

## ***Interactive comment on “Heterogeneous uptake of the C<sub>1</sub> to C<sub>4</sub> 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 #1 for his/her helpful comments on manuscript #acpd-2007-0187 and we feel that the manuscript has greatly improved by making the suggested changes and additions. Below we list the point-by-point reviewer comments and our responses.

1. p 7001, line 16, define “long distances.”

\*\*\*To clarify what is meant by “long distances,” we have changed the text on page 7001, line 15 to read “For example, an estimated 50% of airborne mineral particles from Chinese deserts are transported thousands of kilometers over the remote North Pacific Ocean (Zhang et al., 1997). Additionally, the entrained dust has been found to reach the United States (DeBell et al., 2004) and Canada (McKendry et al., 2001).”

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2. p. 7002, line 9, a few more details of the findings from Falkovich et al. (2004) are in order, given their potential relevance to this work.

\*\*\*Referee #1 makes a good point here. The Falkovich et al. (2004) field study findings are very relevant to our work as they have shown, using multiple analytical techniques, that not only are mineral aerosol particles commonly coated with organic species, but acetic and formic acids are the most common mono-carboxylic acids associated with mineral particles in the atmosphere. Additionally, Falkovich et al. (2004) suggest that the concentration of adsorbed short-chain organic acids, such as those studied here, increases significantly at high ambient relative humidities. Thus, water-assisted heterogeneous uptake of these gases may play an important role in the atmosphere. On page 7002, line 9, we have added a sentence stating “Additional gas chromatography/mass spectrometry and ion chromatography measurements indicated that formic and acetic acids were the most common mono-carboxylic acids found in the mineral aerosol samples.” The statement “suggesting water-assisted uptake onto entrained mineral particles” has been added to the end of the sentence on page 7002, line 11. Additionally, we have added a sentence on page 7016, line 22 that states “This result is in agreement with water-assisted uptake of organic acids on mineral particles suggested by Falkovich et al. (2004).”

3. p. 7004, line 9, it would be valuable to give some estimates here and throughout the work on the errors in the relative humidity and the partial pressures of the organic acids.

\*\*\*We would like to thank Referee #1 for pointing this out. The error in RH has been obtained based on the errors in sample temperature and the partial pressure of H<sub>2</sub>O vapor. We find the error in RH to be less than 10% under humid conditions. This uncertainty has been added to the manuscript on page 7004, line 12 to read “Based on the error in the sample temperature and partial pressure of water vapor, the uncertainty in the RH is less than 10% under humid conditions.” The uncertainty in the partial pressure of the organic acids was determined to be less than 5% based on uncertainty in

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the MS signal and the calibration curves collected prior to each experiment. This error has also been added to the manuscript text on page 7004, line 9 to read “Uncertainty in the organic acid partial pressure is less than 5% for all organic acids studied based on uncertainty in the mass spectrometer signal and the calibration curve collected prior to each experiment.”

4. p. 7007, line 15, organize references chronologically.

\*\*\* The revised manuscript will reflect the correct organization of the references on page 7007, line 15 and throughout the manuscript.

5. p. 7007, line 19, are these relative humidities appropriate for 212 K or were these experiments conducted at room temperature instead? How does temperature affect this process?

\*\*\*Referee #1 makes an excellent point here. The previous experimental studies of Cases et al. (1992) and Newman (1983) were indeed conducted under room temperature conditions. Thus, the relative humidity values reported are appropriate for montmorillonite swelling at room temperature. However, the swelling regimes of montmorillonite clay occur at the reported relative humidity values at all temperatures relevant for the Earth’s troposphere and thus are applicable to the low temperature studies reported in our manuscript. A previous study in our laboratory by Frinak et al. (2005) has shown that water adsorption on montmorillonite clay (SWy-2) as a function of RH is independent of temperature. This study found that water adsorption at 222 K as a function of RH agrees very well with values obtained using experimental (Cases et al., 1992) and theoretical (Hall and Astill, 1989) methods at room temperature. We have clarified the temperature independence of clay swelling in the revised version of our manuscript by adding the statement “Although the swelling regimes of montmorillonite clay have been experimentally investigated at room temperature as a function of RH by Cases et al. (1992) and Newman (1983), previous studies in our laboratory (Frinak et al., 2005) have shown that water adsorption on montmorillonite clay is independent

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of temperature and thus these regimes also apply at upper tropospheric temperatures” to the manuscript text on page 7007, line 20, after the sentence beginning with “Water begins adsorbing”

6. p. 7008, line 5, the authors should state how they “independently” assessed the surface area of the clay.

\*\*\*We agree that we were not very clear as to how we independently confirmed the BET surface area of SWy-2 reported by the Clay Mineral Society. We have added the following statements to the manuscript text on page 7008, line 5: “and independently confirmed by the authors by BET analysis using a volumetric expansion technique with nitrogen as the adsorbate. The calculated BET surface area was within the uncertainty reported by the Clay Mineral Society.”

