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Cover Photograph:

Description: Sampling for ^{222}Rn along the Cockburn River
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Executive Summary

Continuous injection of sulfur hexafluoride (SF_6), a pulse injection of Br^- and the measurement of ^{222}Rn activity disequilibrium in streambed porewater were used to characterise hyporheic exchange in two contrasting reaches of a subtropical stream (Cockburn River, Australia). In a cobble-bottom stream section, hyporheic exchange was rapid, as demonstrated by the short time to reach equilibrium (<1 day) between stream and hyporheic zone SF_6 concentrations. Hyporheic water residence times (t_h) estimated using ^{222}Rn disequilibrium ranged between <0.05 to 0.23 days, consistent with an independent t_h derived from a bromide pulse injection (0.10 day). Modelled parameters for the 1-D advection-dispersion equation with transient storage derived from the pulse Br^- tracer experiment could accurately predict the changes in hyporheic SF_6 concentrations over time, indicating that Br^- and SF_6 are equivalent tracers of hyporheic exchange. In a sand and gravel streambed section, hyporheic exchange was slower and more variable. Hyporheic zone SF_6 concentrations had not reached equilibrium with the stream after 71 hours of continuous injection and t_h derived from ^{222}Rn disequilibrium ranged between <0.05 and 21 days. However, the ^{222}Rn disequilibrium technique may be less reliable for this stream section because hyporheic water could be a mixture of surface water and regional groundwater, the latter with potentially very high ^{222}Rn activity. The use of SF_6 injection and ^{222}Rn hyporheic disequilibrium are promising complimentary techniques to study hyporheic processes, especially in larger streams and rivers where solute injection is less practical.

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1. Introduction

Hyporheic exchange plays an important role in solute transport, nutrient cycling and contaminant attenuation in streams (Thibodeaux and Boyle 1987; Boulton 1993; Jones and Mullholland 2000). However, quantifying the rate of this exchange, in particular in larger streams and rivers, remains a challenge (Hinkle et al. 2000; Stanley and Jones 2000). In-stream tracer additions combined with modelling of breakthrough curves is the most widely used approach to quantify hyporheic exchange in small streams (Stream Solute Workshop 1990; Wagner and Harvey 1997). However, the use of dissolved solutes as tracers is logistically complicated in larger streams and rivers because of the large volume of solution that must be used. Dyes have also been used in rivers (Fernald et al. 2001) but may present aesthetic and environmental concerns when used in streams that are part of drinking water supplies. An alternative to the use of dyes and salts would be the use of inert gases, such as sulfur hexafluoride (SF_6). SF_6 can be used to label large volumes of water because of the large dynamic range over which concentrations can be measured and of its occurrence in only trace concentrations in the atmosphere. One drawback with the use of inert gases is the potential for losses by exchange with the atmosphere. However, this exchange can either be independently estimated (Wanninkhof et al. 1990; Genereux and Hemond 1992; Raymond and Cole 2001) or, in the case of SF_6, is considered to be negligible at smaller spatial scales (hundreds of metres). Examples of current applications of SF_6 in hydrological studies include measurement of gas exchange in rivers (Clark et al. 1994), estimation of longitudinal dispersion in large rivers (Ho et al. 2002), and the tracking of groundwater flow paths (Gamlin et al. 2001).

In addition to injected tracer experiments, it may be possible to characterise hyporheic exchange using naturally-occurring tracers. Radon-222 is an inert gas with a half-life of 3.8 days that is produced by the radioactive decay of uranium-238 series radioisotopes. Virtually all geologic materials produce at least small quantities of ^{222}Rn and it is a commonly used tracer to identify locations of groundwater discharge to streams (Ellins et

al. 1990; Lee and Hollyday 1993; Genereux et al. 1993; Cook et al. 2003). Because of its relatively short half-life, streambed porewater ^{222}Rn activity should rapidly reach secular equilibrium with its parent ^{226}Ra in sediments. However, if hyporheic exchange occurs, secular equilibrium will not be achieved because of dilution by low ^{222}Rn activity surface water. This discrepancy between the expected and measured ^{222}Rn activity in stream sediment porewater could be used to quantify hyporheic exchange.

In this study, we evaluated the potential for two new complementary techniques to estimate hyporheic exchange in streams and rivers: SF_6 tracer injection and ^{222}Rn activity disequilibrium in the hyporheic zone. These techniques were tested at two contrasting sites (a cobble/stone and a sand/gravel reach) in a subtropical river (Cockburn River, New South Wales). Both techniques are relatively simple to apply in the field and use similar equipment, such as nests of mini-piezometers. To further evaluate the validity of both techniques, a pulse addition of bromide was made at one site and hyporheic exchange parameters independently estimated using an advective-dispersive transport with storage model. We discuss the potential limitations, practical applications and further improvements to the SF_6 injection and ^{222}Rn disequilibrium techniques.

