



Using the molecular composition of dissolved organic matter in groundwater to assess the functional stability of subsurface ecosystems

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With surface systems changing rapidly on a global scale, it is important to understand how this will affect groundwater resources and ecosystems in the subsurface. The molecular composition of dissolved organic matter (DOM) integrates essential information on metabolic functioning and could therefore reveal changes of groundwater ecosystems in high detail. Here, we evaluate a 6-year time series of ultrahigh-resolution DOM composition analysis of groundwater from a hillslope well transect within the Hainich Critical Zone Exploratory, Germany. We predict ecosystem functionality by assigning molecular sum formulas to metabolic pathways via the KEGG database. Our data support hydrogeological characterizations of a compartmentalized fractured multi-storey aquifer system and reveal distinct metabolic functions that largely depend on the compartment's relative surface-connectivity or isolation. We show that seasonal fluctuation of groundwater levels, coinciding with cross-stratal exchange can substantially impact the local inventory of functional metabolites in DOM. Furthermore, we find that extreme conditions of groundwater recharge following pronounced groundwater lowstand cause strong alterations of the functional metabolome in DOM even in aquifer compartments, which usually show minimal variation in DOM composition. Our findings suggest that bedrock groundwater ecosystems might be functionally vulnerable to hydrogeological extremes.