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Identifying the contribution of regional groundwater to the baseflow of a tropical river (Daly River, Australia)

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summary

A mixture of older regional-scale groundwater flow and relatively modern local-scale groundwater was identified as the source of baseflow to a perennial river in a tropical savanna. Multiple environmental tracers, including ^{222}Rn , CFCs, SF_6 , and ^4He were measured in the river, groundwater, and springs along a 60 km segment of the Daly River in the Northern Territory of Australia. At the location where a group of springs intersected the river, groundwater discharge contained elevated ^4He and very low concentrations of CFCs and SF_6 . This influx of regional-scale groundwater could be detected at downstream locations in the river and was used to parameterize a one-dimensional model for estimating the groundwater discharge flux. Upstream and downstream of the springs, the source of baseflow is composed of waters containing SF_6 and CFCs from local-scale groundwater sources adjacent to the river. Within 1 km of the river, a redox fence was detected, with reducing conditions leading to degradation of CFCs that could have masked detecting the contribution of local-scale sources. This study confirmed the applicability of a new technique using ^4He to identify regional-scale groundwater flow contributions to rivers, and demonstrated that multi-tracer studies are needed to identify the locations, rates, and sources of baseflow.

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1. Introduction

Determining the groundwater contribution to a river system is a fundamental part of developing conceptual models of water cycling in catchments. Baseflow is integral to both the hydrological and ecological functions of a river system, often supplying the necessary environmental conditions to sustain in-river aquatic habitat and a suitable near-river ecologic state during dry seasons or drought (Hayashi and Rosenberry, 2002). Quantifying the linkage between groundwater and river systems, through characterization of baseflow rates, the locations of groundwater discharge, and the sources of baseflow are essential for water resource planning. However, despite the need to understand contributions from baseflow and its sources, there has been insufficient research on (i) the mechanisms responsible for baseflow, and (ii) development of consistent methods that would allow comparison across different regions (Price, 2011).

The baseflow contribution to rivers is driven by release from groundwater storage, and can be manifested as either diffuse seepage through the riverbed or as discrete flow at locations where springs discharge. Diffuse seepage can include many sources of water: riverbank storage and interaction with alluvial floodplain sediments (Rorabaugh, 1964; Doble et al., 2012); drainage from hillslopes adjacent to the river (Freeze, 1972; Kirkby, 1988); and, contributions from deeper groundwater (Tóth, 1963; Gleeson and Manning, 2008; Frisbee et al., 2011). Similarly, discharge from springs may originate within a catchment (e.g., Ellins et al., 1990), or from an external basin (e.g., Solomon et al., 2010). Thus, variable water sources for baseflow can be expected, and methods for characterization have been

challenged not only to define rates and locations, but also to begin defining flow-weighted mixtures of groundwater spanning different time scales (e.g., Stolp et al., 2010; Solomon et al., 2010).

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Characterization of baseflow has focused on quantifying groundwater discharge rates and

locations using a myriad of hydrograph analyses or chemical and isotopic separation techniques, often at the outlet of a catchment (Hooper and Shoemaker, 1986; Smakhtin, 2001). Several in-river methods, including measurement of water chemistry (Tetzlaff and Soulsby, 2008; McCallum et al., 2012; Frisbee et al., 2012) and synoptic sampling of isotopic tracers (Cook et al., 2003; Gardner et al., 2011a) have begun to unravel the internal dynamics of a catchment that will lead to more comprehensive characterization. Different methods for characterization must be combined to expand the knowledge of groundwater discharge locations, rates, and residence times (McDonnell et al., 2010). For example, Gardner et al. (2011a) described a novel technique to separate the fractions of local-scale and regional-scale groundwater discharge to rivers by synoptically sampling a river for naturally occurring tracers (^{222}Rn and ^4He). These measured concentrations of tracers in the river were then modelled to estimate the total groundwater discharge and to separate local-scale and regional-scale discharge fractions. When combined with other methods to characterize groundwater discharge, an ability to scrutinize the source of baseflow for a given river system can be achieved. Such analyses are needed to refine conceptual models in many catchments and in order to facilitate improved water resource management.