2. Methods

2.1. Study Site

The Cockburn River is a semi-permanent stream draining a catchment of approximately 1126 km^2 in the Southern Highlands of New South Wales, southeastern Australia (Fig. 1). It is formed by the confluence of Swamp Oak Creek and Jamiesons Creek, and flows into the Peel River immediately upstream of the city of Tamworth. The majority of the Cockburn catchment is part of the New England Fold belt and consists of a Cambrian to Silurian ophiolitic sequence, which was uplifted and subjected to mild metamorphism in the Late Carboniferous. In the late Permian, the sediments were intruded

by the New England Batholith (granite), which underlies the Cockburn River. Climate in the region is subtropical, with long hot summers and cool winters. Mean annual precipitation at Tamworth is 670 mm and is relatively evenly
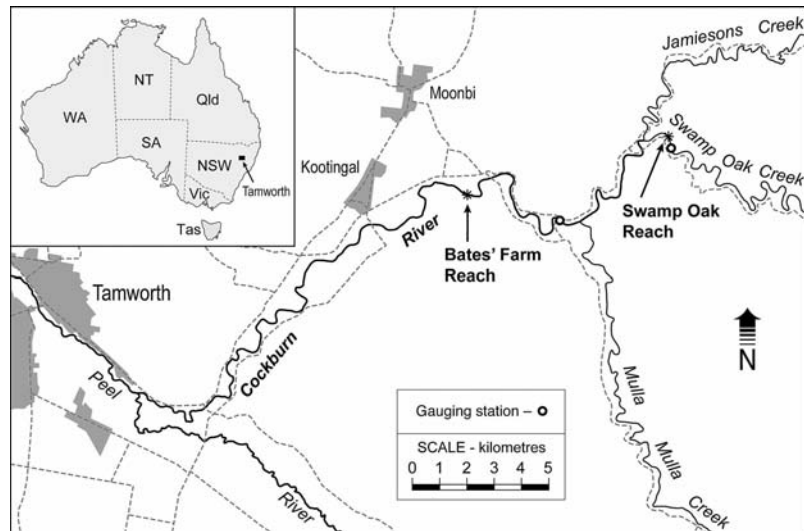
Figure 1: *Location of the Cockburn River (New South Wales) and the two experimental study reaches.*

distributed throughout the year. However, drought periods occasionally occur, at which time the river may become a series of disconnected pools. Land use in the catchment ranges from irrigated agriculture in the lowlands to a mixture of pastures and native *Eucalyptus* forests in uplands area.

Two sites were selected for SF_6 injection experiments and the measurements of ^{222}Rn disequilibrium (Swamp Oak Creek and Bates' Farm; Fig. 1). Swamp Oak Creek is an upland tributary of the Cockburn River (Fig. 1). The study reach in Swamp Oak was the 300 m section of the river downstream from the Swamp Oak Creek gauging station (Fig. 1). This section of Swamp Oak Creek has a shallow (10 – 100 cm) cobble stream bed and a baseflow of approximately 0.08 m^3 s^{-1}. The Bates' Farm study reach was more representative of the lowland section of the Cockburn, with a more gentle gradient, and a more extensive sand to gravel streambed (up to several metres thick) and a baseflow of ~0.5 m^3 s^{-1}.

3.   Theory

3.1. SF_6 and bromide injections

Using the breakthrough curves from pulse or continuous tracer addition experiments, hyporheic exchange can be estimated using the one dimensional advection-dispersion equation combined with a transient storage model (Harvey and Wagner 2000; Packman and Bencala 2000):

$$\frac{\partial C}{\partial t} + \frac{Q}{A}\frac{\partial C}{\partial x} = \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha(C_S - C),$$ (1)

$$\frac{\partial}{\partial t}C_S = -\alpha\frac{A}{A_S}(C_S - C),$$ (2)

where C and C_s are the solute concentrations in the stream and the storage zone, respectively (M L^{-3}; using arbitrary mass, length and time units); Q is the volumetric flow rate in the stream (L^3 T^{-1}); D is the dispersion coefficient (L^2 T^{-1}); A and A_s are the cross-sectional area of the stream and the storage zone (L^2), respectively; q_L is the lateral inflow rate (L^3 T^{-1} L^{-1}); α is the storage exchange coefficient (T^{-1}); t is time (T) and x is the distance along the stream channel (L). The hyporheic water residence time can be estimated from the transport parameters using (Harvey and Wagner 2000):

$$t_h = \frac{A_S}{\alpha A}$$ (3)

These equations assume that there is only one storage zone exchanging water with the stream. In reality, both hyporheic and surface storage (sluggish side pools, etc) will be present (Runkel 1998). Analytical solutions for Equ. 1 and 2 are available for simple boundary conditions (De Smedt et al. 2005) and numerical models are available for more complex problems, such as OTIS and OTIS-P (Runkel 1998).

3.2. Rn-222 disequilibrium

Cook et al. (in press) developed a simple model to quantify the importance of the hyporheic zone as a source of radon to streams. They represented the hyporheic zone by a layer of constant depth beneath the stream bed, with uniform concentration c_h. They further assumed a continual water exchange between the river and the hyporheic zone, although with zero net water flux at each point and hence no significant lateral flow within this zone. The model thus does not allow for large-scale zones of upwelling and downwelling. With this simplification, the solute mass balance within this zone can be expressed:

$$Q_h c - Q_h c_h + \gamma w h \theta - \lambda w h \theta c_h = 0 \qquad (4).$$

Where c and c_h are the radon activities within the river and the hyporheic zone respectively, Q_h is the flux of water into and out of the sediments (m^3 m^{-1} day^{-1}), γ is the production rate within the hyporheic zone (units of concentration per day), h is the mean depth of the hyporheic zone (m) and θ is its porosity, w is the river width (m) and λ is the decay coefficient for radon (day^{-1}). The concentration within the hyporheic zone is then given by re-arrangement of (3):

$$c_h = \frac{Q_h c + \gamma h w \theta}{Q_h + \lambda h w \theta} \qquad (5).$$

The mean residence time of water within the hyporheic zone, t_h, is given by:

$$t_h = \frac{w h \theta}{Q_h} \qquad (6).$$

Substitution of (5) into (4) gives:

$$c_h = \frac{c + \gamma t_h}{1 + \lambda t_h}$$ (7).

Thus, the radon activity within the hyporheic zone is only a function of the activity in the river and of the hyporheic zone turnover time. The significance of this is that t_h (a parameter difficult to measure in the field) can be estimated from c and c_h, which are relatively easy to measure.