7. p. 7008, paragraph starting at line 8. If I understand the procedure correctly, the experiments were conducted entirely on samples that been initially dried by pumping for extended periods. They were then exposed to the organic acid under either dry or enhanced relative humidity conditions. I am comfortable with the dry measurements but for those under enhanced RH, how are they to be interpreted given that some degree of water uptake will be occurring during the extent of the experiment? The clay has not fully swelled or reached equilibrium with the relative humidity, but neither is it entirely dry. How can the authors be confident that the initial uptake coefficient measurements are not affected by swelling to some degree (p 7008, line 17)? Would it not have been preferable to have conditioned the clay samples to the appropriate relative humidity prior to exposure to the organic acid, and then expose them to the organic acid once equilibrium with water had been reached? Could a few experiments of this nature be reported for the ACP version of the paper?

\*\*\*Initially, we had attempted to perform experiments in which we first added water vapor and allowed the SWy-2 clay to swell prior to introducing the organic acid; therefore, measuring the heterogeneous uptake on the already swollen clay. Unfortunately,

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at the temperatures and water pressures used in our measurements, the clay did not reach equilibrium with the water vapor even after six hours of exposure! This is consistent with the findings of Frinak et al. (2005) who showed that the  $1/e$  loading times of water adsorption on SWy-2 get to be very long at very low temperatures and water partial pressures, as discussed on page 7008, lines 10-16. Because the clay is not fully swollen within six hours of exposure to water vapor, we do not know the surface area of the clay under these conditions. Even if the surfaces had fully equilibrated first with the water vapor, it would still not be clear what surface area to use because the gases may require multiple collisions with the clay surface to penetrate the pores. Thus, the full (swollen) surface area is useful to determine the total coverage at equilibrium, but it is less useful for determination of gamma. From our preliminary experiments, we concluded that the surface area is most accurately known under “dry” conditions upon initial simultaneous exposure to the organic acid and water vapor. Although we cannot obtain an accurate gamma because we do not know the surface area, FT-IR measurements do indicate that formic and acetic acid were indeed taken up by the previously swollen wet clays. Indeed, we find from our preliminary measurements that after heating and evaporation of water, the infrared absorption band of the remaining carboxylate peak is similar in strength whether water and the organic acid are adsorbed simultaneously or sequentially. This is now indicated on page 7010, line 28 by adding the following statement to the text: “We also find that after heating and evaporation of water, the infrared absorption band of the remaining carboxylate peak is similar in strength whether water and the organic acid are adsorbed simultaneously or sequentially.” Because we do not know the surface area and it is experimentally difficult to maintain stable conditions for the 8-10 hours necessary for sequential experiments we did not pursue these measurements further. To address the comments of the Referee #1, we have added the following statement on page 7005 at the end of the paragraph ending on line 25 that reads “Our measurements were limited to studying the uptake of the organic acids on SWy-2 upon simultaneously exposing the samples to the gas phase water and organic acid because the surface area of the clay under swollen conditions

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is unclear and the time for the clay to reach equilibrium with the water vapor exceeds six hours. Although we cannot obtain an accurate initial uptake efficiency from experiments in which the clay is sequentially exposed first to gas phase water and then to the organic acid vapor because we do not know the clay surface area under the swollen conditions, as discussed below, FT-IR measurements do indicate that formic and acetic acid were taken up by the previously swollen wet clay. Referee #1 also refers to the fact that some degree of water uptake will be occurring during the extent of the experiment. Since swelling (water adsorption) is very slow under the conditions studied, the measurement of the initial uptake efficiency from simultaneous exposure of water and acetic acid has minimal impacts from saturation effects. From our FT-IR measurements, based on time resolution of 11 seconds, of water adsorption on SWy-2 in the presence of  $1 \times 10^{-4}$  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  $1640 \text{ cm}^{-1}$ . Assuming one monolayer (ML) is  $1 \times 10^{15} \text{ molec/cm}^2$  and the BET surface area is  $318.2 \text{ cm}^2/\text{mg}$ , we estimate that there is less than 8% of a ML of water after 11 seconds of exposure. Additionally, as discussed in our responses to Referee #2, we estimate that less than 1% of a ML of acetic acid is present after 2 seconds of exposure from our mass spectrometer measurements under the same conditions. Thus, although more than 91% of the surface sites are still available for uptake and surface saturation effects will be minimal, the occupation of surface sites at the time of the initial uptake efficiency measurement will result in slightly low initial uptake efficiencies. A sentence stating “As discussed in further detail later, surface saturation and swelling effects have a minimal impact on the  $\rho_0$  measurement” has been added to page 7008, line 19. We have also included this discussion in the revised version of the manuscript by adding a paragraph on page 7016, after the paragraph beginning on line 4, that clearly states that the reported initial uptake efficiencies may be slightly low due to surface saturation and swelling effects that may be occurring within the first two seconds of exposure to the SWy-2 sample.

