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Microbial assimilation of dissolved organic matter in shallow aquitards constrained using organic speciation and stable carbon isotopes

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Low-permeability aquifer sediments (aquitards) are globally widespread and exert important controls on groundwater quality by decreasing flow rates and limiting gas exchange. Dissolved organic matter (DOM) in aquitards is likely to be a prime substrate for anaerobic microbial metabolism, with potential to facilitate the reduction of important groundwater contaminants, such as nitrate (NO_3-). However, it is difficult to estimate microbial assimilation based solely on DOM stable isotope composition (d13C) because interactions with the aquifer matrix (e.g. DOM adsorption/desorption) also alter d13C values. We constrained the extent of microbial fractionation of DOM by modelling the proportion of DOM fractionation due to changes in (13C enriched) hydrophilic DOM (HiDOM) and (13C depleted) hydrophobic DOM (HoDOM) in two shallow aquitard systems (0 to ∼40 m depth) with contrasting vadose zone (VZ) thicknesses, overlying deep gravel aquifers (∼40 to ∼150 m depth). Results indicate that adsorption of HoDOM was most important in the aquitard with a 20m VZ, but minimally important in the system with 1-2m VZ. Microbial fractionation of DOM in deep, anaerobic groundwater coincided with decreases in terminal electron acceptor concentrations at the same depth. The availability of reactive DOM, influenced by unsaturated zone thickness and flow rates, is therefore likely to be an important control on aquitard redox chemistry.