There is a limit in the range in t_h where the ^{222}Rn disequilibrium technique will be applicable. In addition, both the range in applicability and the resolution of the method at a given t_h will be
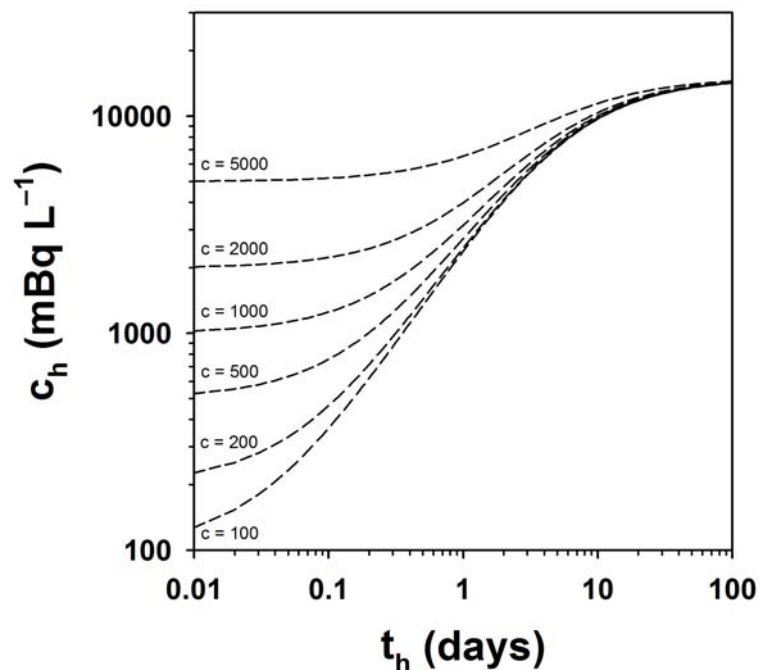
Figure 2: *Theoretical variation in radon activity within the hyporheic zone as a function of hyporheic water residence time and surface water radon activity (c; in mBq L^{-1}). Model assumes γ/λ = 15,000 mBq L^{-1}, a typical value for the Cockburn River (see Results).*

determined in part by surface water ^{222}Rn activity (Fig. 2). For conditions typical of the Cockburn River, the upper limit in t_h that could be estimated would be ~30 days, regardless of surface water ^{222}Rn. However, the resolution of the method (the change in t_h per unit change in c_h) is low when $t_h > 10$ days. The lower limit in measureable t_h decreases when surface water ^{222}Rn activities are lower. For example, when surface water ^{222}Rn activities are high in the Cockburn River (~5000 mBq L^{-1}), t_h could be estimated only down to ~0.5 day. However, at low surface water ^{222}Rn activities (100–200 mBq L^{-1}), hyporheic water residence times of 0.01 day or less could be measured. In general, the resolution of the method also

increases at lower surface water ^{222}Rn activities (Fig. 2). In other words, the error for a given t_h will tend to be smaller when surface water ^{222}Rn is low. Overall, the ^{222}Rn disequilibrium technique is applicable over the range in t_h that is often of interest in hydrological studies (hours to days).

4. Field Experiments

4.1. Bromide injection

A bromide pulse injection was carried at Swamp Oak reach on 18 October 2005. An inflatable swimming pool was filled with 40 L of bromide brine ($\sim$1.13 kg L^{-1}) and injected in the stream using a peristaltic pump connected to a spraying system designed to release the brine over most of the stream width. Downstream sampling stations were set-up 110 m (Station 1) and 295 m (Station 2) from the point of injection. Brine was injected in the stream for 40 minutes, at which time the injection was stopped (with $\sim$38.4 L injected). Sampling occurred at the downstream stations at 1 to 4 minutes intervals, with a higher sampling frequency when the bromide pulse was detected (as assessed by simultaneous electrical conductivity measurements). Water samples were collected mid-stream using 125 mL polyethylene bottles. Sampling proceeded until 150 minutes after the injection was started. Stream discharge was 0.085 m^3 s^{-1} and remained constant throughout the injection. Bromide concentrations were measured by ion chromatography.

4.2. Mini-piezometers

Nests of mini-piezometers were installed 200 m and 400 m downstream from the point of SF$_6$ addition at Swamp Oak and Bates' Farm, respectively (Table 1). The mini-piezometers were made of 6 mm OD by 4 mm ID nylon tubing, with their bottom ends screened with fine mesh cloth, and fastened to 5 mm dia. wooden rods. Each nest consisted of one shallow (30 to 41 cm below the streambed) and one deeper (60 to 104 cm) piezometer (Table 1). The minipiezometer nests were installed using a technique similar to the one outlined in Boulton (1993). Briefly, casings (20 mm OD PVC) were first installed in

the streambed down to one metre, or as far as practical, using a percussion technique

Table 1: *Details of mini-piezometers at the Swamp Oak and Bates' Farm reaches (range in width and wetted perimeter from three cross-sections at Swamp Oak; average values estimated at Bates' Farm).*

Reach (m)	Width (m)	Wetted perimeter (m)	Q ($m^3 s^{-1}$)	Mini-piezometer	Depth below stream bed (cm)	Water depth (cm)	Stream velocity ($m s^{-1}$)
Swamp Oak	4.6 – 15	0.35 – 1.4	0.085	MP1–S	35	30	0.06
				MP1–D	75		
				MP2–S	30	30	0.06
				MP2–D	60		
Bates' Farm	~20	~4	0.5	MP3–S	30	19	~0.15
				MP3–D	104		
				MP4–S	41	59	<0.01
				MP4–D	91		
				MP5–S	39	10	~0.15
				MP5–D	92		

(Boulton 1993). The mini-piezometer nests were then inserted within the casings, which were then gently removed while the nests were held in place using the wooden rods. The two nests at Swamp Oak (MP1 and MP2) were located in a shallow cobble-bottom pool three metres from one another (Table 1). At Bates' Farm, one nest of mini-piezometers was located at the head of a riffle (MP3), another at the toe of the same riffle (MP5) and a last one (MP4) in a sluggish side pool 30 metres downstream from the riffle section (Table 1). It was hypothesised that hyporheic exchange would be large and similar in MP1 and MP2. Hyporheic exchange was hypothesised to be smaller at the Bates' Farm reach and to vary in the order MP3>MP5>MP4 due to preferential recharge of hyporheic water at the head of the riffle and lower stream velocities in the MP4 pool.