8. p. 7008, line 26, state how much correction is made for loss of the acid to the “sample mount.”

\*\*\*We find that less than 20% of the organic acid lost from the gas phase is taken up by the sample wafer, mount and chamber walls from an average of blank experiments under all conditions studied. This statement was added to the revised version of the manuscript on page 7009, line 11.

9. p. 7010, line 27 and following. It is claimed that the small peaks in the IR that remain after the sample has warmed to room temperature are due to carboxylate species on the surface of the true. This is probably true and they indicate uptake of organic acids, but these measurements have been made after the sample has been warmed to room temperature and all the surface water has pumped away. How confident are the authors that these interactions were indeed occurring under the low temperature, enhanced relative humidity conditions of the experiment? Also, it is stated (line 3, p 7011) that these measurements are only made when the clay is swollen. But, it is stated earlier (p. 7010, line 10) that the uptake of water is fully reversible. If it is fully reversible, how can the clay be swollen at room temperature, after all the water has been pumped away? What is the picture we are supposed to leave the paper with? A few carboxylates trapped in between the non-swollen (or swollen?) layers of the clay?

\*\*\*We may not have been clear in our original manuscript regarding the adsorbed carbonyl species on the clay surfaces. Our FT-IR measurements suggest carboxylate species on the surface of the clay after removing all water and organic acid vapor from the chamber and warming the sample to room temperature to drive off adsorbed water. There is no evidence for either the carboxylate, dissociated, or the carboxylic acid, not dissociated, in the presence of water vapor due to possible masking of the carboxylic acid peak by the water bend. Thus, it is unclear as to whether the organic acid dissociates in the presence of adsorbed water or once the adsorbed water is removed. We had initially attributed formation of the carboxylate to a possible interaction with the interlayer cation. However, in this regard, it is difficult to determine whether the interlayer

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cations play a significant role in uptake. Regardless of the mechanism of organic acid dissociation, with or without adsorbed water, this result indicates irreversible uptake of the organic acid and a change in the clay composition upon atmospheric processing with the organic acids. We have now replaced the statements on pages 7010 line 28 through page 7011, line 7 with the following argument reflecting our statements above: “However, it is unclear as to whether dissociation occurs under humid conditions when adsorbed water is present and the clay is swollen, or if the carboxylic acid dissociates upon removal of adsorbed water when warming the sample to room temperature. Regardless of the mechanism for dissociation, results from infrared analysis suggest irreversible uptake of organic acids on SWy-2 resulting in a change in the chemical composition of the clay. Thus, atmospheric processing through heterogeneous uptake of short-chain mono-carboxylic acids and transport through varying humidity conditions can result in modified chemical composition of the particles which may impact the optical properties and further reactivity toward other trace gases in the atmosphere.” Referee #1 also points out some confusion in our manuscript on page 7010 and 7011. Indeed the SWy-2 clay has fully reversible water adsorption, as reported previously by Frinak et al. (2005). The statement on page 7011, line 3 refers to the fact that the peak at 1615  $\text{cm}^{-1}$  is only observed for the experiments performed under humid conditions (not dry measurements) and only after warming to room temperature to drive off adsorbed water. The confusion lies in the wording of the statement, because we did not clarify the fact that it is observed “only after warming to room temperature to drive off adsorbed water.” In order to clarify these results, the statements made on page 7011, line 3 has been replaced with the discussion in the previous paragraph.

10. p. 7011, line 22. I question the conclusion that there is “significant enhancement” in the water content observed in the presence of the organic acids. In Figure 3, I only see one point that lies above the “water only” points, and not very far above. Also, in that Figure the “water only” points are for 222 K. How much of a difference does the 10 degree difference make, given that the experiments with the acid were at 212K? It should also be pointed out that the partial pressures of the acids in these experiments



were much above those that prevail in the atmosphere. Isn't it more accurate to state that the acids will not affect the clay water content in the atmosphere under these conditions?

