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Heterogeneous uptake of the C₁ to C₄ organic acids on a swelling clay mineral

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Abstract. Mineral aerosol is of interest due to its physiochemical impacts on the Earth's atmosphere. However, adsorbed organics could influence the chemical and physical properties of atmospheric mineral particles and alter their impact on the biosphere and climate. In this work, the heterogeneous uptake of a series of small organic acids on the swelling clay, Na-montmorillonite, was studied at 212 K as a function of relative humidity (RH), organic acid pressure and clay mass. A high vacuum chamber equipped with a quadrupole mass spectrometer and a transmission Fourier transform infrared spectrometer was used to detect the gas and condensed phases, respectively. Our results show that while the initial uptake efficiency was found to be independent of organic acid pressure, it increased linearly with increasing clay mass. Thus, the small masses studied allow access to the entire surface area of the clay sample with minimal effects due to surface saturation. Additionally, results from this study show that the initial uptake efficiency for butanoic (butyric) acid on the clay increases by an order of magnitude as the RH is raised from 0% to 45% RH at 212 K while the initial uptake efficiency of formic, acetic and propanoic (propionic) acids increases only slightly at higher humidities. 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. Surface saturation results in sub-monolayer coverage of organic acid on montmorillonite under dry conditions and relevant organic acid pressures that increases with increasing humidity for all organic acids studied. Additionally, the presence of large organic acids may slightly enhance the water content of the clay above 45% RH. Our results indicate that heterogeneous uptake of organic acids on swelling clay minerals provides an important irreversible heterogeneous sink for these species.

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