4.3. SF$_6$ injection

Continuous SF$_6$ injection experiments were carried out from 15–18 October 2005. Two 600 mL stainless steel vessels were filled with SF$_6$ to pressures of 623 and 764 kPa. The tanks were then attached to 25 m of 3 mm diameter silicone tubing, via a regulator that maintained the pressures in the tubing at approximately 60 kPa. One apparatus was submerged on the bed of the river at each study reach (approximately 15 km apart). The first

apparatus was installed at 9:35 at Swamp Oak and the second at 15:15 at Bates' Farm both on October 15. The hydrograph on the first day of the injections was the tailing end of a storm, but stream flow was constant from October 16 onward (Fig. 3). The pressure in the tanks was measured at
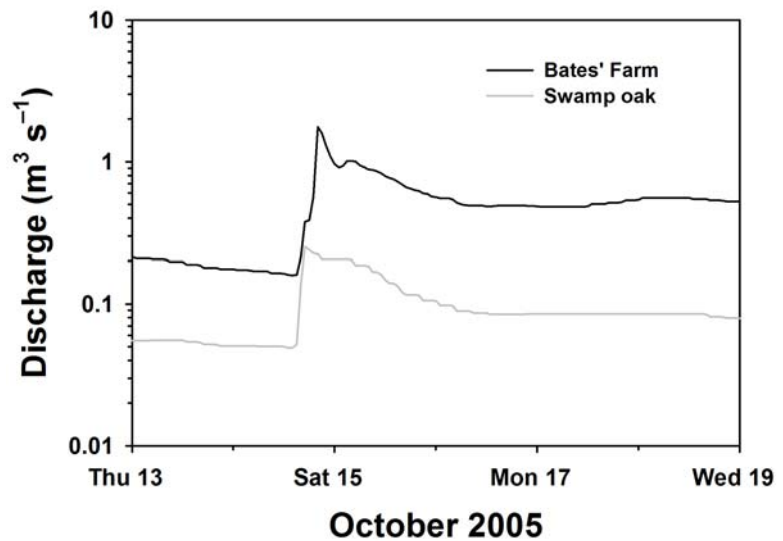

Figure 3: *Hydrographs for Swamp Oak Creek and the Cockburn River near Bates' Farm, 13–19 October 2005.*

regular intervals to ensure that a constant injection rate was maintained. Based on the rate of pressure decrease in the tanks, injection rates were approximately $3.31 \cdot 10^{-5}$ moles min^{-1} at Swamp Oak and $2.03 \cdot 10^{-5}$ moles min^{-1} at Bates' Farm.

SF_6 in stream water was sampled by submerging pre-weighed and pre-evacuated collection tubes (10 mL Vacutainer, Becton-Dickinson) and inserting a needle through their rubber septa until they were approximately half full. Each sample was collected at least in duplicate and later weighed in the lab to determine the exact volume of water collected. Surface water samples were collected at the mini-piezometer locations once or twice a day until the end of the experiment (October 18). More detailed longitudinal sampling for SF_6 occurred on October 17 along the length of the Cockburn River downstream from the Swamp Oak gauging station (Cook et al. in press). SF_6 concentrations were measured on a gas chromatograph equipped with an electron capture detector using a head space method as described by Clark et al. (1994).

The sampling frequency for SF_6 concentration in the hyporheic zone was a trade-off between the need to sample hyporheic water often enough to characterise the SF_6

breakthrough curves and the need to minimise the artificial induction of hyporheic exchange by removing large volumes of porewater. A cautious sampling frequency was chosen, where SF_6 concentration was measured no more than twice a day on a given mini-piezometer. Hyporheic water samples were collected with a hand-held peristaltic pump connected to the mini-piezometers using tightly fitting silicone tubing. Each mini-piezometer was first flushed for two standing water volumes prior to sample collection. Following flushing, while gentle pumping proceeded (~0.5 mL s^{-1}), the free end of the peristaltic tubing was fitted with a narrow gauge needle (0.5 x 16 mm) and inserted into a collection tube until half full. Each hyporheic SF_6 sample was collected in duplicate. The combination of purging and collection of duplicate samples removed between 16 to 25 mL of hyporheic water per sampling round for a 30 cm and 100 cm mini-piezometer, respectively. Assuming a porosity of ~0.4 in the hyporheic zone and an isotropic porous medium, the volume of hyporheic zone sampled per each sampling round would represent a sphere with a radius of ~2.3 cm for the shorter piezometers and ~2.7 cm for the longer piezometers. Thus, the volume of hyporheic water removed is significant but will not produce a large artefact if hyporheic flushing is relatively rapid (as expected in the coarse substrates sampled).