\*\*\*There are actually two points (propanoic acid, triangle and butanoic acid, bowtie) that are approximately a factor of two above the water only measurements in Fig. 3. In response to referee #2's comment h and the above comment, the revised version of the manuscript includes an inset in Fig. 3 expanding the y-axis so that the water uptake in the presence of the organic acid and the symbols can be clearly seen. We feel that a factor of two could be a "significant" increase in the water content above the water only measurements. However, we have no problem with removing the word "significant" from this statement and have done so in the revised version of the manuscript on page 7011, line 22. With regards to the temperature dependence of water adsorption (i.e., water only measurements at 222 K and water adsorption in the presence of organic acids at 212 K), previous measurements of water adsorption on SWy-2 in the absence of organic acid vapor at 222 K (Frinak et al., 2005) show that water adsorption on SWy-2 is independent of temperature up to 298 K. Thus, the 10 K difference in experimental temperatures between the measurements we are comparing should have no effect on the adsorbed water content reported in Fig. 3. This is now more clearly stated in the text of the revised manuscript on page 7011, after the sentence ending on line 17. Additionally, we have replaced the sentence beginning on page 7011, line 26 with a statement that reads "Additionally, the organic acid partial pressures used in our experiments are much larger than those that prevail in the atmosphere; therefore, organic acids may have less of an impact on water adsorption in the Earth's atmosphere."

11. p 7012, line 21. It is stated that only for the low mass samples do the gas signals recover fully after exposure to the clay. This cannot be discerned from the data in Figure 4. Can the data in the figure for the 1.6 mg sample be blown up to demonstrate this conclusion? For example, is it within the S/N of the experiment to conclusively say that this is so? Could the signals appear to recover in the lowest mass case only

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because there is little mass to drive uptake? I am puzzled why only the low mass samples would display this long time uptake behavior. Instead, I suspect that all the samples exhibit the long-term uptake observed in the higher mass samples, and that this uptake arises from the continual uptake of water by the initially dry clay material. If so, there is information content in the degree to which the signal does not saturate.

\*\*\*We have added an inset to Figure 4 showing the region of uptake for the 1.6 mg sample on an expanded scale. As stated in the original version of our manuscript, the mass spectrometer uptake curve for the 1.6 mg sample still appears to recover to within error of the baseline mass spectrometer values. We have replaced the statements that begin on page 7012, line 20 and end on page 7013, line 5 and added the following sentences to the revised version of the manuscript. “The inset of Fig. 4 shows an expanded view of the propanoic acid uptake curve on a 1.6 mg SWy-2 sample. Similar traces are observed for the other organic acids studied. These uptake curves show that the uptake of organic acids on small SWy-2 samples appears to reach saturation within the 200 second time scale of exposure, indicated by complete recovery, within error, of the mass spectrometer signal to baseline values. The incomplete recovery of the mass spectrometer for the larger sample masses prior to closing the cup may indicate diffusion into and adsorption on the underlying clay layers at longer exposure times. Since larger sample masses show incomplete recovery of the mass spectrometer signals, longer exposure times are required to accurately determine the organic acid coverage at steady-state. Thus, the organic acid content is more accurately known for the small sample masses used in the RH and pressure studies, discussed below.” Additionally, in accordance with our response to comment #7, even if continued uptake is due to water-assisted uptake from continual water adsorption, we would not be able to obtain meaningful gammas from the uptake at longer exposure times because the surface area is not known.

12. p. 7017, line 10. What is meant by “independent”? \*\*\*The revised version of our manuscript now states on page 7017, line 10 that we performed “additional measure-

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ments” rather than “independent measurements” since we performed these measurements in our laboratory in an effort to understand the results reported in the current manuscript.

13. Discussion and Atmospheric Implications. I recommend that it be pointed out that the clay samples were not equilibrated with the reported ambient relative humidity. Also, I think there is evidence that the water uptake is not affected by (high partial pressures of) the organic acids. Finally, I think the potential impacts will not be so much on the ability of these dust particles to act as CCN but, perhaps, as ice nuclei instead. Dusts are very good ice nuclei but they are in relatively low number abundance, and so will probably not affect CCN number all that much (except perhaps the number of giant CCN). Knowing their surface composition under atmospheric conditions is important.

\*\*\*We have added a statement on page 7018, line 1 reading “Although our reported initial uptake efficiencies were measured under conditions where the clay samples were not equilibrated with the reported RH, we use the initial uptake efficiencies for  $\tilde{E}$ ” Additionally, we have removed the statement in the atmospheric implications section referring to the enhancement of water content in the presence of organic acids on page 7019, line 5 beginning with “Additionally, we find that the presence of the organic acid  $\tilde{E}$ ” and ending on line 9. Instead, we include the following statements: “Additionally, our results indicate that atmospheric processing of swelling clay minerals with water vapor and organic acids results in modification of the chemical composition of the gas phase and the entrained clay particle during transport through the atmosphere, which may lead to modified cloud properties such as ability of these particles to become giant CCN or ice nuclei in addition to a possible modification of the optical properties of these minerals in the atmosphere.” The abstract has also been modified by replacing the sentence beginning on page 7000, line 20 with “Our results indicate that heterogeneous uptake of organic acids on swelling clay minerals provides an important irreversible heterogeneous sink for these species.”

References

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