In this paper, we demonstrate a method to identify the contribution of regional-scale groundwater discharge to a perennial river using a suite of environmental tracers (^{222}Rn , CFCs, SF_6 , and ^4He). We evaluate the applicability of the technique described by Gardner et al. (2011a), and further illustrate that redox conditions at the interface between surface water and groundwater may render specific environmental tracers (i.e., CFCs) unsuitable for detecting modern baseflow sources. Consideration of local-scale and regional-scale processes must be considered when defining baseflow sources. From samples collected in-river, directly from spring

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vents, and from groundwater at different points along the end of a subsurface flow path, we show that regional-scale groundwater discharge is a discrete, yet major water source for a perennial tropical river. The knowledge gained from identifying sources of baseflow and mixing between local- and regional-scale groundwater advances the conceptual understanding that is the foundation of quantitative models.

2. Study area

This study focused on a segment of the Daly River in the Northern Territory of Australia (Fig. 1) previously studied by Cook et al. (2003), who developed a method for estimating groundwater influx to surface water by sampling of ^{222}Rn and CFCs. The present study builds on this work by expanding the suite of tracers used to investigate the sources of baseflow and by sampling tracers from additional locations. In addition to sampling the river and springs, groundwater was sampled at observation wells that did not exist at the time of the study by Cook et al. (2003). Revisiting this tropical river system allowed the opportunity to test the applicability of the method described by Gardner et al. (2011a) and determine sources of baseflow in an environment where interaction with a regional aquifer was hypothesized to exist.

The Daly River is one of the largest perennial rivers of northern Australia, with a catchment area of approximately 53,000 km². The study area is characterized by a large inter-annual variability in rainfall, with an average annual total of 1020 mm and approximately 95% (975 mm) occurring in the wet season between November and May. Coinciding with the wet season is a period of high potential evapotranspiration (1015 mm; approximately 52% of annual potential evapotranspiration); classifying the region as water-limited on an annual basis (i.e., tropical savanna, or Aw in the Köppen–Geiger climate classification). Annual river flows are dominated by wet season rain events and dry season flows represent a small portion of the total annual flow (Fig. 2). Dry season flows, however, are dominated by groundwater discharge, which occurs regardless of the previous season's river flow or rainfall. Groundwater discharge in the dry season (referred to as low flow in this study) occurs through numerous discrete springs and diffuse seepage zones that have been mapped in the region (Tickell, 2002). The combination of springs and seepage increase the Daly River low flow by approximately 2.5 times in the study area, supporting a diverse aquatic ecosystem (Blanch et al., 2005) that is of central importance to the local indigenous culture (Jackson, 2004).

The Daly River catchment is underlain by the Cambrian–Ordovician Daly Basin, which is composed of four distinct layers. From the bottom to top of the Daly Basin, these are the Tindall Limestone aquifer, the Jinduckin Formation (siltstone and mudstone aquitard), the Ooloo Dolostone aquifer (differentiated into upper and lower units), and the Florina Formation. The Ooloo Dolostone aquifer (Fig. 1) is a significant groundwater resource and supplies approximately 5 GL/year of water for irrigated horticulture. There is increasing pressure to further develop this resource, which is licensed for 25 GL/year. Balancing the apparent competition between the environment and agriculture for groundwater resources will rely on characterizing sources of baseflow for the Daly River.

3. Methods

3.1. Sampling and analytical methods

Field investigation focused on locations where a major spring zone intersected the Daly River (Fig. 3), and utilized a suite of environmental tracers to identify the location of groundwater discharge (^{222}Rn) and differentiate modern versus old water (CFCs, of major spring zones along the Daly River are highlighted and shown with the extent of the uppermost aquifers in the Daly Basin. The study area is outlined with a dashed line and shown on Fig. 3. Fig. 2. Mean daily flow of the Daly River measured at the gauging station (0 km) shown on Fig. 3. Vertical dashed lines indicate the sampling times in November 2009 and May 2010.

SF_6 , ^4He). In this study, multiple tracers have been used, each having a different

