Atmospheric Chemistry and Physics Discussions

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Interactive comment on "Heterogeneous uptake of the C_1 to C_4 organic acids on a swelling clay mineral" *by* C. D. Hatch et al.

C. D. Hatch et al.

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We would like to thank Referee #2 for his/her helpful comments on manuscript # acpd-2007-0187 and we feel that the manuscript has improved by making the suggested changes and additions. Below we list the point-by-point reviewer comments and our responses.

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?

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***We have added the following statement on page 7009, line 11: "Under all conditions studied, less than 20% of the organic acid lost from the gas phase is taken up by the sample wafer, mount and chamber walls." To address the uncertainty in our calculations as a result of this correction, we have added a sentence to page 7007, line 8 that states: "A correction for blank experiments introduces an uncertainty of approximately 7% into the calculation of γo, based on the reproducibility of blank measurements." Similarly, a sentence has been added to page 7009, line 13 that states "Uncertainty in the organic acid content due to blank experiments is approximately 9%, based on the reproducibility of blank measurements." We have included this error in the overall error associated with our calculations of initial uptake efficiency and indicate this by replacing the sentence on page 7014, line 10 with "Error in the initial uptake efficiency represents the average uncertainty, $\pm$36%, due to measurement reproducibility of uptake on the clay and blank wafer under similar conditions." In accordance with this statement, we have included this error in our reported initial uptake efficiencies on page 7014, line17. We have also included this error as the error bars in Fig. 8a and added a sentence to page 7015, line 14 stating "Error in the reported γo values shown in Fig. 8a are based on the combined uncertainty from the reproducibility of uptake on the clay and blank silicon wafer." As for the uncertainty in the organic acid content, we have added a sentence on page 7016, before the sentence beginning on line 17 that states "The error in the organic acid content, $\pm$32%, represents the combined uncertainty due to the reproducibility of uptake measurements on the clay and blank silicon wafer." We have also changed the error bars in Figures 6, 8a and 8b to reflect these errors. We believe that addition of the above statements clearly states the contribution to the error in our calculations due to uncertainty in the blank measurements.

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?

***To clarify the time at which gammas zero is calculated, we have replaced the original sentence on page 7006, line 16 "The initial drop in the mass spectrometer signal of the organic acid upon exposure to the sample is used to quantify heterogeneous uptake efficiency, γo." with "The initial drop in the mass spectrometer signal of the organic acid upon opening the cup reaches a minimum in the first two seconds of exposure, followed by recovery due to surface saturation. Thus, the mass spectrometer signal upon opening the Teflon cup used for the calculation of the initial heterogeneous uptake efficiency, γo, was collected at two seconds after exposure." We have also changed the statement beginning on page 7007, line 3, to read "Ěthe mass spectrometer signal of organic acid after two seconds of exposure, corrected for blank experimentsĚ" Referee #2 also suggests the possibility of error caused by the sampling technique (the location of the MS with respect to the clay surface) and the experimental limitations of the measurement (2 second resolution). Because we operate in the molecular flow regime, any pressure gradients in our system should be minimal. We have now added a statement that reads "For the experiments reported here, organic acid pressures ranged from 8×10^{-6} to 1.3×10^{-4} hPa in order to maximize signal while staying in the molecular flow regime" to page 7004, line 9. If, however, there is a pressure gradient surrounding the clay surface due to uptake prior to the initial measurement, this could result in an underestimate of the initial uptake coefficient. Unfortunately this error is difficult to quantify. To address Referee #2's comments, we have added the following statements to the revised version of the manuscript on page 7016 before the paragraph beginning on line 13: "Additional error in the initial uptake efficiencies reported here may arise from a possible pressure gradient surrounding the clay surface due to uptake prior to the initial measurement by the mass spectrometer. However, because we are in the molecular flow regime, any pressure gradients in our system should be minimal. In any case, experimental uncertainty may result in an underestimate of the true initial uptake efficiency." Additionally, it may be the case where the mass spectrom-