4.4. Rn-222 sampling

Hyporheic ^{222}Rn activity was sampled prior to the beginning of the SF_6 injections in a manner similar to hyporheic SF_6. Following purging of the wells and while gentle pumping continued, 14 mL of hyporheic water was collected without exposure to the atmosphere by inserting the needle of a glass syringe inside the open end of the pump tubing. The sample was then immediately injected into a pre-weighed 22 mm Teflon-coated PTFE scintillation vial containing 6 mL Packard NEN mineral oil. Radon activity was counted in the laboratory by liquid scintillation, on a LKB Wallac Quantulus counter using the pulse shape analysis program to discriminate alpha and beta decay (Herczeg et al. 1994).

For surface water ^{222}Rn, larger sample volumes are required as the radon activity is much lower than in hyporheic water. Surface water samples for radon analysis were

collected in 1250 mL plastic bottles without leaving a headspace. Within 24 h of collection, [222]Rn was extracted by first discarding ~50 mL of water and by adding 20 mL of mineral oil scintillant from a pre-weighed scintillation vial. The bottle was then capped and shaken for four minutes to equilibrate the radon between the air-water-scintillant phases. After allowing the scintillant to settle at the top of the bottle (about 1 minute), the scintillant was returned to the vial and sealed. Efficiency of radon extraction and counting was approximately 50%, and duplicates were within 5%.

Measurements of radon emanation were made on sediments collected from the bed of the river. For each study reach, four ~40 g of oven-dried sediment was sealed in 60 ml brass containers, with 20 ml of mineral oil scintillant. The balance of the volume (~ 20 ml) was filled with distilled water. After a period of several weeks, the radon activity within the chamber will reach a constant value as the radon production rate from the sediment will be exactly balanced by the radon loss due to radioactive decay. After allowing six weeks for this secular equilibrium condition to be reached, the mineral oil was sampled and its radon concentration was measured. By using a series of radium standards, the efficiency of this process (percentage of emanated radon that is captured in the scintillant) was determined to be approximately 61%. The radon activity in the mineral oil is used to calculate the total radon emanation rate, E (Bq kg^{-1}), which is related to the radon production rate, γ (Bq L^{-1} day^{-1}) by:

$$\gamma = \frac{E(1-\varepsilon)\rho_s \lambda}{\varepsilon} \qquad [8]$$

where ρ_s is the density of the solid phase (kg cm^{-3}) and ε is the porosity (cm^3 cm^{-3}).

4.5. Hyporheic exchange parameter estimation

The models OTIS and OTIS-P were used to estimate the parameters of Equ. 1 and 2. Model details can be found in Runkel (1998). Briefly, OTIS and OTIS-P can provide numerical solutions for advective-dispersive transport with transient storage under a variety of conditions (including steady or unsteady flow, pulse or continuous injection, etc), including parameter optimisation with the latter model. For the bromide injection experiment, we used the observed Br^- concentration curve at Station 1 as the input function for the tracer. The best fit for the Br^- breakthrough curve at Station 2 was estimated by allowing the model to optimise the values for D, A, A_s and α. Stream discharge was set at 0.085 m^3 s^{-1} and it was assumed that lateral inflow of groundwater and surface water was negligible ($q_L = 0$) between stations 1 and 2. The model parameters derived from the Br^- injection were then used to predict the SF_6 breakthrough curves in surface water and in the hyporheic zone at MP1/MP2 during the SF_6 injection experiment. Because stream discharge was still receding at Swamp Oak on the first day of the SF_6 injection (Fig. 3), the SF_6 breakthrough curves were predicted using the OTIS unsteady flow option (Runkel 1998), where Q and A can be adjusted for every time step. Only Q was adjusted in our simulations.

5. Results

5.1. Bromide injection

The peak in the breakthrough curves occurred at 49 and 80 min at stations 1 and 2, respectively, and were both characterised by trailing tails indicative that exchange with a storage zone is occurring (Fig. 4). Modelling of the Station 2 breakthrough curve indicated that the storage zone for this stream
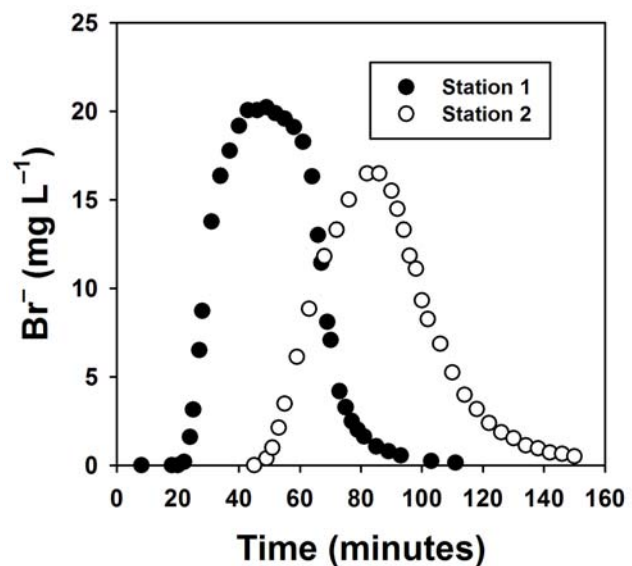

Figure 4: *Breakthrough curves for the Swamp Oak Creek Br^- tracer injection, 18 October 2005.*

section (A_s = 0.53 m^2) was approximately half that of the stream cross-sectional area (A = 0.97 m^2; Table 2). While the optimised fit for all four parameters gave a good match between the observed

and predicted Br$^-$ curves, it was felt that a better fit could be made for the tail end (the part of the curve most influence by exchange with a storage zone). Thus, additional OTIS-P runs were made for fixed α values while the remaining three parameters (A, A_s and D) were still being optimised. The best fit of the tail end of the curve was for $\alpha = 7.5 \cdot 10^{-5}$ (Fig. 5), with minimal differences on the values of the other parameters (Table 2). Assuming that only hyporheic exchange occurs and using Eq. 3, the average water residence time in the hyporheic zone is is ~0.10 day. The parameter values obtained with $\alpha = 7.5 \cdot 10^{-5}$ were used

Table 2: *Estimated parameters for 1-D advective-dispersive solute transport with transient storage for the bromide injection. Mean ± SD.*

	Optimised for all four parameters	With α constrained
D (m^2 s^{-1})	0.54 ± 0.053	0.64 ± 0.036
A (m^2)	0.97 ± 0.013	1.0 ± 0.008
A_s (m^2)	0.53 ± 0.090	0.66 ± 0.17
α (s^{-1})	$9.8 \cdot 10^{-5} \pm 1.0 \cdot 10^{-5}$	$7.5 \cdot 10^{-5}$

to predict the surface water and hyporheic SF$_6$ breakthrough curves.