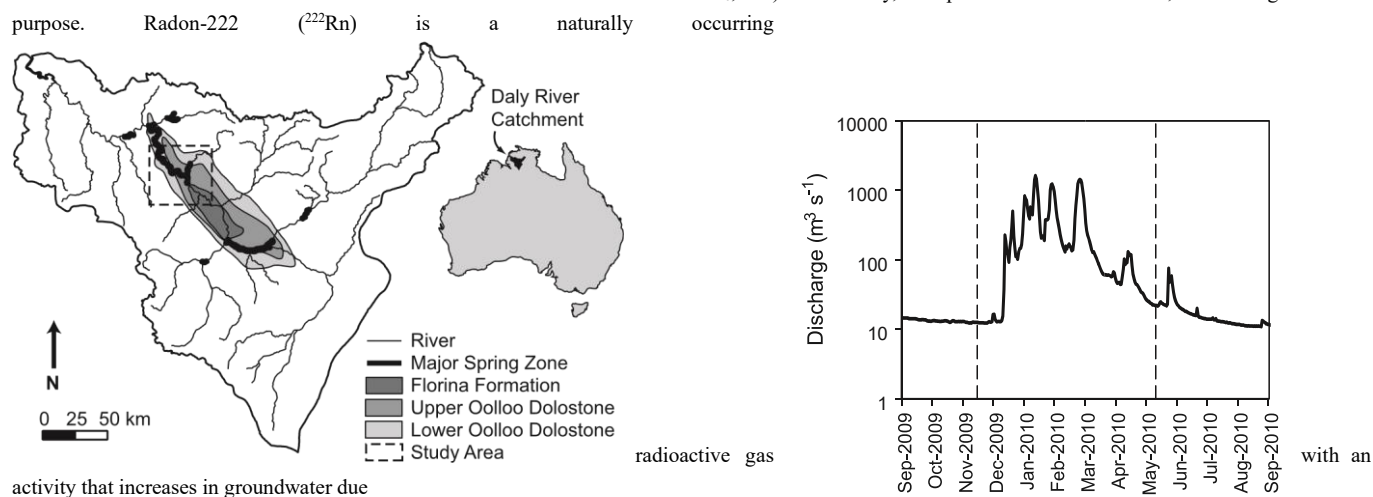


Fig. 1. The Daly River catchment in the Northern Territory of Australia. The location

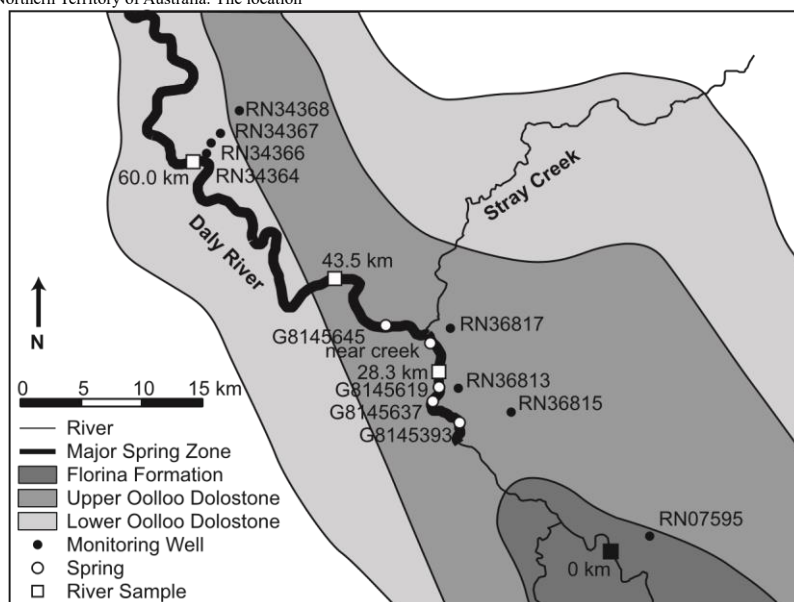


Fig. 3. Location of groundwater, spring, and river sampling sites for the study area outlined in Fig. 1.

to the decay of uranium and radium in aquifer materials, and rapidly decreases where it equilibrates with the atmosphere. These characteristics allow ^{222}Rn to be a useful tracer for identifying groundwater discharge to surface water (e.g., Ellins et al., 1990; Cook et al., 2003; Gardner et al., 2011a), but provides no information on subsurface residence times greater than a couple of weeks. An ability to quantify timescales associated with groundwater flow is provided by environmental tracers present in the atmosphere (e.g., CFCs, SF_6) and tracers that accumulate in groundwater over long periods (e.g., ^4He). CFCs and SF_6 have concentrations that have increased since the 1960s and allow identification of a modern component (i.e., decades) in surface water and groundwater. Helium-4 (^4He) is a non-radioactive noble gas that accumulates slowly in groundwater due to the decay of uranium in aquifer materials. These characteristics allow ^4He to be a suitable tracer for groundwater with a subsurface residence time of greater than 1000 year. By using a combination of environmental tracers that allow detection of water of different residence times, the approach of this study was to identify young water cycling through the shallow aquifer system and much older baseflow sources coming from a regional-scale groundwater flow system. In addition to the environmental tracers, redox indicators were assessed to determine whether a reducing environment could be degrading CFC concentrations. Field investigation made use of observation wells installed by the Northern Territory Government to monitor the Ooloo Dolostone aquifer (Fig. 3).

