ENVIRONMENTAL TRACERS FOR QUANTIFYING SURFACE WATER-GROUNDWATER INTERACTION

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Declaration of originality

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Sarah Anne Bourke

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Co-Authorship

Sarah A. Bourke is the primary author on all manuscripts in this thesis. On all submitted papers, the co-authors provided intellectual supervision and editorial content.

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Summary

As demand for water resources intensifies, quantification of surface water-groundwater interaction has become increasingly important for effective water resource management. Various hydraulic and tracer techniques have been developed for quantifying these exchanges, each sensitive to particular scales or modes of exchange. In order to capture the entire spectrum of exchange fluxes in any given system, it is often necessary to employ several of these methods. Chapter 1 outlines the need for new methods, with different sensitivities than previously published methods, which will be valuable additions to the suite of available techniques. In this thesis, two new techniques are presented, using gas tracers to quantify 1) hyporheic exchange in losing streams, and 2) groundwater discharge to gaining streams. Additionally, groundwater age indicators and noble gases are applied in a novel setting to quantify the re-circulation of groundwater associated with mine dewatering operations.

Chapter 2 presents a new method for quantifying hyporheic exchange in losing streams based on measurements of radon-222 along the stream. A longitudinal mass balance approach is used to interpret measurements of streamflow and radon along the stream in terms of hyporheic (beneath the stream) and parafluvial (beside the stream) exchange fluxes. The results of this new method are compared to two existing methods; streambed radon disequilibrium and transient storage modeling of the breakthrough curves of an injected tracer. Transient storage modeling characterized rapid hyporheic exchange with a mean residence time of 4 minutes, storage zone area of 0.6 m^2 and storage exchange flux of 224 m^2 d^{-1}. This is consistent with the results of the streambed radon disequilibrium method, which suggest that the rapidly flushed hyporheic zone was at most 0.1 m thick. In contrast, the radon influx of 5.4 x 10^4 Bq m^{-1} d^{-1} was dominated by (≥80%) long-path parafluvial exchange with residence times of days, spatial scales of tens to hundreds of metres, and an exchange flux on the order of 10 m^2 d^{-1}. The new radon-based method is particularly sensitive to return flow paths on spatial scales of tens of meters, with sub-surface residence times of days or more, which were not captured by the pre-existing methods. Concurrent application of this new method, with existing methods using injected tracers, will provide a more complete estimate of the spectrum of return flows in losing stream systems.

In Chapter 3, the application of carbon-14 (^{14}C) in dissolved inorganic carbon (DIC) as a tracer of groundwater discharge to gaining streams is presented. A mass balance model for ^{14}C in DIC is developed, which allows for the isotopic equilibration rate to be expressed as an effective

transfer velocity for ^{14}C in DIC. A controlled experiment was conducted over 72 days to quantify the rate of isotopic equilibration of ^{14}C in DIC in groundwater exposed to the atmosphere. The method was then tested at an artificial groundwater discharge zone in the Pilbara region of Western Australia. The effective transfer velocities of these systems were as expected based on the pH and gas transfer velocity of CO_2, with values of 0.013 and 0.025 m d^{-1} respectively. The method was then applied across a previously mapped spring discharge zone in the Daly River, in northern Australia. The ^{14}C activity of DIC in the stream decreased from 83 to 76 pMC across the major discharge zone, which was used to estimate the ^{14}C activity of the discharging groundwater at between 60 and 66 pMC. The effective transfer velocity was estimated at between 0.09 and 0.15 m d^{-1}, which is between 8 and 13% larger than would be expected based on the gas transfer velocity of CO_2 and pH of this system. This increased rate of equilibration, above that predicted by carbonate speciation, is likely to be driven by in-stream CO_2 production through biotic respiration or the conversion of dissolved organic carbon to DIC. In spite of these additional sources of DIC in the stream, the signal of groundwater discharge in stream ^{14}C activity persisted for at least tens of kilometers. This persistence of the changes in ^{14}C activity caused by groundwater discharge over longer distances than other gaseous tracers allows for a larger spatial sampling interval and may allow for smaller groundwater fluxes to be quantified than is possible with other gaseous tracers.

In Chapter 4, groundwater age indicators (^{14}C and CFC-12) and noble gases are used as tracers of recharge by surplus mine water that is discharged to streams. In environments where groundwater is effectively re-circulated, quantification of the relative proportions of natural and anthropogenic recharge can be difficult. Groundwater age indicators, in particular gases, are likely to be more sensitive tracers of recharge than stable isotopes or chloride in this setting. This is because, unlike stable isotopes or chloride, they undergo a process of equilibration with the atmosphere, and historical atmospheric concentrations are known. Ternary mixing fractions were calculated based on ^{14}C and CFC-12 concentrations measured along three transects of piezometers perpendicular to the creeks, and from dewatering wells. The three end-members were defined to reflect the historical atmospheric concentrations of these tracers, and the history of mining operations. Uncertainty in calculated mixing fractions was estimated using a Monte Carlo approach. Recharge by mine water that had been discharged to the creeks was present in all samples, with the largest proportions within 250 m of the creeks. These results are supported by seepage estimates based on the chloride mass balance along the creeks, which suggests that between 85 and 90% of mine water discharged to the creeks recharges the aquifer. Based on the duration of discharge, recharge by mine water is predicted to extend between 110 and 730 m from the creeks. Ternary mixing ratios in dewatering wells suggest that recharge by mine water accounted for between 10 and 87 % of water currently abstracted by dewatering wells. These results are supported by estimates of excess air and terrigenic helium-4 amounts, with correlations between the amount of mine water and excess air, and the amount of regional groundwater and terrigenic helium-4. These methods could also be used to quantify recharge associated with agricultural irrigation or wetland supplementation and will be most successful when the duration of the activity is short, relative to the timescale of variation in atmospheric tracer concentrations.

Chapter 5 discusses how the new methods demonstrated in this thesis can be used in conjunction with pre-existing methods to improve field-based estimates surface water-groundwater interaction. Future work will involve the further validation of these new methods and their application at other field sites.

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