5.2. SF$_6$ injection

At Swamp Oak Creek, SF$_6$ concentration in surface water increased rapidly and concentrations varied between 2500 and 2900 pmol L^{-1} after 24 h of injection (Fig. 6a). However, the change in
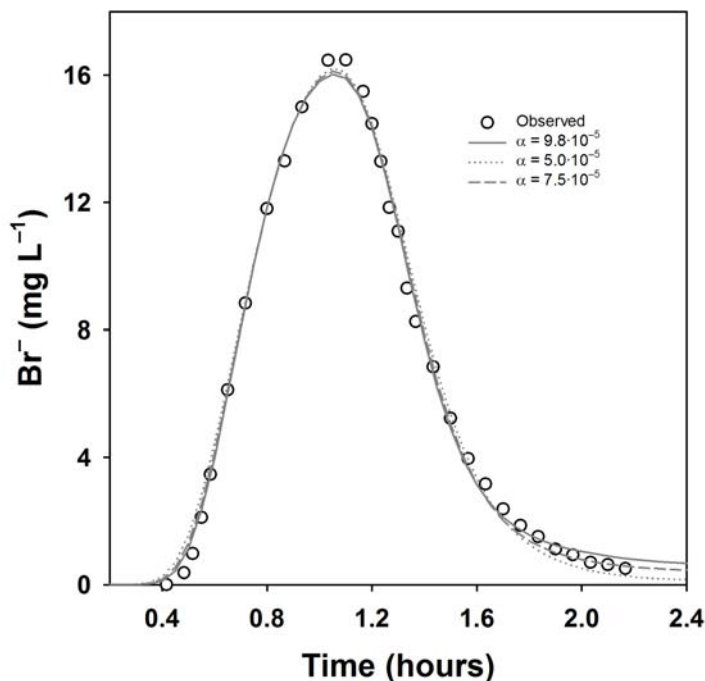
Figure 5: *Observed and predicted Br$^-$ breakthough curves at Station 2 for different estimates of α.*

surface water SF_6 concentration during the first 24 h of injection was due to a combination of a decrease in stream flow during that period (less dilution of the tracer; Fig. 3) and the time for the SF_6 plume to travel 200 m downstream to MP1 and MP2 (<2 hours). SF_6 concentrations in MP1 and MP2 also increased rapidly but were less than surface water concentrations at $t = 8$ h, especially in the deeper piezometers. However, stream and mini-piezometer SF_6 concentrations were within analytical error at $t > 8$ h. As for the trends in surface water SF_6 concentrations, decreasing flow rates during the first 24 h of injection probably increased the time required to reach constant hyporheic SF_6 concentrations. This would have been due to changes in surface water SF_6 concentrations and possibly variations in hyporheic exchange rate at different flow rates.

Surface water SF_6 concentrations did not increase as rapidly at Bates' Farm but appear to have stabilised after $t > 24$ h (Fig. 6b). Unlike at Swamp Oak Creek, SF_6 concentrations in mini-piezometers appeared not to have reached equilibrium with surface water after three days of injection. There were also significant differences in SF_6 concentrations between and within mini-piezometer nests. SF_6 concentrations were highest in the MP3 piezometers (top of riffle), lowest in MP4 (pool), and were generally more elevated in the shallower piezometers. This suggests that hyporheic exchange is slower and more variable, the hyporheic zone larger, and that several hyporheic flowpaths co-occur at the Bates' Farm reach.
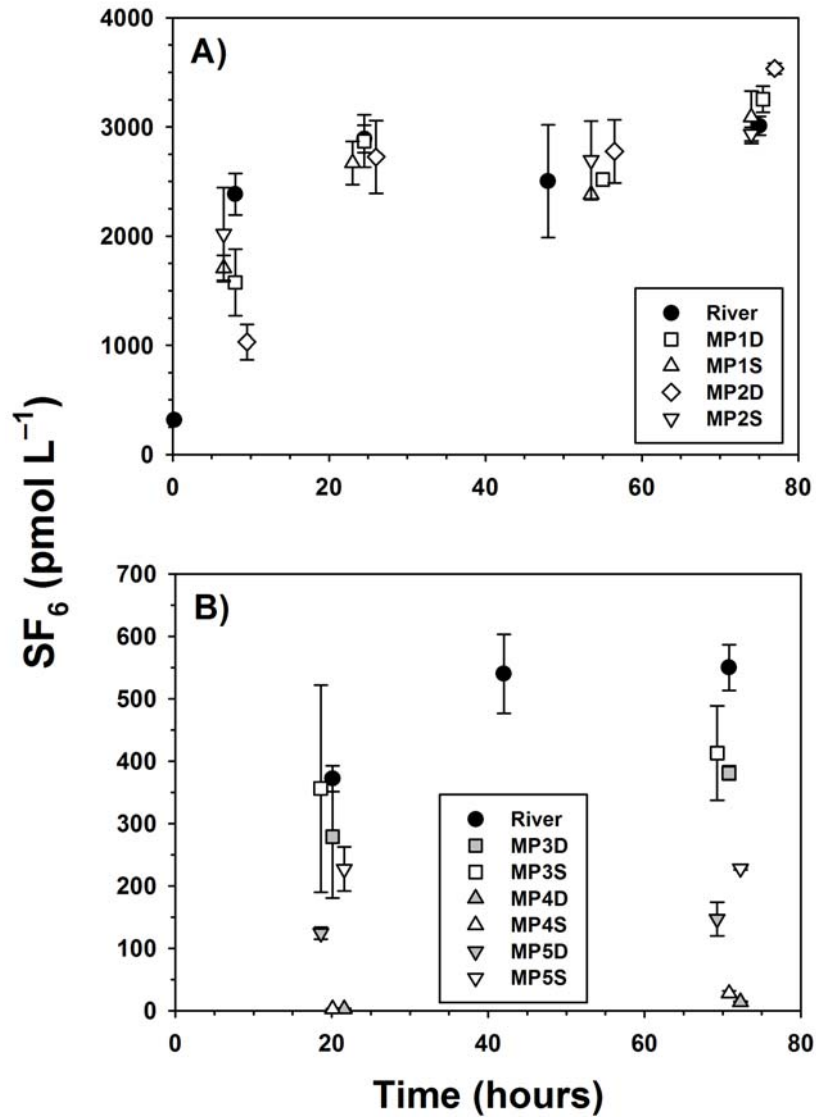
Figure 6: *Observed SF$_6$ concentrations at A) Swamp Oak and B) Bates' Farm in surface water and the hyporheic zone (mean ± SD). Hyporheic zone sampling occurred at* t *= 8.0, 24.5, 55.0 and 75.5 h at Swamp Oak and* t *= 20.1 and 70.8 h at Bates' Farm. Some hyporheic concentrations were slightly offset on the x-axis for clarity.*

