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Interactive comment on "Semi-continuous measurements of gas/particle partitioning of organic acids in a ponderosa pine forest using a MOVI-HRToF-CIMS" *by* R. L. N. Yatavelli et al.

Anonymous Referee #2

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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

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Interactive Discussion

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are listed below.

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?

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?

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.

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.

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?

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

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.

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?

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.

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.

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?

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17327, 2013.