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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "High gas-phase mixing ratios of formic and acetic acid in the High Arctic" *by* Emma L. Mungall et al.

Anonymous Referee #3

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Mungall et al. present field observations of formic and acetic acid in the gas-phase, and of formate and acetate in rain water samples taken at Alert, Nunavut during a the early summer 2016. Surprisingly high and variable gas-phase concentrations are at odds with our current understanding about sources of biogenic VOC precursor molecules, or possible other sources in the remote arctic atmosphere.

The manuscript is generally well written, and the topic falls well within the scope of ACP. The work is of considerable quality, and leverages state-of-the-art instrumentation. I recommend publication after the below points have been addressed.

Comments: 1) The abstract points out that the scarcity of measurements at high latitudes is a hindrance to understanding these acids and their sources. Yet the authors seem to be making a conscious choice to limit discussion to previous measurements

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Discussion paper

of FA and AA. Why? In terms of the sources for acids, it is not obvious why there should be anything special about FA and AA, other than that they reside primarily in the gas-phase. There is a rich history of acid measurements in the condensed phase at Alert, that dates prior to the advent of online techniques, and includes measurements of annual cycles of organic acids in aerosols in 1987-1988 (published approximately a decade later). Early work by Kimi Kawamura in aerosols, and also Len Barrie comes to mind. A thorough literature review might reveal other information. This should be discussed. A paragraph that summarizes what other acids measurements have revealed about sources of other acids at Alert is currently missing.

2) The lifetime of FA and AA is listed as 1-2 days in the introduction. Does this apply to the conditions at Alert? How different are the environmental conditions characterized in Paulot et al 2010 to those during the wet/cool period, and to the photochemical period? Variables such as boundary layer height, dry and wet deposition rates are likely quite different for the different periods studies, and a shallow boundary layer at Alert may affect that lifetime?

3) The experimental section mentions estimates of mixing height from radiosondes deployed by the EC weather station at Alert. At what frequency are these observations available? What is known about the boundary layer height during the cold/wet and photochemical period? What gaps are there in our understanding of boundary layer height at Alert? A thorough discussion of boundary layer height is missing, and is not only relevant to lifetimes (see point 2); also the dilution of a surface source flux, the observed wind-speed dependence of the photochemical cycle, previous observations of extremely shallow inversions (few m-10m) above ground in the arctic point to a key role of boundary layer height, etc. Please expand this discussion. Data of mixing height is missing in Figure 3.

4) Figure 4: Maybe I missed it, but was the acid spike in Figure 4 observed with high or low light conditions? Maybe this could be clarified by using a second y-axis to illustrate a subset of other variables. It is later suggested (page 17, line 29) that changes in pH

due to precipitation may drive atmospheric variability of acid concentrations here. A reference to Figure 4 seems appropriate here (currently missing) - and revising Figure 4 would benefit from showing other parameters to support the claim, if at all possible.

5) A minor point, but somewhat disconcerting: Table 3 lists R2 for FA*WS as 0.8, while Figure 6d lists that same number, for the same period as R2 = 0.87 - which is correct?

6) Is there no data about the enrichment factor of acids at surfaces of snow crystals, or as a result of freeze thaw cycles? Concentration is likely, and well established for halogens (e.g. frost flower mechanism of halogen activation). The assumptions underlying estimates of gas-phase acid concentrations on page 15, lines 28f seem very crude. How much acid can realistically be expected to be rationalized if the assumption of equilibrium partitioning is refined, or conversely, how much of a change in pH, or surface concentration enrichment is needed to explain the observations?

7) There is no mentioning of aerosols as a source for FA and AA. Why is this? Can the authors rule out that aerosols are incubators for FA and AA formation?

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