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Kinetics of calcium carbonate precipitation in soil

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We are interested in secondary calcium carbonate precipitation in soil as a result of increases in pH caused by, for example, release of base from plant roots or root-associated organisms, or from reactions of fertilizers or other materials added to the soil. To generate information of generic use, we measured $CaCO_3$ precipitation caused by base formed in urea hydrolysis (a) in a solution system equilibrated with CO_2 to which NH_3 was added at a constant rate, and (b) in soils incubated with urea. The effects of inhibition by urea, Mg, P and DOC and of seeding with $CaCO_3$ crystals were assessed. In the soil systems, the time courses of pH and the concentrations of Ca^{2+}, NH_4^+, P and DOC in the soil solution and soil solid following urea addition were measured, and the rates of $CaCO_3$ precipitation were inferred from the first differential of a logistic equation fitted to the time courses of precipitation. The following rate laws described precipitation in the solution systems

$$R = kw^n \mathrm{e}^{-a[P]}\ \mathrm{e}^{-b[C]}(\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-})/K_{SP},$$

and in the soils

$$R = \alpha\ kw^n \mathrm{e}^{-c[P]}\ \mathrm{e}^{-d[C]}\mathrm{e}^{-e[P][C]}(\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-})/K_{SP},$$

where R = rate of precipitation, k = rate constant, w = mass of newly-formed $CaCO_3$ per unit solution volume, [P], [C] = concentrations of P and DOC in solution, K_{SP} = solubility product of calcite, α = soil-specific factor and n, a, b, c, d and$e$= coefficients. The concentrations of P and DOC required to halve the rate of precipitation were an order of magnitude larger in the soils than in the solution system, and the inhibition coefficients were correspondingly smaller. However in all the soils studied,

large increases in dissolved P and DOC occurred as a result of the increase in pH with urea hydrolysis and decrease in Ca^{2+} with $CaCO_3$ precipitation. We incorporated the results in a model of $CaCO_3$ precipitation induced by base released from plant roots or root-associated fungal hyphae, allowing for the transport of base away from the root or hyphae and transport of Ca^{2+} and other reactants in the opposite direction. We made a sensitivity analysis of the model for realistic combinations of plant and soil parameters.