Nonequilibrium Conditions for Ammonium Adsorption-desorption During Flow in Soils

In a recent study, Ardakani and McLaren (1977) investigated the kinetics of ammonium adsorption-desorption using batch and column experiments. Their data pointed out that instantaneous equilibrium was not achieved between solution and adsorbed ammonium phases. Thus, the assumption of instantaneous equilibrium required by several simulation models for ammonium transport and transformations was questioned by these authors.

The data presented by Ardakani and McLaren (1977) are of interest, but leave several questions concerning their data unresolved. For example, in deriving Eq. [1] from first-order reversible kinetics, a linear equilibrium adsorption isotherm was implicitly assumed. Therefore, excellent agreement between the measured data from batch adsorption experiment (Expt. A; Fig. 1) is not consistent with the nonlinear adsorption isotherm data obtained from the column study (Expt. B; Fig. 3). This apparent contradiction in the data from their two experiments was not discussed by the authors. Experimental data of Preul and Schroepfer (1965) and Misra et al. (1974) indicate that for low ammonium concentrations (0 - 100 μg/ml), equilibrium adsorption isotherms are linear. The nonlinear isotherm data in Fig. 3 illustrates an unusual case in that the ability of the soil to adsorb ammonium increased with an increase in ammonium solution concentration.

On the basis of their data (Fig. 1 and 3), Ardakani and McLaren (1977) concluded that “in the absence of local equilibrium, solution and adsorbed NH₄⁺ are not related by an adsorption isotherm.” The implication appears to be that adsorbed and solution ammonium concentrations were not related in an ordered manner prior to equilibrium; however, the contrary is true. For a linear equilibrium adsorption isotherm, a linear relationship exists at all times prior to achieving equilibrium between the adsorbed and solution concentration (see Fig. 3 of Selim et al., 1976). Furthermore, using Eq. [1] and [2] of Ardakani and McLaren (1977), it can be shown that the adsorption partition coefficient, (NH₄⁺)a/NH₄⁺, increases with time until an equilibrium value of 0.485 ml/g is attained.

Ardakani and McLaren (1977) suggest that “equilibrium was not achieved between NH₄⁺ in a moving solution and exchangeable NH₄⁺ after flow in a soil column for 26 days.” These authors suggest that local equilibrium was achieved only after downward solution flow was stopped for 1 hour. We have simulated their Expt. B (data in Fig. 2) using Eq. [3] to describe transport and transformations was questioned by these authors. The question raised by Rao and Davidson would be resolved if we accept both Expt. A and B as equally valid. The apparent contradiction in the data from their two experiments was not discussed by the authors. Experimental data of Preul and Schroepfer (1965) and Misra et al. (1974) indicate that for low ammonium concentrations (0 - 100 μg/ml), equilibrium adsorption isotherms are linear. The nonlinear isotherm data in Fig. 3 illustrates an unusual case in that the ability of the soil to adsorb ammonium increased with an increase in ammonium solution concentration.

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monotonically decrease with soil depth for cases when adsorption equilibrium was not attained. These simulations of the nonsystematic variations in NH₄⁺ solution concentrations, as measured by Ardakani and McLaren (1977), can be attributed to the absence of local equilibrium for NH₄⁺ during flow; apparently, other factors or processes were responsible for the observed data.

Ardakani and McLaren (1977) stated that the solution concentrations in the moving solution measured in the experiment varied nonsystematically within the column.” Since these data were not included, we were unable to compare the simulated and observed solution concentration profiles at times less than 10 days. Examination of these data and additional experimental results might provide answers to the unresolved questions pointed out here.

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Nonequilibrium Conditions During Ammonium Transport in Soils: A Reply to Criticism

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