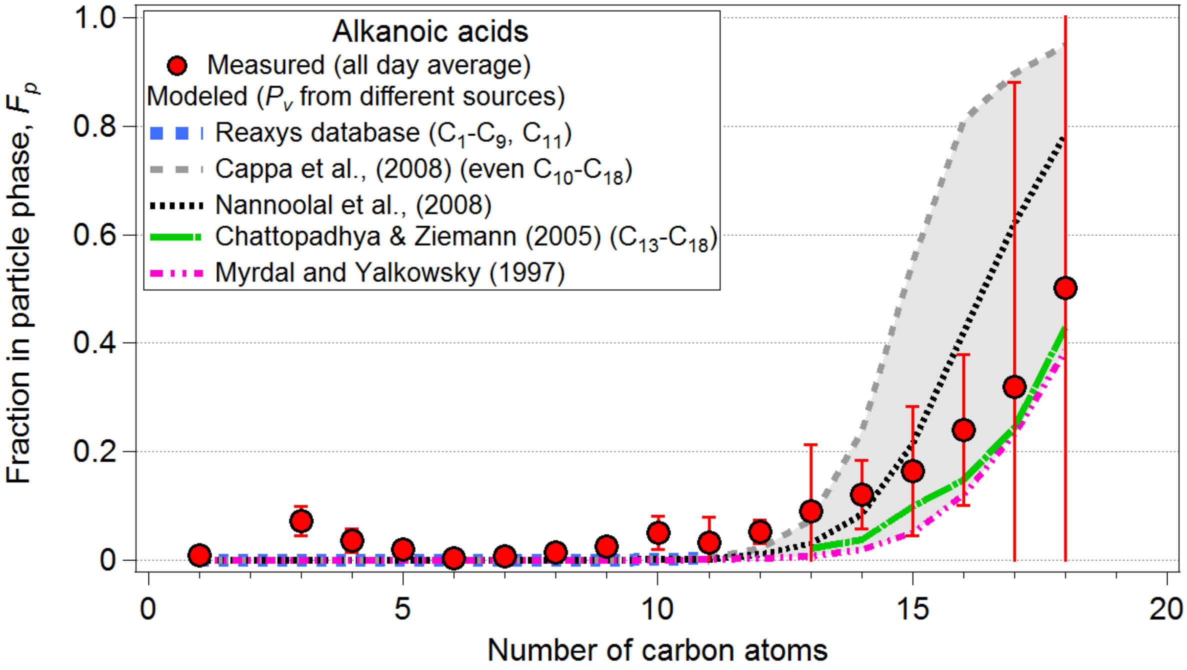
R1.9, p.17349 line 14 (and throughout): "Data" is plural, please check the verb agreement.

We corrected the sentence as:

"Despite all the uncertainties, the data clearly indicate that semi-volatile acids undergo reversible phase partitioning, …"

R1.10, Fig. 3: It's not really possible to distinguish the lines, even when the image is in color.

The figure has been slightly modified to make the lines easier to distinguish, see below. It has to be noted that the line for data from Reaxys Database was not visible because of overlapping lines. Also, it had the same line pattern as Cappa et al. (2008) which is for different carbon number alkanoic acids.



R1.11, Fig 6-14: it’s not immediately clear that the black lines correspond to temperature. I suggest including the black line with the other curves in a legend for each figure.

The figures have been modified as suggested.

Responses to Comments from Anonymous Referee #2

R2.0, Summary: This manuscript describes in situ measurements of gas- and particle-phase organic acids in a forested environment, using a new chemical ionization mass spectrometer (CIMS). The focus of this work is on phase partitioning of the acids. It is found that absorptive partitioning into an absorbing organic phase is sufficient to qualitatively explain the observed gas-particle partitioning for most semivolatile species. However higher- and lower-volatility species are not as well-described; possible reasons for such discrepancies are put forward. This is a strong paper, providing new insights into an important topic in atmospheric chemistry (phase partitioning of organic species), and is certainly worthy of publication in ACP. Specific comments that need to be addressed are listed below.

R2.1. P. 17335, second paragraph: Does acetate-CIMS measure nothing but carboxylic (and inorganic) acids? Might other acidic organic species (e.g., functionalized alcohols) be measured as well? Have the sensitivities of this technique to such species been investigated?

The reviewer raises a good point, and we have revised this text as follows:

"Acetate ion selectively ionizes acids by abstracting a proton from the carboxyl hydrogen (Veres et al., 2008). Both, organic and inorganic acids are ionized, but here we focus exclusively on organic acids. We note that acidic alcohols such as nitrated phenols that have gas-phase acidities higher than that of acetic acid will also be ionized and can also be measured by proton abstraction (Mohr et al., 2013), while species such as glyoxal, methylglyoxal and levoglucosan can be measured by clustering with acetate (depending on the declustering settings of the ToF), but with far lower sensitivity (Aljawhary et al., 2013)."

R2.2, Section 2.5: It would be useful to have a sense of the magnitude of background signal that was present. For example, what was the ratio of ambient-to-blank signal for the alkanoic acids of different carbon numbers?

