



Large-scale study on groundwater dissolved organic matter reveals strong heterogeneity and a complex microbial footprint

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Dissolved organic matter (DOM) in fresh groundwater is generally low in concentration compared to other fresh waters. However, the overall amount of groundwater DOM is huge, as there is 100 times more fresh groundwater than fresh surface water. To date, research on groundwater DOM has merely focused on specific threats to humans such as e.g. DOM and heavy metal complexations and DOM from hydrocarbon contamination. Only few studies targeted to understand DOM as energy source of groundwater food webs and the role of groundwater DOM in the global carbon cycle. While research on these two subjects in surface waters flourish, a comprehensive, large-scale study of groundwater is still missing. Since a major fraction of Earth's microbial biomass is found in the subsurface, mainly in aquifers, this represents a major knowledge gap. Moreover, researchers found that groundwater DOM concentrations worldwide increase alarmingly. Here, for the first time, we examine DOM properties and heterogeneity in a large-scale approach with regards to aquifer characteristics and physical-chemical as well as microbial features. We hypothesize that groundwater DOM quality shows high diversity and plays an important, yet complex role in these ecosystems, where bioavailability is influenced by intrinsic molecular properties, as well as environmental conditions.

We analyzed 1000 water samples from 100 groundwater bodies all over Austria with regards to their DOM quantity, quality and bacterial abundance (BA). From fluorescence excitation-emission-matrices (EEMs) we derived indices and components to describe DOM quality. Next, we explored this data with principal component analysis, where we used convex-hull areas to estimate the heterogeneity of DOM composition within the groundwater bodies. In parallel, the similarity of DOM quality was evaluated with self-organizing maps on EEMs to test if we captured the heterogeneity of the data set sufficiently with the previous analysis. DOM quantity and quality was then related to BA and physical-chemical parameters.

Our results show that water from fractured and karstic aquifers exhibit significantly higher terrestrial DOM origin and less degraded DOM than porous aquifers. This result can be explained by abiotic factors such as adsorption of large, aromatic compounds, as well as biological factors, specifically, larger surface areas for biofilm development in porous aquifers. The latter is supported by our observation that porous aquifers showed higher BA values. Remarkably, we found that BA was related to different DOM quality in each aquifer type: In porous aquifers BA was

related to large, aromatic DOM molecules indicating that these are important for bacterial growth, while in fractured and karstic aquifers BA was related to fulvics and highly degraded humic compounds. Bacterial growth and degradation of complex DOM might be limited by low retention times in some of these aquifers. Also, we found that groundwater bodies located in river valleys display high heterogeneity in DOM quality spanning across the whole DOM compositional diversity found in this study. This finding could either be explained by surface water infiltration in some parts and younger groundwater or the fact that river valleys are main settlement areas.