Water samples were collected from the observations wells and at three locations in the Daly River in November 2009 and analysed for ^{222}Rn , CFC-11, and CFC-12. November is the end of the dry season, and annual low flow gauging on the Daly River was completed by the Northern Territory Government in October 2009

explicit finite difference in a spreadsheet for the river length (60 km) shown in Fig. 3. For specified river dimensions and flow, tracer characteristics, and measurements of tracer concentrations in groundwater, a longitudinal profile of groundwater inflow was determined.

Model parameters were based on values measured in the present study (e.g., river geometry, tracer concentrations) and those reported by Cook et al. (2003) for the previous study of the Daly River (e.g., gas transfer velocity). The present study incorporates measured groundwater data heretofore unknown, an additional timeframe with a higher river discharge, and additional environmental tracers. Specific details of the hyporheic zone of the Daly River are unknown and difficult to measure given the annual flooding. However, Cook et al. (2006) found that exclusion of a hyporheic zone led to an overestimate of groundwater discharge. For this study a hyporheic zone of 1.0 m depth, 0.4 porosity, and having a residence time of 0.25 days was assumed. This assumption yielded a small amount of ^{222}Rn production along the length of river studied similar to Gardner et al. (2011a) and had no effect on other environmental tracers.

4. Results

4.1. ^{222}Rn

Radon activities are shown on Table 1. In groundwater samples, radon activities varied from 0.7 to 18.0 Bq/L, with mean values of 9.1 and 7.4 Bq/L for November 2009 and May 2010, respectively. Radon activity decreased from approximately 10 Bq/L in groundwater samples near the river to 5 Bq/L at distances greater than 1 km from the river. Radon activity measured at the spring vents was found to span a narrower range than groundwater collected

Sample Location		November 2009			May 2010			
		^{222}Rn (Bq L ⁻¹)	CFC-11 (pg kg ⁻¹)	CFC-12 (pg kg ⁻¹)	^{222}Rn (Bq L ⁻¹)	CFC-11 (pg kg ⁻¹)	CFC-12 (pg kg ⁻¹)	SF ₆ (pg kg ⁻¹)
Groundwater	RN07595	–	–	–	–	7	2	0.095
	RN36813	0.7	88	61	5.1	36	19	0.183
	RN36817	1.0	–	69	7.5	32	16	0.096
	RN34364	9.6	73	58	10.9	70	31	0.058
	RN34366	18.0	3	0	10.6	70	27	0.095
	RN34367	–	79	61	8.6	84	51	0.088
	RN34368	–	133	92	5.1	138	82	0.127
Daly River	28.3 km	3.3	181	110	1.3	243	117	0.159
	43.5 km	2.1	186	116	1.2	233	115	0.162
	60.0 km	1.2	209	125	0.7	–	127	0.175
Springs ^a	G8145393	–	–	–	13.2	14	6	0.001
	G8145619	–	–	–	7.9	25	15	0.026
	Near creek	–	–	–	17.3	48	36	0.054
	G8145645	–	–	–	15.9	50	47	0.089

^a Springs were not sampled in November 2009.

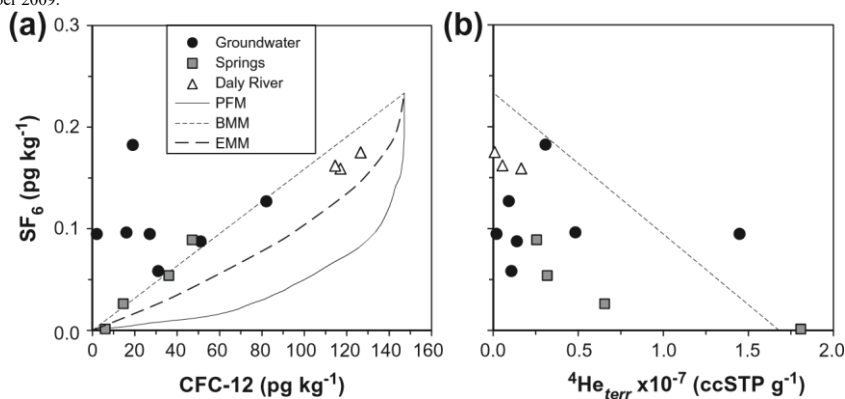


Fig. 4. Tracer plots of (a) SF₆ versus CFC-12 and (b) CFC-12 versus terrigenous helium (⁴He_{terr}). Data are plotted relative to the hypothetical mixing models for piston flow (PFM), a binary mixture (BMM), and an exponential mixture (EMM).

from the monitoring wells, varying from 7.9 to 17.3 Bq/L. In the Daly River, radon activities were found to increase in the downstream direction of the study area, with higher activities (1.2–

3.3 Bq/L) in November 2009, compared with May 2010 (0.7–1.3 Bq/L). The observed trend and activities for November 2009 were approximately the same as those measured by Cook et al. (2003) for similar sampling locations in 2001.