Theoretical surface and hyporheic SF$_6$ concentrations were estimated at Swamp Oak

Creek reach using OTIS and the transport and exchange parameters derived from the Br$^-$

injection experiment. Predicted surface water SF$_6$ concentrations slightly underestimated the

observed surface water SF$_6$ breakthrough curve (Fig. 7). However, the match between the

predicted and observed SF$_6$ concentrations in the hyporheic zone was better. It is possible

that the bromide-derived transport and hyporheic exchange parameters were not optimal for

the first day of the SF$_6$ injection, when stream flow was slightly larger (Fig. 3). In addition, the

modelled SF$_6$ concentrations were probably not optimal at early times because A probably increased at the higher flow rates but was maintained constant in the simulations. Despite these shortcomings, these results suggest that SF$_6$ and bromide are equivalent tracers to characterise advective-dispersive transport with transient storage at Swamp Oak Creek.
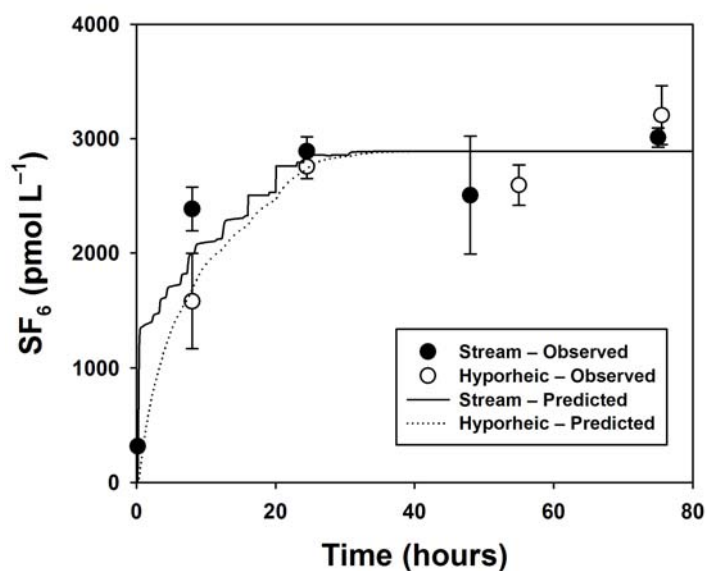

Figure 7: *Observed and predicted SF$_6$ concentrations in surface and hyporheic water (mean ± SD for all mini-piezometers) at the Swamp Oak Creek reach. Predicted curves estimated with OTIS using A, A$_s$, D and α values derived from the Br$^-$ injection experiment.*

5.3. Radon–222

Hyporheic [222]Rn activities were dissimilar between the two study reaches (Table 3), ranging between 420 to 950 mBq L^{-1} at Swamp Oak and 2060 to 12,740 mBq L^{-1} at Bates' Farm. Hyporheic [222]Rn activities were higher than in surface water, which was 426 ± 48.7 mBq L^{-1} (mean ± standard deviation from eight samples) at Swamp Oak and 2307 ± 976 mBq L^{-1} ($n = 6$) at Bates' Farm. Cook et al. (in press) determined that radon production rates were 2500 ± 650 and 2800 ± 850 mBq L^{-1} day^{-1} (mean ± SD) in sediments from the Swamp Oak and Bates' Farm reaches, respectively. From Eq. 7, hyporheic mean water residence time ranged between <0.05 and 0.23 days at Swamp Oak and <0.05 to 21 days at Bates' Farm (Table 3). At the latter site, residence times were longest in the sluggish pool and

shortest at the head of the riffle. At Swamp Oak, the average hyporheic water residence

time estimated using ^{222}Rn-disequilibrium (0.11 day) was similar to the one estimated

Table 3: *Radon activities in water samples extracted from mini-piezometers estimated hyporheic water residence times (from Equ. 7).*

Piezometer	Radon-222 (mBq L^{-1})	t_h (days)
MP1D	660	0.098
MP1S	560	0.056
MP2D	950	0.23
MP2S	420	<0.05
MP3D	3160	0.38
MP3S	2060	<0.05
MP4D	9630	6.9
MP4S	12740	21
MP5D	3960	0.79
MP5S	3530	0.57

independently using the Br$^-$ injection (0.10 day).