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eter does not respond fast enough to accurately measure the initial uptake efficiency. Thus, a few surface sites may already be occupied after 2 seconds of exposure, also leading to an underestimate of the initial uptake efficiency. From our measurements of 1x10-4 Torr acetic acid uptake on 1.5 mg SWy-2 at 29% RH, we find that there is less than one percent of a monolayer (ML) on the SWy-2 clay after two seconds of exposure, assuming 1 ML is 1x1015 molec/cm2. Thus, the effect of acetic acid surface saturation is expected to be minimal. Also, from FT-IR measurements (based on time resolution of 11 seconds) of water adsorption on SWy-2 in the presence of 1x10-4 Torr acetic acid at 29% RH, we can estimate the amount of water adsorbed to SWy-2 after 11 seconds of exposure to water and acetic acid according to the method used by Frinak et al. (2005) and Mashburn et al. (2006) using the water bend at 1640 cm-1. Assuming one monolayer (ML) is 1x1015 molec/cm2 and the BET surface area of 318.2 cm2/mg, we estimate that there is less than 8% of a ML of water after 11 seconds of exposure. Experimental error due to surface saturation will result in an underestimate of the true initial uptake efficiency. This discussion has also been added to the revised version of the manuscript after the paragraph ending on page 7016, line 12.

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 um2 cm-3 of dust, in spheres of d=2um, 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.

***Referee #2 makes an excellent point here. To address this issue, we have replaced the sentence beginning on page 7019, line 1 and the sentence beginning on line 3 with

the following discussion: "However, the initial uptake efficiency is not appropriate for use at longer exposure times due to saturation of surface sites, as demonstrated by the rapid recovery of the mass spectrometer signal in Fig. 4, within approximately one minute. Thus, the lifetime for removal of these organic acids may be much longer than predicted. To explore the effect of surface saturation on atmospheric dust particles, we can assume that there are two parts per billion by volume (ppbv) acetic acid (Talbot, 1995) in a dust storm of 150 μm2/cm3 dust (de Reus et al., 2000) at 5 km. Using our measured acetic acid content of 5 mgorg/gclay at 29% RH from Fig. 8b and assuming 2 μm diameter particles with a density of 2.2 g/cm3, we estimate that up to 40% of the gas phase acetic acid will be removed from the atmosphere. Thus, based on these values, heterogeneous uptake of organic acids on mineral aerosol may be a significant, yet limited, removal mechanism for carboxylic acids in troposphere." We believe that the addition of these statements clarifies the effect of surface saturation effects at longer exposure times in our Atmospheric Implications section.

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 increases 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 values of gamma is appropriate to use over the lifetime of a dust particle? And at what point will uptake cease due to saturation of the available surface sites?

***Yes, in the sentence beginning on page 7000, line 15, "increase" should be "increases." We have fixed this in the revised version of the manuscript. Replacing the word "uptake" on page 7000, line 18 with "initial uptake efficiency" should clear up the confusion regarding the seemingly contradictory statements. The initial uptake efficiency is measured in the initial moments of exposure to the gas phase organic acid while the organic acid content is measured after longer exposure times under

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equilibrium conditions. Thus, the organic acid content and initial uptake efficiency are measured at different times during the uptake measurement and the different trends in the two parameters are probably due to different physical properties of the organic acids and their effects on uptake. Our results suggest that organic acid uptake on SWy-2 is time dependent and surface saturation occurs on the timescale of minutes. Thus, the revised version of the abstract will include the following statement after the sentence ending on page 7000, line 19 regarding the time dependent uptake and the appropriate use of the uptake coefficient in atmospheric chemical models: "However, the initial uptake efficiency decreases significantly in a short amount of time due to surface saturation effects. Thus, although the initial uptake efficiencies are appropriate for initial times, the fact that the uptake efficiency will decrease over time as the surface saturates should be considered in atmospheric models."

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.

***The revised manuscript indicates the IUPAC names along with common names in the abstract for indexing purposes. We will also change propionic to propanoic acid and butyric to n-butanoic acid throughout the manuscript. Additionally, all partial pressures reported in Torr will be converted to hPa.