For this very reason we had already included Fig. S3 in the ACPD version. We now realize that we did not describe this figure in the main text and we thank the reviewer for pointing out the need for this information. We have added the following text to section 2.5 to address this point:

"Fig. S3 shows the background and ambient signals for C_1-C_{18} alkanoic acids for August 26th. Data from other days are similar. Background signals are about an order of magnitude lower than gas and particle signals, although there is some variation with carbon number."

R2.3, P. 17338, Equation 3: The molecular weight (MW) here is that of the acid, consistent with the treatment by Donahue et al. (ES&T 40:2635, 2006). However Pankow (Atmos Environ, 28:185, 1994) uses MW of the absorbing organic mass instead (see Eq 15). Cappa (AMT, 3:579. 2010) presents a formulation that includes both (see Eq 11). A brief discussion of the "proper" MW to use would be helpful.

This is an interesting observation. As discussed in the paper we indeed use the formulation of Donahue et al. (2006). In this formulation C_i* is the saturation concentration of species *i* in mass units, and thus the MW to be used in the equation (our equation (3), same as equation (5) in the Supp. Material of Donahue et al., 2006) is the MW of the partitioning species. We were aware of the slightly different treatment of Pankow (1994), but not of that of Cappa (2010). We have added the following text to the manuscript to address this point:

"Alternative formulations of partitioning theory have been presented by Pankow (1994) and Cappa (2010). The differences in these three formulations are on the order of MW_i/MW_{OA}, and similar or smaller than uncertainties in vapor pressures and activity coefficients, and therefore we do not consider them further."

R2.4, Figure 3: What is the source of the very large error bars for the largest (C17-18) acids in Figure 3? From the text (p. 17340, line 3) it sounds like this is just from low signal-to-noise; but since the range of values within the error bars is from 0 to 1, it seems these two points should be eliminated as well.

Yes, the large error bars are because of the low signal-to-noise ratio, especially in the gas-phase data. Although noisy, the averages still follow the increasing trend of the other acids. Here the error bars do not capture the whole statistical information content of the data points, and the fact that e.g. they reach 0 does not mean that the data points do not have any information content, from a statistical standpoint. Thus we have not modified the figure.

R2.5, P. 17341 (and throughout text): a number of possible reasons for model-measurement discrepancy in F_p is given here; one that is missing is nonideal partitioning (activity coefficients deviating from 1). This should be mentioned, and possibly explored in some detail. Could non-ideal partitioning (with a fixed activity coefficient) explain any of the results?

The reviewer raises a good point. We have added the following text to the manuscript to address this point: (P17341 L23):

"Differences in formulations of partitioning theory (Pankow, 1994; Cappa, 2010) vs. the Donahue (2006) formulation used here, and/or activity coefficients different from the value of one assumed here could also result in some differences. However both effects should only result in limited changes of the calculated $F_{p.}$ As discussed above, differences between the partitioning formulations are on the order of MW_i/MW_{OA}, and should only be substantial for the lightest acids. Recent studies have shown that activity coefficients for oxidized organics deviate only by a factor of 2-3 from 1 (Donahue et al., 2011; Shiraiwa et al., 2013), which is not large enough to change the model results substantially."

R2.6, P. 17341, line 25: "absorption" rather than "adsorption"?

Corrected as suggested.

R2.7, P. 17343, line 9-12: The focus here is on the RO2 chemistry at the site, but the acids measured were probably not formed right there, and rather were formed somewhere upwind. What matters then is the RO2 chemistry of the airmass over the last several hours/days.

The reviewer makes a good point that the history of the air masses impacting the site is important and we had already noted in the text (P17341 L4-7) that those changes were not considered. In any case this text refers to the choice of functional groups for the estimation of *C** of the bulk acids, and it is already stated (P17343 L7-8) that "Addition of a hydroperoxyl group (–OOH) reduces *C** by approximately a factor of 2.3×10^{-3} which is in between the addition of a –OH and a –C(O)OH group." The abstract already reflects this possibility when it states "Partitioning of bulk acids is more consistent with model predictions for hydroxyacids, hydroperoxyacids, or polyacids, and less so for ketoacids." From the point of view of the analysis in Fig. 4 & 5, not considering –OOH groups explicitly was done to reduce visual clutter. Thus we have not modified the manuscript in response to this comment.

R2.8, Fig 5: The focus here is on carbonyl and hydroxyl groups; what about nitrates? Would these be measured as such by the CIMS (or would they decompose as they do in the AMS)? Were any nitrated acids measured?

We have added the following text to address this point (P17343 L12):

"Organic nitrates were present at the site and their aerosol concentration was quantified by two different methods, which showed good agreement (Fry et al., 2013). According to Fry et al. (2013) molecules with an organic nitrate group comprised about 6-20% of OA. From our calibrations (not shown here) we estimate organic acids to comprise 30% of OA, some fraction of which could be nitrated acids. Quantifying the fraction of acids that have a nitrate group might be possible from the high-resolution spectra, and should be explored in future studies."

While interesting, the determination of nitrated acids from the high-resolution spectra is a very complex and difficult topic that is beyond the scope of the current manuscript. A manuscript in preparation (Stark et al., in prep) will address the information content of the high-resolution spectra from the CIMS in this study.