6. Discussion

Overall, the inferences made about hyporheic processes were consistent between the

bromide injection, the SF$_6$ injections and the ^{222}Rn hyporheic disequilibrium techniques. At

Swamp Oak reach, hyporheic exchange was rapid, as demonstrated by the short t_h

estimated using the Br$^-$ injection and ^{222}Rn disequilibrium techniques, and the short time (<1

day) required for hyporheic zone SF$_6$ concentrations to reach equilibrium with stream SF$_6$

concentrations. By contrast, hyporheic exchange was slower at Bates' Farm and several

hyporheic flow paths with different t_h may have been present. Unlike at Swamp Oak,

hyporheic SF$_6$ concentrations did not reach equilibrium with stream SF$_6$ concentrations at

Bates' Farm. In particular, only trace SF$_6$ concentrations were found in the MP4 piezometer

nest after 72 hours of injection, consistent with the long t_h inferred from ^{222}Rn disequilibrium.

However, the ^{222}Rn disequilibrium and the SF$_6$ data are not entirely consistent at Bates'

Farm. At piezometer MP3, the short t_h inferred from ^{222}Rn disequilibrium (<0.05 – 0.38 day)

implied that hyporheic SF$_6$ concentrations should have had equilibrated after 72 hours of

injection, but this was not observed.

Regional groundwater mixing with hyporheic water could bias t_h estimates based on the ^{222}Rn disequilibrium technique. Regional groundwaters tend to have higher ^{222}Rn activities than hyporheic waters, with activities ranging from 4000 to 580,000 mBq L^{-1} in Cockburn catchment groundwaters depending on the local geology (Cook et al. in press). Quantifying the impact of groundwater discharge on ^{222}Rn disequilibrium-derived t_h values is not straightforward. In addition to its large range in potential activity, the ^{222}Rn signature of regional groundwater could be modified during transit through alluvial aquifers when they form an interface between regional aquifers and the hyporheic zone. If regional groundwater transit in an alluvial aquifer is longer than 20 days, regional groundwater will tend to have a similar ^{222}Rn signature as hyporheic water at secular equilibrium (assuming that sediments in the alluvial aquifer and in the hyporheic zone have similar γ). Overall, the effect of the mixing of regional groundwater with hyporheic water will tend to yield longer apparent ^{222}Rn-derived t_h values, especially if the residence time of regional groundwater in the alluvial aquifer is less than 20 days.

There are two options to assess the role of regional groundwater discharge on ^{222}Rn disequilibrium-derived t_h values. If hyporheic ^{222}Rn activities are greater than what can be achieved by equilibrium with hyporheic sediments, mixing with regional groundwater is likely and the ^{222}Rn disequilibrium method should not be used. In this study, all hyporheic ^{222}Rn activities were lower than the maximum values that can be achieved by equilibrium with hyporheic sediments (~15,000 mBq L^{-1}; Fig. 2). However, this does not prove that hyporheic waters were only derived from surface water because mixing with regional groundwater that has transited for more than ~20 days through an alluvial aquifer or that as low ^{222}Rn activity is still possible. Mixing of surface water and regional groundwater in the hyporheic zone can be assessed using long-term SF$_6$ injection experiments. In cases where hyporheic waters are a mixture between surface water and groundwater discharge, hyporheic SF$_6$ concentrations will tend to plateau at concentrations lower than in surface water, commensurate to the proportion of groundwater in the hyporheic zone. In such cases, the ^{222}Rn disequilibrium

technique should either not be used or modified to account for the input of ^{222}Rn from groundwater.

6.1. Conclusion

SF$_6$ injection and ^{222}Rn disequilibrium appear promising techniques to study hyporheic exchange processes. The advantage of the SF$_6$ technique is that large volumes of stream and hyporheic waters can be labelled with relative ease. The SF$_6$ injection system used in this study can be installed by one person in less than an hour and can be left largely unattended for days. No large pieces of equipment were required (such as inflatable swimming pools, pumps, generators, etc) which enabled to set-up the injection points away from roads. In contrast, a three-day bromide injection experiment at Bates' Farm would have required approximately 11,500 L of brine and a pumping system capable of delivering at least 160 L h^{-1}. On the other hand, unlike solute and dye injection, it was not possible to assess the progress of the SF$_6$ injections in the field. Thus, a further improvement to the technique would be to measure SF$_6$ concentration in the field continuously using a Portable GC system. Further improvements could also be made to sampling for SF$_6$ in the hyporheic zone. The use of smaller tubing connected to a larger wellhead could be use to reduce the volume of water that needs to be purged from mini-piezometers, without increasing the chances of clogging by fine sediments. The volume of hyporheic water sampled could also be reduced by half without unduly compromising the precision of the SF$_6$ analyses.

The main advantage of ^{222}Rn disequilibrium technique is that it is a simple method to estimate hyporheic water residence times *in situ*, without the need of injected tracers. It could be used to independently validate hyporheic water residence times estimated with injected tracers, or to gain some understanding of the variability in hyporheic exchange within a given study reach. The disadvantages of the ^{222}Rn disequilibrium technique are that it can only measure hyporheic water residence times over a restricted range (hours to days) and

may not be applicable in cases where mixing of surface and regional groundwater occurs in the hyporheic zone.

7. References

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