

Interactive comment on “Heterogeneous uptake of the C₁ to C₄ organic acids on a swelling clay mineral” by C. D. Hatch et al.

Anonymous Referee #2

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This manuscript presents very systematic, clearly-organized experiments about the uptake of small organic acids onto montmorillonite. These acids have been observed in the troposphere, and their behavior may affect the pH of the particles to which they are exposed. The suggestion that acids dissociate on the surfaces of montmorillonite suggests additional chemistry which could be considered subsequent to the uptake of organic acids. Also important is the realization that acid uptake can affect water uptake, and vice versa. The results presented are interesting and quite relevant to current work in the field, although a bit more rigor may be called for when extrapolating the lab results to the atmosphere.

I have three significant concerns about the scientific basis of this work. Once they have been resolved, I believe this manuscript will make a valuable contribution to the

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community's understanding of the chemical role of dust in the atmosphere.

1) The uptake of organic acid onto the sample mount and other surfaces in the "blank" exposures is alluded to but not sufficiently quantified. As the authors note, this correction is necessary for obtaining accurate results. Thus, an average or typical value should be reported. Does 1% of the acid lost from the gas phase stick to the sample mount? 90%? What is the uncertainty introduced into the calculations as a result of this correction for blank losses?

2) The time at which gamma zero is calculated really should be specified. Only on page 7008 (line 17) is there any implication, but no explicit statement, of the point at which the "initial" uptake is defined. Since Figure 4 clearly shows that the uptake is time dependent, the protocol employed should be defined. If gamma zero really is calculated after only two seconds of exposure, the authors should address the uniformity of the partial pressure in the chamber at that time. Is the mass spectrometer really reporting faithfully the conditions at the gas/dust interface?

3) The calculation of atmospheric uptake of acids onto dust surfaces presented in Section 5 is incomplete. The phenomenon of saturation must be addressed in this section. By my (rough) calculations, 1 ppbv of acid at 5 km would provide more than twice the saturation coverage reported in Figure 8b for acetic acid uptake at 29% RH. Thus, under plausible conditions, complete removal of acids from the gas phase may never be achieved (150 $\mu\text{m}^2 \text{ cm}^{-3}$ of dust, in spheres of $d=2\mu\text{m}$, with a density of 2.2g cm^{-3} ; 5mg acetic acid uptake per g of dust at 29% RH), invalidating the conclusion that removal of all organic acids occurs in four days or less.

Furthermore, as shown in Figure 4, gamma zero is not a relevant quantity after some early exposure period, yet this is not acknowledged in the calculation presented.

Additional questions, corrections and suggestions:

a) The abstract seems contradictory: "the organic acid content increased significantly

with increasing humidity." But two sentences later: "the uptake of formic, acetic and propionic acids increase only slightly at higher humidities." (In this sentence, should "increase" actually be "increases" to match with "uptake"? Also, the abstract should explain how others should use the results of this study. What value of gamma is appropriate to use over the lifetime of a dust particle? And at what point will uptake cease due to saturation of available surface sites?

b) I strongly urge the use of IUPAC standard names throughout, while also including common names in abstract (or elsewhere) for identification and indexing purposes. Likewise, pressures should be in Pa, or at least haP.

c) pg 7003, lines 17-8: the subject and verb of this sentence don't match. Do you mean: reactor . . . is used or: reactor is equipped . . . spectrometer and spectrometer are used.

d) pg 7004: heater specifications could be given.

e) pg 7009: why is "steady state" defined to occur at 5000 sec? Why is the data extrapolated with a double exponential?

f) Table 1: is Max et al. meant to be Max and Chapados?

g) Fig. 2: what does "structural OH" mean? Also, the file I have doesn't seem to have letters in the figure, only in the caption.

h) pg 7011, Fig 3: please expand the y-axis of the figure so the "almost a factor of two" increase in water uptake can be clearly seen. Also, it is difficult to discern the symbols in the figure I see. Is that a bow-tie and a triangle sitting above the rest? Can you please explain the error bars shown? I think I am supposed to see that your data (C3 and C4, 45% RH) sit significantly above (i.e., outside the error bars of) the measurements of water only. Yet, the highest RH water only point seems to sit equally far above the rest of the water only data points. Are you truly comfortable that your water uptake measurements would continue to sit above the reported "water only"

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points of extrapolated to other RHs?

i) pg 7012 / Reversibility: given the potentially significant sticking of acids to non-dust surfaces in the chamber, as alluded to in the discussion of blanks, have you been able to demonstrate 100% recovery of any "sticky" gas when flow is discontinued? Is it possible that more than 20% is released from the dust but not sampled by the MS?

j) Fig 5 and pg. 7013: again, please define the time at which you have calculated $(I_0 - I_t)/I_t$.

k) Section 3.2.4: When RH is varied and the clay begins to swell, is the surface area used in the analysis (Eq 1) adjusted?

l) pg 7017, line 26: I don't understand what you mean by "if this mechanism counters . . . other removal mechanisms"

m) pg 7014 line 25: Fig 7 looks to me as though propanoic acid does, in fact, saturate, because the coverage at the highest pressure is not larger than the point at the second-highest pressure. The pattern looks exactly the same as that for butanoic acid. What evidence leads you to state that it does not saturate?

n) pg 7017, line 10: please provide a reference for the "independent measurement".

o) Fig 8b: do you have any speculation why propanoic acid has a higher saturation coverage than the other acids?

p) pg 7017: lines 15-18 and 22 seem to be in contradiction. Can you please clarify how "mineralogy of the reactive surface strongly influences the heterogeneous uptake . . . " if "steady-state coverage of acetic acid on SWy-2 (is)... on the same order as adsorbed acetic acid observed on other minerals."

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6999, 2007.

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