4.2. CFCs and SF₆

Measured concentrations of CFC-11, CFC-12, and SF₆ are shown on Table 1. CFC concentrations varied from below lab detection limits (25 and 20 pg/kg for CFC-11 and CFC-12) to 243 pg/kg for CFC-11 and 127 pg/kg for CFC-12. Groundwater samples within 1 km of the Daly River and a sample from an observation well completed up-gradient and deep in the Ooloo Dolostone (RN07595; Fig. 3) had CFC-12 concentrations less than 30 pg/kg. Groundwater discharge at the spring vents was less than 50 pg/kg for CFC-11 and CFC-12. Samples collected from the Daly River were on the order of 180 and 120 pg/kg for CFC-11 and CFC-12 in November 2009, and 240 and 120 pg/kg for CFC-11 and CFC-12 in May 2010.

SF₆ was only sampled in May 2010 and concentrations in the groundwater varied from 0.058 to 0.183 pg/kg with a trend of increasing concentration with increasing distance away from the Daly River. Samples collected at spring vents were found to contain between 0.001 and 0.089 pg/kg SF₆, and concentrations in the Daly River were found to vary from 0.159 to 0.171 pg/kg.

The concentrations of CFC-12 and SF₆ are shown on a bivariate plot (Fig. 4a) that includes hypothetical mixing models often used

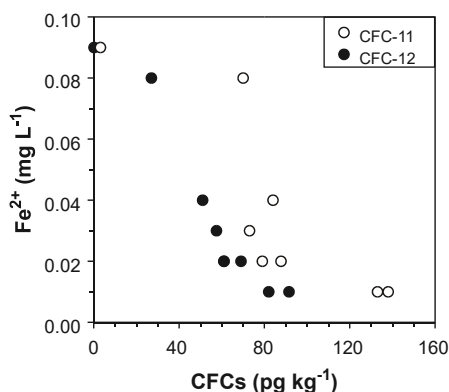


Fig. 5. Concentration of dissolved iron (II) versus CFCs for groundwater samples.

to explain observed concentrations of environmental tracers (Solomon et al., 2010; Gardner et al., 2011b): the binary mixing model (BMM), which represents sampled water that is a mixture of two end members (i.e., modern and very old); an exponential mixing model (EMM), which represents sampled water that contains an exponential distribution of groundwater travel times; and, the piston flow model (PFM), which represents sampled water that has not mixed by hydrodynamic dispersion during transport.

4.3. Fe²⁺

Concentrations of dissolved Fe²⁺ were 0.01–0.02 mg/L in groundwater sampled further than 1 km from the Daly River. At distances less than 1 km from the river, Fe²⁺ concentrations in groundwater samples increased to 0.09 mg/L. Fe²⁺ data are shown on Fig. 5 and plotted with CFC concentrations. Measured Mn²⁺ concentrations follow a similar result and have not been presented for brevity.

4.4. Noble gases

Measured concentrations of dissolved noble gases and N₂, calculated ⁴He_{terr}, and fractionation factors are shown on Table 2. The concentrations of ⁴He_{terr} are within the range of 1.9e-9 and 1.4e-7 ccSTP/g for groundwater. Samples collected from the springs had higher ⁴He_{terr} concentrations, in the range of 2.5e-8 to 1.8e-7 ccSTP/g. In-river ⁴He_{terr} concentrations were found to be between 8.5e-10 and 1.6e-8 ccSTP/g.

Concentrations of ⁴He_{terr} are shown on a bivariate plot with SF₆ (Fig. 4b). Similar to the plot for modern environmental tracers (Fig. 4a), the BMM is shown for modern and very old end members of groundwater observed in this study. To plot the BMM for ⁴He_{terr}, a helium production rate was assumed. Given average crustal U and Th composition, the steady-state production rate of ⁴He is approximately 1:7 lccSTP=m³_{aquifersolid}=year (Solomon, 2000). Assuming a porosity of 0.3 and complete transfer from the rock to the aqueous phase the production rate in groundwater is approximately 4lccSTP=m³_{water}=year, and the time needed for ⁴He_{terr} concentrations to equal the atmospheric ⁴He concentration is 10,000 years.