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.

***We meant to say that the "high vacuum flow reactorĚis used. This has been corrected in the revised version of the manuscript.

d) pg 7004: heater specifications could be given.

***We have added more detail regarding the heating of the clay sample by changing

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the sentence beginning on page 7004, line 17 to read: "The temperature is set by resistively heating against the liquid nitrogen using a Watlow heater controlled by an 818 Eurotherm temperature controller. Two Type T thermocouples attached to either side of the sample mount monitor the temperature of the sample."

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

***To clarify why our data are extrapolated with a double exponential fit, we have added the following statement to page 7009, line 8: "Similar to previous studies (Al-Abadleh and Grassian, 2000; Frinak et al., 2004), we have found that a double exponential fit represents the shape of the uptake curve more accurately than a single exponential fit." We arbitrarily assigned 5000 seconds as "steady-state" although our experiments were found to recover to constant MS values within the 200 seconds of exposure. To address this issue, we have changed the sentence beginning on page 7009m line 8 to read "The number of organic acid molecules adsorbed at steady-state, norg, is obtained by extrapolating the data collected during a 200 second experiment to 5000 seconds. Extrapolation to 5000 seconds resultes in less than 10% increase in the calculated organic acid content values. However, extrapolation beyond 5000 seconds does not change the calculated steady-state organic acid content. Thus, extrapolation to 5000 seconds is a sufficient to obtain realistic coverage values on the montmorillonite clay."

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

***Yes, Max et al., should be Max and Chapados. This has been corrected in the revised version of the manuscript in Table 1.

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.

***To address the ambiguity of the "structural OH stretch," we have added the sentence: "This region represents stretching of the hydroxyl groups bound directly to the

aluminosilicate structure of the montmorillonite clay" to page 7010, line 5. We have also added letters to the images in Fig. 2 as well as the figure 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" points of extrapolated to other RHs?

***We have added an inset to Fig. 3 showing the y-axis expanded so that the water uptake increase in the presence of the organic acid can be seen. We have also clarified the symbols in the text on page 7011 by changing the statement beginning on line 22 to "Similar to the nitric acid study, Fig. 3 shows that, at 45% RH, an enhancement in the adsorbed water content is observed in the presence of propanoic (triangle) and butanoic (bowtie) acids by almost a factor of two compared to water only measurements (Frinak et al., 2005)." Additionally, the direction of the bowtie is also changed in all figures so that it is easier to distinguish in Fig. 3. The error bars are explained in the text pg. 7011 lines 14 and 15. To address the probability of continued enhanced water adsorption at higher RH values, we have added the following discussion to page 7011, line 26: "The inset of Fig. 3 shows the enhanced water content at 45% RH on an expanded scale. As measurements of the water content above 45% RH were not attainable in the experimental system, we cannot be certain that this trend will continue at higher humidities. However, nitric acid adsorption showed continuously higher water contents above 30% RH compared to water only measurements. The results reported here may indicate that the same trend will occur as the RH is raised above 45% RH and we could expect more adsorbed water at higher RH values compared to water only

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measurements. However, more studies are needed at higher RH values to validate this assumption." This discussion will replace the sentence beginning on page 7011, line 26.

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?

***To address this issue, we have removed the statement on page 7012, line 12 "This result suggests irreversible adsorption of organic acids on SWy-2 clay, in agreement with the observation of the dissociated carbonyl stretch by FT-IR observed for experiments performed under humid conditions upon removal of adsorbed water" and replaced it with the following discussion: "However, as mentioned previously, up to 20% of the organic acid lost from the gas phase was due to adsorption on the sample wafer, mount and chamber walls. Thus, it is possible that some of the desorbed organic acid remains on the exposed wafer and mount and would therefore not be measured by the mass spectrometer. This would result in an overestimate of the irreversibility of organic acid uptake. However, the fact that an organic spectral signature remains on the clay even after warming to room temperature indicates that the adsorption is at least partially irreversible."