To our knowledge the possible thermal decomposition of nitrates during detection in the MOVI-CIMS has not been studied.

R2.9, Figures 6, 7, 9, 10, 12, 13: A legend should be provided that indicates that the colored traces correspond to partitioning whereas black traces correspond to temperature.

The ambient temperature trace is now added to the legend to make this clear.

R2.10, Section 3.3.2: I was confused by the switch back to alkanoic acids after all the discussion of bulk acids and excess oxygen. It might make more sense to move this section (and the accompanying figures) to earlier in the paper (right after section 3.1) before discussing the bulk acids.

We had this discussion repeatedly and reordered the figures more than once before submission. After considering both options, we decided to show the average F_p as a function of carbon number for both alkanoic acids and bulk-averaged acids, before showing the F_p time series, since that allowed us to discuss the partitioning as a function of carbon number for all species, followed by a discussion of time series for all species. We thank the reviewer for the suggestion but we think that the present format is the best possible way to describe the results.

R2.11, On a related note: there is no discussion of alkenoic acids (oleic, etc.); these have no excess oxygen but are distinct from the saturated fatty acids. Were these measured? If so, what was their partitioning behavior?

Yes, alkenoic acids are also measured but alkanoic acids, because they have the highest possible positive mass defect from their nominal mass for organic acids and are most clearly identifiable in the mass spectrum. On the other hand, alkenoic acids have lower positive mass defects because of two less hydrogen atoms than the alkanoic acids and therefore have the potential for interferences from other ions and we therefore are less certain in terms of identification. Also, vapor pressure data is readily available for C_1-C_{18} alkanoic acids. Hence, we choose to analyze alkanoic acids for this manuscript.

R2.12, Throughout: It is stated that “hundreds” of organic acids were measured. But only a small fraction of these (the alkanoic and terpenoic acids, accounting for <30 species) are discussed specifically. What are the overall characteristics of the others? Distributions of numbers of carbon/oxygen/hydrogen/nitrogen atoms would be interesting values to report. Do these exhibit the same general partitioning behaviors as the alkanoic and terpenoic acids?

We note that the partitioning behavior of the bulk acids is reported in the manuscript, e.g., Figs 4-8. In terms of their compositional parameters, we agree with the reviewer that such information is very interesting. However, it is voluminous and needs to be described in detail. Thus it clearly exceeds the scope of this paper. A detailed description of the hundreds of observed acids, the distributions of C, O, H and N atoms, along with the peak fitting procedure employed to obtain the elemental compositions are in a forthcoming paper in preparation for ACPD (Stark et al., in prep.).

References

Aljawhary, D., Lee, A. K. Y., and Abbatt, J. P. D.: Application of high resoltuion chemical ionization mass spectrometry (CI-ToFMS) to study SOA composition: focus on formation of oxygenated species via aqueous phse processing, Atmos. Meas. Tech. Discuss., 6, 6147-6186, 2013.

Cappa, C. D.: A model of aerosol evporation kinetics in a thermodenuder, Atmos. Meas. Tech., 3, 579-592, 2010.

Cappa, C. D., Loverjoy, E. R., and Ravishankara, A. R.: Evaporation rates and vapor pressures of the even-numbered C8-C18 monocarboxylic acids, J. Phys. Chem. A, 112, 3959-3964, 2008.

Compernolle, S., and Muller, J.-F.: Henry's law constants of di-acids and hydroxypolycids: recommended values, Atmos. Chem. Phys. Discuss., 13, 25125-25156, 2013.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303-3318, 2011.

Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.1 - HENRYWIN v 3.2 (2013), United States Environmental Protection Agency, Washington, DC, USA, Available at Accessed on

Fry, J. L., Draper, D. C., Zarzana, K. J., Campuzano-Jost, P., Day, D. D., Jimenez, J. L., Brown, S. S., Cohen, R. C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B. L., and Grossberg, N.: Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011, Atmos. Chem. Phys., 13, 8585-8605, 2013.

Hodzic, A., Madronich, S., Aumont, B., Lee-Taylor, J., Karl, T., Camredon, M., and Mouchel-Vallon, C.: Limited influence of dry deposition of semivolatile organic vapors on secondary organic aerosol formation in the urban plume, Geophys. Res. Lett., 40, doi:10.1002/grl.50611, 2013.

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prevot, A. S. H., Xu, L., Ng, L. N., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton, J. A.: Contribution of nitrated phenols to woob burning brown carbon light absorption in Detling, United Kingdom during winter time, Environ. Sci. Technol., 47, 6316-6324, 2013.

Pankow, J. F.: An absorption Mmodel of gas/particle partitioning of organic compounds in the atmosphere, Atmos. Environ., 28, 185-188, 1994.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., and Cass, G. R.: Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, Environ. Sci. Technol., 25, 1112-1125, 1991.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., and Cass, G. R.: Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants, Environ. Sci. Technol., 27, 2700-2711, 1993.

Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-particle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Phy. Chem. Chem. Phys., 15, 11441-11453, 2013.