As shown on Table 2 and Fig. 6a, F(²⁰Ne) was relatively close to 1, F(⁴He) for groundwater samples varied from 1 to 2, and F(⁴He) for the springs varied from 1.5 to 4.7. Furthermore, a comparison of ⁴He_{terr} and F(⁴He) indicated a good correlation (Fig. 6b), implying that F(⁴He) would be suitable for modelling of groundwater discharge rather than modelling the low concentration values.

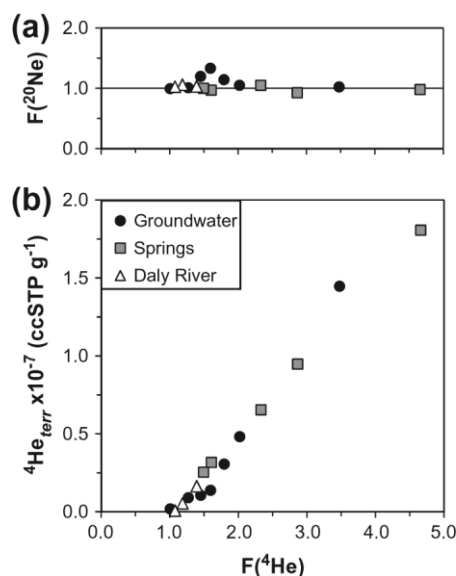


Table 2

Dissolved noble gas and N_2 concentrations, calculated terrigenous helium concentrations, and fractionation factors $F(^4\text{He})$ and $F(^{20}\text{Ne})$ for May 2010.

Sample location		4	20	40	N_2 (ccSTP g ⁻¹)	4	$F(^4\text{He})$	$F(^{20}\text{Ne})$
		He (ccSTP g ⁻¹)	Ne (ccSTP g ⁻¹)	Ar (ccSTP g ⁻¹)		He_{terr} (ccSTP g ⁻¹)		
Groundwater	RN07595	2.0E-07	2.1E-07	3.3E-04	1.4E-02	1.4E-07	3.5	1.0
	RN36813	8.9E-08	2.0E-07	2.8E-04	1.2E-02	3.1E-08	1.8	1.1
	RN36817	1.0E-07	1.9E-07	2.8E-04	1.2E-02	4.8E-08	2.0	1.0
	RN34364	7.4E-08	2.2E-07	3.0E-04	1.3E-02	1.1E-08	1.5	1.2
	RN34366	4.9E-08	1.7E-07	2.8E-04	1.1E-02	1.9E-09	1.0	1.0
	RN34367	8.5E-08	2.5E-07	3.1E-04	1.2E-02	1.4E-08	1.6	1.3
	RN34369	5.3E-08	1.6E-07	2.6E-04	7.1E-03	9.1E-09	1.3	1.0
Daly River	28.3 km	6.6E-08	1.8E-07	2.9E-04	1.3E-02	1.6E-08	1.4	1.0
	43.5 km	6.1E-08	2.0E-07	3.1E-04	1.4E-02	5.4E-09	1.2	1.1
	60.0 km	5.2E-08	1.8E-07	2.9E-04	1.4E-02	8.5E-10	1.1	1.0
Springs	G8145393	2.3E-07	1.6E-07	2.6E-04	1.0E-02	1.8E-07	4.7	1.0
	G8145637	1.4E-07	1.6E-07	2.6E-04	9.9E-03	9.5E-08	2.9	0.9
	G8145619	1.2E-07	1.9E-07	2.9E-04	1.2E-02	6.5E-08	2.3	1.0
	Near creek	7.7E-08	1.7E-07	2.8E-04	1.1E-02	3.2E-08	1.6	1.0
	G8145645	7.5E-08	1.8E-07	2.8E-04	1.1E-02	2.5E-08	1.5	1.0

Fig. 6. (a) Noble gas fractionation factors for ^{20}Ne and ^4He relative to water in equilibrium with the atmosphere. (b) Terrigenous helium ($^4\text{He}_{\text{terr}}$) calculated from a closed equilibrium model versus fractionation factor for ^4He . $F(^4\text{He})$ greater than 1 (e.g., springs) indicate increased concentration with travel time, revealing a component of regional-scale groundwater.

