Nonequilibrium Conditions for Ammonium Adsorption-desorption During Flow in Soils

In a recent study, Ardakan 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 Ardakan 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), Ardakan 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 Ardakan and McLaren (1977), it can be shown that the adsorption partition coefficient, (NH₄⁺/NH₄⁺)ₐ/NH₄⁺, increases with time until an equilibrium value of 0.485 ml/g is attained.

Ardakan 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 convective-dispersive ammonium transport. Based upon excellent agreement between measured data and Eq. [1], first-order reversible kinetics were assumed for ammonium adsorption-desorption. The sink/source term, Σφ, in Eq. [3] was neglected. The values of the forward and backward rate coefficient, obtained from Fig. 1, were 4.94 and 1.94 hours⁻¹, respectively. The equilibrium adsorption coefficient was 0.485 ml/g. Other experimental parameters necessary to numerically solve Eq. [1] and [3] are given by Ardakan and McLaren (1977).

Simulated ammonium solution concentrations at all depths in the soil column after 26 days of continuous NH₄⁺ application were equal to the input NH₄⁺ concentration (75 µg/ml). These simulated results suggest that the measured kinetic rate coefficients were apparently large enough for equilibrium to be achieved between solution and adsorbed ammonium during flow. Additional simulations using larger flow velocities and smaller rate coefficients illustrated that the solution concentrations would monotonically decrease with soil depth for cases when adsorption equilibrium was not attained. These simulations also suggest that the nonsystematic variations in NH₄⁺ solution concentrations measured by Ardakan and McLaren (1977) cannot be attributed to the absence of local equilibrium for NH₄⁺ adsorption during flow; apparently, other factors or processes may have been responsible for the observed data.

Ardakan and McLaren (1977) stated that "ammonium concentrations in the moving solution measured periodically during the experiment varied nonsystematically with depth in the soil column." Since these data were not included in their paper, we were unable to compare the simulated and experimental NH₄⁺ solution concentration profiles at times less than 26 days. A closer examination of these data and additional experiments may yield answers to the unresolved questions pointed out here.

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Literature Cited

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

The questions raised by Rao and Davidson would be resolved if we accept both Expt A and B as equally valid instead of basing our argument on Expt. A alone. The apparent inconsistency between Expt. A and B regarding NH₄⁺ adsorption isotherm is due to the difference between the two experiments in the extent of NH₄⁺ adsorption.

In Expt. A a small initial section of the isotherm corresponding to exchangeable NH₄⁺ values of from 0 to 2.3% of C.E.C. was examined while in Expt. B a larger section of the isotherm was investigated by filling up to 51% of exchange sites with NH₄⁺. Thus, it can be seen from Fig. 3 that even though the adsorption isotherm is nonlinear as a whole, it is initially linear and as such confirms Expt. A within its limits.

The increase in the rate of NH₄⁺ adsorption at higher NH₄⁺ concentrations considered to be unusual by Rao and Davidson can be explained in two ways. For simplicity, we can attribute this rate increase to a dispersion of soil particles resulting from a replacement of Ca⁺⁺ by NH₄⁺ on the exchange sites. More specifically, we can apply Jenny's formulation of the kinetic theory of ion exchange to explain the observed nonlinearity on a