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

***The time at which It was obtained (2 seconds) has been clarified in the revised version of the manuscript on page 7013 and in Fig. 5 caption. We have changed the sentence beginning on line 9 to read "Figure 5 shows (Io-It)/It, where It is measured after two seconds of exposure and corrected for blank experiments, as a function of SWy-2 mass for each of the organic acids studied."

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?

***We have not adjusted the surface area in Eq.1 used to calculate the initial uptake efficiency as the RH is varied. To clarify this, we have changed the sentence beginning on page 7014, line 7 to "The initial uptake efficiency was determined using Eq. 1 assuming the external BET surface area of the clay is available for uptake."

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

***To clarify this statement, we have changed the first sentence in the paragraph on page 7017, line 25 to: "The heterogeneous removal of organic acids from the atmosphere by uptake onto mineral aerosol must occur on fast enough time scales compared to other removal processes in order to be important in the Earth's atmosphere (Ravishankara, 1997)." We believe that this should clarify any ambiguity in the statement.

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?

***Although further measurements at higher propanoic acid partial pressures could verify the saturation of propanoic acid, Fig. 7 does appear to show that the propanoic acid could be saturated at pressures above 8×10^{-5} Torr, although it is difficult to tell within the given errors. We have changed the two sentences starting on page 7014, lines 24 and 26 to: "Sub-monolayer coverages of formic and acetic acids are found to increase linearly with organic acid pressure, never reaching saturation within the range of pressures studied. However, butanoic and perhaps propanoic acids appear to saturate at approximately one monolayer for pressures greater than 2.7×10^{-5} hPa."

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

***The term "independent measurement" implies reference to other literature data. The revised version of our manuscript will clearly state on page 7017, line 10 that we performed "additional measurements" rather than "independent measurements" as we performed these measurements in our laboratory in an effort to understand the results reported in the current manuscript.

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

***We have added the following discussion as a paragraph following the paragraph on page 7016, line 13 regarding our speculation as to why the propanoic acid has the highest saturation coverage than the other acids. "The propanoic acid shows the largest increase in adsorbed mass with RH, increasing by a factor of five from 0.3% to almost 2% propanoic acid by mass from 0% to 45% RH. It is interesting to note that propanoic acid has the highest Henry's law constant of the four acids studied (Khan et al., 1995). This may suggest that more soluble organic acids will adsorb to the swelling clay to a greater extent than less soluble species under humid conditions. Additionally, the trend in coverage matches the trend in pKa with pKa going from 3.75 (formic), 4.76 (acetic), 4.83 (butanoic), to 4.86 (propanoic) (Lide, 2004). Thus, the swelling properties of montmorillonite clay provide an aqueous environment under humid conditions that appears to impact the adsorption of oxygenated organics." In accordance with the addition of the above paragraph to the revised version of the manuscript, we have also removed the sentence on page 7016, line 18 ("The propionic acid showsĚ") as it is now the first sentence in the above paragraph.

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?"

***Again, our wording may be a little confusing. To clarify we have modified the sen-

tences on page 7017, lines 14 to 17 to read "We conclude that the discrepancy in measured initial uptake efficiencies is a result of the different reactivity of the substrates studied. The mineralogy of the reactive surface appears to influence the initial heterogeneous uptake efficiency of organic acids on mineral aerosol in the troposphere, and thus should be considered in atmospheric models." We have also changed the sentence on page 7017, line 20 and added the following discussion: "Based on our results shown in Fig. 7b, we estimate the steady-state coverage of acetic acid on SWy-2 at 8x10-4 hPa to be near 4x1012 molec/cm2; on the same order as acetic acid coverage observed on other minerals at room temperature and dry conditions (Carlos-Cuellar et al., 2003). Thus, in contrast to the γo, the steady-state coverage of organic acids on mineral aerosol does not appear to depend on the mineralogy of the dust. However, since montmorillonite clay provides an aqueous environment under humid conditions, the organic acid coverage will increase as the RH is raised. More studies of organic acid adsorption on other metal oxides and non-swelling clays are needed to determine the role mineralogy plays in the adsorbed organic acid adsorption under humid conditions."

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