4.5. Groundwater discharge modelling

Modelling was completed for low flow conditions during November 2009 (10.2 m³/s) and the May 2010 sampling period at higher flow conditions (22.0 m³/s). The groundwater discharge was modelled by achieving a visual best-fit for measured in-river environmental tracer concentrations (^{222}Rn , CFC-12, SF_6 , and $F(^4\text{He})$) by adjusting the rate of groundwater inflow. Groundwater inflow concentrations were specified from values measured (Tables 1 and 2). Each tracer used in this study was used for a different purpose: ^{222}Rn identified inflow locations, CFC-12 and SF_6 identified modern water sources, and ^4He identified older regional-scale sources. Modelled groundwater discharge, reported here as m³ per day, per linear m (m³/d/m), is the result of balancing the estimated groundwater inflow rate, measured concentrations of environmental tracers, and an approximation of in-river processes (e.g., evaporation, gas exchange, and ^{222}Rn production in the hyporheic zone).

Local-scale groundwater inflow was assigned a ^{222}Rn activity of

4 Bq/L, CFC-12 concentration of 25 pg/kg, SF_6 concentration of

0.08 pg/kg, and $F(^4\text{He})$ of 1. Where regional-scale groundwater inflow occurred, corresponding to the location of a major spring zone between 26 and 32 km on Fig. 3, inflow was assigned a ^{222}Rn activity of 12 Bq/L, CFC-12 and SF_6 concentrations of 0 pg/kg, and $F(^4\text{He})$ of 4. The remaining parameters for the groundwater discharge model are shown on Table 3.

Modelled and observed in-river concentrations of ^{222}Rn , CFC-12, SF_6 , and $F(^4\text{He})$ are shown on Fig. 7. The results of Cook et al. (2003) have been plotted for comparison and to help define the longitudinal profile of modelled river concentrations for ^{222}Rn and CFC-12. The modelled groundwater discharge was found to peak at the onset of the major spring zone, with inflow rates of 180 $\text{m}^3/\text{d}/\text{m}$ from 26 to 27 km, 120 $\text{m}^3/\text{d}/\text{m}$ from 27 to 29 km, and 50 $\text{m}^3/\text{d}/\text{m}$ from 29 to 32 km. Across the remainder of the study area, modelled groundwater discharge was found to be 10 $\text{m}^3/\text{d}/\text{m}$.

Across the major spring zone the majority of groundwater discharge (26–29 km) is entirely composed of a regional-scale source, which had $F(^4\text{He})$ of 4 and an absence of CFC-12 and SF_6 . At the downstream end of the major spring zone (29–32 km), the regional-scale source diminishes and there is a higher inflow rate of groundwater discharge that contains CFC-12 and SF_6 . The increase

Table 3
Parameters for the groundwater discharge model.

Symbol	Description	November 2009	May 2010
Q_0	River flow ($\text{m}^3 \text{s}^{-1}$)	10.2	22.0
E	Evaporation (mm d^{-1})	7	5
w	River Width (m)	50	55
d	River depth (m)	1.5	2.0
h	Hyporheic zone depth (m)	1.0	1.0
h	Hyporheic zone porosity	0.4	0.4
t_h	Hyporheic zone residence time (d)	0.25	0.25
c	Hyporheic zone ^{222}Rn production (Bq $\text{L}^{-1} \text{d}^{-1}$)	0.2	0.2
c0-RN	Initial ^{222}Rn activity	0.5	0.5
c0-CFC	Initial CFC-12 concentration (pg kg^{-1})	135	135
c0-SF6	Initial SF_6 concentration (pg kg^{-1})	–	0.15
c0-HE	Initial $F(^4\text{He})$	–	1.0
kRN	^{222}Rn gas transfer velocity (m d ⁻¹)	1.0	1.0
kCFC	CFC-12 gas transfer velocity (m d ⁻¹)	1.0	1.0
kSF6	SF_6 gas transfer velocity (m d ⁻¹)	–	0.9
kHE	$F(^4\text{He})$ gas transfer velocity (m d ⁻¹)	–	2.5
k	^{222}Rn decay (d ⁻¹)	0.181	0.181
Q_1	Tributary inflow at 32.8 km (Stray Creek; $\text{m}^3 \text{s}^{-1}$)	0.6	1.2
c1-RN	Tributary ^{222}Rn activity (Bq L^{-1})	1	1
c1-CFC	Tributary CFC-12 (pg kg^{-1})	135	135
c1-SF6	Tributary SF_6 (pg kg^{-1})	–	0.15
c1-HE	Tributary $F(^4\text{He})$	–	1.0

