

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 #1

Received and published: 24 June 2007

Hatch et al. present new measurements on the uptake of small carboxylic acid gases by montmorillonite, a clay material found in the atmosphere as a component of desert dusts. Experiments have been conducted using both mass spectrometry, to monitor the uptake of the trace gases, and infrared spectroscopy to study changes in the clay samples upon gas uptake. Tolbert and co-workers have a long-standing reputation for performing measurements of this type in a reliable manner, and so the data are expected to be solid. In addition, they have done prior work with montmorillonite which proves to be a difficult substrate to study because it swells under enhanced relative humidity. The potential importance of the chemistry is that uptake of this type may affect the nature of the dust aerosols that exist in the atmosphere and also represent a sink for the small acids themselves. The key findings from this work are the kinetics

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

of the uptake of the small acids, and that they appear to strongly bind in an irreversible manner, at least over the timescale of the expt. However, I also have some questions concerning the interpretation of the data and one suggestion for more experiments.

Comments:

1. p 7001, line 16, define “long distances”
2. p. 7002, line 9, a few more details of the findings from Falkovich et al. are in order, given their potential relevance to this work.
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
4. p. 7007, line 15, organize references chronologically
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?
6. p. 7008, line 5, the authors should state how they “independently” assessed the surface area of the clay
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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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?

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

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?

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?

11. p 7012, line 21. It is stated that only for the low mass samples do the gas signals

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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 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.

12. p. 7017, line 10. What is meant by “independent”?

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 numbers all that much (except perhaps the number of giant CCN). Knowing their surface composition under atmospheric conditions is important.

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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)