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## Rn as a geochemical tool for estimating residence times in the hyporheic zone and its application to biogeochemical processes

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The hyporheic zone is at the interface between groundwater and surface water systems. It is also often a geochemical and redox boundary between typically reduced groundwater and oxic surface water. It experiences dynamic physical and chemical conditions as both groundwater fluxes and surface water levels vary in time and space. This can be particularly important for processes such as biogeochemical processing of nutrients and carbon. There has recently been an increasing focus on coupling residence times of surface water in the hyporheic zone with biogeochemical reactions. While geochemical profiles can be readily measured using established geochemical sampling techniques (e.g. peepers), quantifying surface water residence times and flow paths within the hyporheic zone is more elusive. The nobel gas radon offers a method for quantification of surface water residence times in the hyporheic zone. Radon activities are typically low in surface waters due to degassing to the atmosphere and decay. However once the surface water flows into the hyporheic zone radon accumulates along the flow path due to emanation from the sediments. Using simple analytical equations the water residence time can be calculated based on the difference between measured 222Rn activities and 222Rn activities at secular equilibrium, with a maximum limit of about 20 days (depending on measurement precision). Rn is particularly suited to residence time measurements in the hyporheic zone since it does not require addition of tracers to the stream nor does it require complex simulations and assumptions (such as 1D vertical flow) as for temperature measurements.

As part of the biogeochemistry course at the University of Bayreuth, we have investigated the coupling of redox processes and water residence times in the hyporheic zone using 222Rn as a tracer for residence time. Of particular interest were nitrate and sulfate reduction and methane and CO2 production. Measurements were made in a sandy section of the Mistelbach, a second order stream running through agricultural land near the city of Bayreuth. Radon was measured at 1-3 locations on two occasions and at 5 different depths (-5 to-25 cm). Geochemical parameters NO<sub>3</sub>-, NO<sub>2</sub>-, SO<sub>4</sub>-, Fe<sub>2</sub>+, CO<sub>2</sub> and CH<sub>4</sub> was measured in peepers with a vertical resolution of 1-2 cm to a depth of 50 cm as well as in the same samples as the Rn. Groundwater activities were measured in incubation experiments and by the deepest sampling point in the hyporheic zone. The results showed that there was a clear dependence of biogeochemical processes on the residence time. Nitrate was reduced within 2 days, while sulfate reduction began after 5 days while Fe2+ was produced after 10 days. CH4 production occurred at >20 days, which is above the upper limit of residence time detection using Rn. Obviously, biogeochemical processes are controlled by the balance between reaction rates and advection rates in the hyporheic zone, and that the ratio of these rates (i.e. the Damköhler number) will control the efficiency of material processing. The uncertainty in the method increases towards longer residence times, as secular equilibrium activities and measured activities converge. It is also influenced by the heterogeneity of emanation in the sediments. However, research within the hyporheic zone is usually focused on residence times shorter than two weeks, and emanation can be quantified in the laboratory. Thus Rn appears well suited to the study of time scales over which biogeochemical processes occur in the hyporheic zone.