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Quantification of submarine groundwater discharge and its short-term dynamics by linking time-variant end-member mixing analysis and isotope mass balancing (222-Rn)

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Submarine groundwater discharge (SGD) plays a crucial role for the water quality of coastal waters due to associated fluxes of nutrients, organic compounds and/or heavy-metals. Thus, the quantification of SGD is essential for evaluating the vulnerability of coastal water bodies with regard to groundwater pollution as well as for understanding the matter cycles of the connected water bodies.

Here, we present a scientific approach for quantifying discharge of fresh groundwater (GWf) and recirculated seawater (SWrec), including its short-term temporal dynamics, into the tide-affected Knysna estuary, South Africa. For a time-variant end-member mixing analysis we conducted time-series observations of radon (222Rn) and salinity within the estuary over two tidal cycles in combination with estimates of the related end-members for seawater, river water, GWf and SWrec. The mixing analysis was treated as constrained optimization problem for finding an end-member mixing ratio that simultaneously fits the observed data for radon and salinity best for every time-step. Uncertainty of each mixing ratio was quantified by Monte Carlo simulations of the optimization procedure considering uncertainty in end-member characterization. Results reveal the highest GWf and SWrec fraction in the estuary during peak low tide with averages of 0.8 % and 1.4 %, respectively. Further, we calculated a radon mass balance that revealed a daily radon flux of 4.8 * 108 Bq into the estuary equivalent to a GWf discharge of 29.000 m^3/d (9.000-59.000 m^3/d for 25th-75th percentile range) and a SWrec discharge of 80.000 m^3/d (45.000-130.000 m^3/d for 25th-75th percentile range). The uncertainty of SGD reflects the end-member uncertainty, i.e. the spatial heterogeneity of groundwater composition.

The presented approach allows the calculation of mixing ratios of multiple uncertain end-members for time-series measurements of multiple parameters. Linking these results with a tracer mass balance allows conversion of end-member fractions to end-member fluxes.