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Inhibition of carbon transfer across the vadose zone by 20th century acid rain

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Carbon sequestration to pedogenic carbonates, forming in unsaturated zones or in aquifers further down the flow path, relies on the downward flux of carbon with infiltrating groundwater. During 2012, we measured seasonal dynamics of water movement, soil gas CO_2, and pore water chemistry in four multi-level profiles through a 4-6 m thick sandy unsaturated zone of an agricultural barley field 10 km south of Ikast, Denmark. The residence time of water in the unsaturated zone was close to one year. Soil gas CO_2 concentrations were 1-3vol% during winter, increasing to 4-7vol% during summer. Post-harvest soil gas CO_2 concentrations remained elevated into fall, indicating CO_2 production by root decay. CO_2 production occurred primarily in the upper 0.3-0.5 m, reflecting a root zone constrained mostly to the (moist) plow layer and not extending into the (much dryer) sand underneath. Nevertheless, CO_2 produced in the root zone was evenly distributed over the underlying unsaturated zone by gas diffusion. Dissolved inorganic carbon (DIC) concentrations in pore water collected below the root zone to $\sim$2 m depth, were up to 3.0 mM in March, increasing to 3.6 mM in September. In the same depth range pore water pH-values were between 6 and 6.5. Below $\sim$2 m depth, however, a pH front was encountered, at which the pH dropped to $<$5, along with a decrease in DIC to 2.0 mM (March) and 2.7 mM (September). The decrease in DIC was caused by the protonation of bicarbonate to carbonic acid, followed by the degassing of its contained carbon as CO_2 to the soil gas. Near-equilibrium for amorphous and crystalline gibbsite was observed above and below the pH front, respectively. At all depths, a jurbanite-like $AlSO_4OH$-phase appears to be present, as based on equilibrium calculations, and on the observation that dissolved SO_4 concentrations showed a remarkable linear and season-independent increase with depth, from 0.05 mM near the pH front, to 0.8 mM near the groundwater table. A PHREEQC transport model, applying equilibrium with the above three mineral phases and the observed soil gas CO_2 pressure, reproduced the overall observed development of pH, DIC and SO_4 over depth. An implication of these results, in addition to the immediately reduced DIC leaching to the groundwater, is that less residual DIC will be available for potential carbonate precipitation further downstream. The acidified zone observed below $\sim$2 m is believed to be a relict of the zone acidified in preceding decades by acid rain, which could also have caused the deposition of SO_4. Previous research in the same area suggests that acid rain during the 20th century must have caused widespread acidification of carbonate free unsaturated zones in industrialized regions of the world. Ongoing work includes leaching of sediment samples to further elucidate the role of the jubanite-like phase, and the setup of a Hydrus HP1-model to couple processes of transient water movement, chemistry and gas diffusion.