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A novel silicon diffusion membrane method for high-resolution continuous quantification of groundwater-surface water interaction using 222-Rn

H. Hofmann (1,2), B. Gilfedder (1,2), I. Cartwright (1,2)

(1) Monash University, School of Geosciences, Clayton, Australia (harald.hofmann@monash.edu), (2) National Centre for Groundwater Research and Training, Flinders University, Adelaide, SA, Australia

^{222}Rn is a naturally produced radioactive isotopic tracer that is commonly used to quantify groundwater discharge to streams, rivers, and wetlands. Traditional sampling and analysis techniques are usually confined to point measurements taken at a specific time. However, it is difficult to constrain short- or medium-term processes occurring at the groundwater-surface water interface using single measurements. Here we describe a method for high-resolution, autonomous, and continuous, measurement of radon in rivers and streams using a silicon diffusion membrane system coupled to a solid-state radon-in-air detector (Durridge RAD7). In this system, water is pumped through a silicon diffusion tube placed inside an outer air circuit tube that is connected to the radon-in-air detector. Radon diffuses from the water into the air loop and is measured by the detector. By optimising the membrane tube length, wall thickness, and water flow rates through the membrane, it was possible to quantify the variability of ^{222}Rn concentrations over timescales of about 3 hours and qualitatively observe changes in as little as 20 minutes. The detection limit for the entire system with 20 minutes counting was 0.018 Bq/L at the 3σ level, which is solely determined by the sensitivity of the detector. Results from the diffusion membrane agree well with conventional measurements of ^{222}Rn made using a RAD7 and an air-water exchanger at both high (20 Bq/L) and low ($<$1 Bq/L) concentrations. The silicon membrane system is suitable for continuous and autonomous monitoring of groundwater-surface water interactions on hourly to monthly times scales. Unlike unshielded diffusion membranes (such as the Membrana system), the system is not prone to clogging with sediment or biofilms even in turbid water; additionally, the silicon membrane is flexible and can be coiled for installation at sites where space is restricted. While the response times are slower than air-water exchangers, the silicon membrane system uses less. The system has been deployed on an urban stream for 3 days and in a wetland for periods of $>$30 days without requiring attendance. In both cases the system showed variability in ^{222}Rn concentrations that have allowed the short-timescale variations in groundwater inflow and degassing to be constrained and which allow the dynamic processes in these environments to be addressed.