



Soil and Water Science

Research Brief

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Multiprocess Transport of Hydrazinium Cations During Water Flow in Soil

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The basic, difunctional, polar hydrazine molecule (N_2H_4) is a powerful reducing agent used widely in the synthesis of various pesticides, as rocket fuel (Fig. A), as an antioxidant, and as an oxygen scavenger. Hydrazine is a toxic environmental carcinogen suspected of being a human carcinogen. Extensive commercial usage of this toxic compound combined with high solubility in water implicate hydrazine as a potential surface and ground water contaminant.



Fig. A. Photo of Titan rocket

For acid aqueous conditions, hydrazine exists primarily as nonmetallic, inorganic

N_2H_5^+ cations (99.99% at pH 4). Acidic N_2H_5^+ solutions tend to be stable, in contrast to alkaline conditions where N_2H_4 undergoes abiotic autooxidation. During transport in soil, sorption of N_2H_5^+ cations is strongly influenced by humic substances and to a lesser extent by clay minerals. N_2H_5^+ cations are known to undergo four multiple retention processes: (1) reversible ion exchange, (2) partially reversible complexation of N_2H_5^+ ions with cations on exchange sites associated with reactive soil constituents, (3) irreversible condensation (i. e., chemisorption) of N_2H_5^+ ions with carbonyl groups of humic components, and (4) microbiological degradation of N_2H_5^+ ions by soil microorganisms. Cation exchange is well known to be a major retention mechanism for N_2H_5^+ on humic acids under acid conditions.

Acidic aqueous 0.01 N CaCl_2 solutions with specified N_2H_5^+ concentrations using $\text{N}_2\text{H}_5\text{Cl}$ were miscibly displaced through columns of Ca-saturated sandy soil during steady saturated flow conditions. Low, medium, and high N_2H_5^+ concentrations were used in influent. Soil columns were packed with samples of Ap, E1, and E2 horizons from Arredondo fine sand. Organic C content in the Ap horizon was 13.14 times that in the E2 horizon and 2.43 times that in the E1 horizon.

Observed breakthrough curves (BTCs) for concentrations of N_2H_5^+ , Ca^{2+} , and H^+ ions in effluent from Ca-saturated soil columns during displacement of acidic solutions of

N_2H_5^+ and Ca^{2+} ions were characterized with 4 features: (i) competitive ion exchange heavily influences solute retention; (ii) mass loss of applied N_2H_5^+ also implies an additional irreversible retention such as chemisorption; (iii) asymmetry of Ca^{2+} BTCs suggests that chemisorption for a fraction of exchangeable N_2H_5^+ results in a decrease in the effective soil CEC.; and (iv) exchange of H^+ ions is of minor importance due to relatively low concentrations in solution.

A multiprocess, multi-component numerical model was developed to describe the major features of fate/transport of N_2H_5^+ and competing Ca^{2+} and H^+ cations applied in acidic solutions to columns of $\text{Ca}^{2+}/\text{H}^+$ -saturated sandy soil during steady saturated flow conditions. Instantaneous ternary H^+ - Ca^{2+} - N_2H_5^+ cation exchange (Gaines-Thomas approach) was assumed the primary retention mechanism. It was combined with a secondary chemisorption mechanism for a fraction of exchange-phase N_2H_5^+ ions. Chemisorption was assumed to provide irreversible and kinetic behavior. Exchange sites were assumed to be carboxyl groups associated with organic matter. Exchange-mediated chemisorption of N_2H_5^+ was assumed to occur via chemical binding of N_2H_5^+ ions located on carboxyl-group exchange sites to nearby carbonyl groups. Consequently chemisorption was perceived to decrease the effective CEC of the soil. The cation exchange submodel utilizes effective soil CEC which decreases from the constant soil CEC as chemisorption proceeds. Biodegradation of N_2H_5^+ was omitted from the model since column experiments occurred for only a few days.

The multiprocess transport model provided valid approximation for N_2H_5^+ fate and transport during miscible displacement. Observed (discrete points) and simulated N_2H_5^+ and Ca^{2+} BTCs are shown (Fig. B) for effluent from Arredondo Ap soil column injected with a pulse of high hydrazinium

concentration ($22.15 \text{ mol}_c \text{ m}^{-3}$). A comparison of simulated BTCs with and without chemisorption of exchange-phase N_2H_5^+ reveals the quasi-catalytic behavior of N_2H_5^+ chemisorption. Simulations for both N_2H_5^+ and Ca^{2+} with chemisorption was clearly an improvement. Unrecovered N_2H_5^+ in the observed BTC was attributed to the chemisorption mechanism. The unrecovered N_2H_5^+ from the column effluent was also observed to be unrecoverable from the soil.

The multiprocess transport model successfully described the transport of Ca^{2+} and N_2H_5^+ cations, but further work is needed to verify the exchange-mediated chemisorption mechanism in other soils.

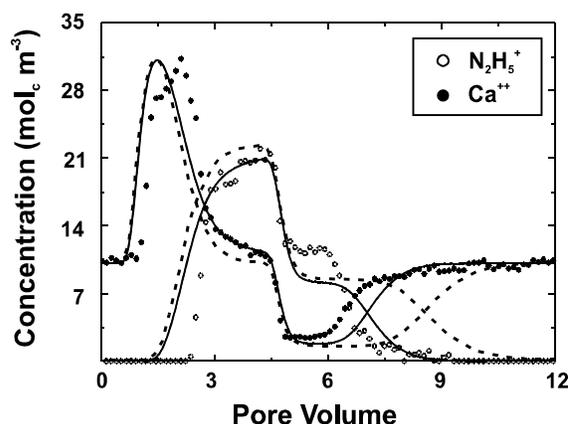


Fig. B. Observed (points), simulated with (lines) and without (broken lines) chemisorption BTCs for Ca and hydrazinium (Mansell et. al. 2001)

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