

## Disentangling dissolved oxygen sources in shallow riparian groundwater by stable isotope analysis

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Dissolved oxygen (DO) is one of the strongest oxidation agents in aquatic environments. Besides gas-water-exchange, mixing and mineral oxidation, it is a key player in fundamental biogeochemical processes such as respiration and photosynthesis. These processes also systematically influence stable isotope ratios of DO and of dissolved inorganic carbon (DIC). Simultaneous measurements of DO and DIC concentrations in conjunction with their stable isotope ratios ( $\delta^{18}\text{O}_{\text{DO}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$ ) can thus provide useful tools to quantify oxygen and carbon sources and sinks in natural waters.

This study focused on the Selke River in the Harz Mountains (Germany) with steep DO gradients between the stream water and the shallow, adjacent groundwater and associated stable isotope shifts.  $\delta^{13}\text{C}_{\text{DIC}}$  values decreased from -13 ‰ to -18 ‰ versus the Vienna Pee Dee Belemnite standard (VPDB) from May to November 2016 and indicated the dominant influence of microbial respiration on the observed DO gradients. With such respiration dominance, we have expected a simultaneous enrichment of  $\delta^{18}\text{O}_{\text{DO}}$  to values higher than the one of atmospheric  $\text{O}_2$  (+23.9 ‰ versus Vienna Standard Mean Ocean Water standard - VSMOW). However, our measurements revealed anomalously low  $\delta^{18}\text{O}_{\text{DO}}$  values between +22 ‰ and +18 ‰ versus VSMOW for the same time period. These  $\delta^{18}\text{O}_{\text{DO}}$  values were lower than those found in the river. Latter were close to equilibrium with the atmosphere (24.9 ‰ versus VSMOW). The observed  $\delta^{18}\text{O}_{\text{DO}}$  ratios in the shallow groundwater can be explained with DO from the river that is subject to fractionation by microbial respiration with a typical fractionation factor ( $\alpha_r$ ) of 0.995. In addition, mass balances revealed that this oxygen pool receives contributions of up to 25 % by diffused oxygen from the vadose zone. Consequently, isotope shifts by respiration and admixture with surface water are masked by diffusion effects that result in a decoupling of carbon and oxygen isotope systematics in the near river subsurface environment. They also demonstrate that DO in shallow groundwaters has additional sources than admixture from surface waters alone.