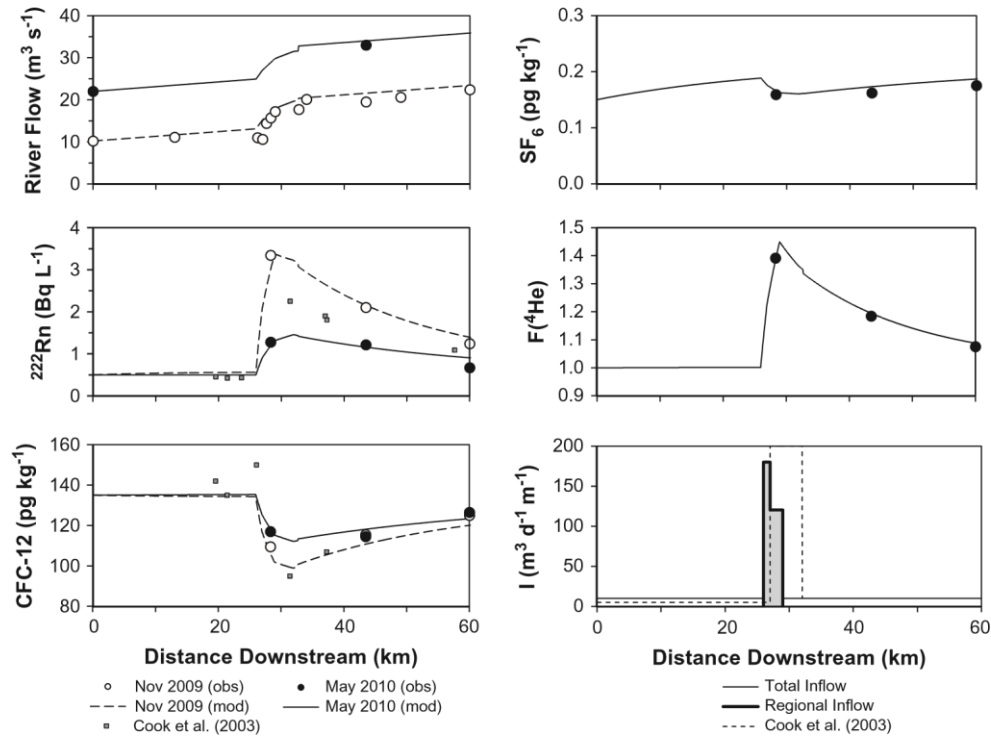


Fig. 7. Observed and modelled concentrations of environmental tracers in the Daly River for November 2009 and May 2010. Data from Cook et al. (2003) is shown for comparison of similar low flow conditions. Modelled groundwater inflow is illustrated by the total inflow and the portion sourced from regional-scale groundwater.

in river discharge measured between the gauging stations at 0 and 43.5 km was 900 ML/d in November 2009, and 950 ML/d in May 2010. The groundwater discharge modelling results indicate an increase of 940 ML/d across the same interval, with 420 ML/d originating from regional-scale sources. Over the river reach between these gauging stations, the fraction of groundwater discharge from regional-scale sources is 45%.

5. Discussion

Concentrations of $^4\text{He}_{\text{terr}}$ were found to be elevated in deeper groundwater in the Daly Basin, in groundwater discharge occurring at the major spring zone, and in the Daly River downstream of the major spring zone. Stolp et al. (2010) noted that tracer concentrations measured in-river are related to inflow rate and subsequent losses, and Gardner et al. (2011a) further defined the following ratio when sampling for helium in rivers:

$$\frac{F \delta^4\text{He}_{\text{eq}}}{\delta^4\text{He}_{\text{eq}}} \times \frac{1}{\text{km}_{\text{gw}}} \quad \delta^4\text{He}_{\text{eq}}$$

where a ratio greater than 0.05 would be sufficient to detect elevated $^4\text{He}_{\text{terr}}$ concentrations in a river. Across the major spring zone on the Daly River, $F(^4\text{He})$ values were approximately 4 for groundwater discharge, corresponding to an indicator ratio between 3.5 and 5.2 given the modelled rates of groundwater inflow. These findings suggest that the technique described by Gardner et al. (2011a) is applicable where regional-scale groundwater discharge rates are large and have a moderate $^4\text{He}_{\text{terr}}$ concentration. When these results are plotted in relation to the geologic formations present in the Daly Basin (Fig. 8a), it is observed that groundwater elevated in $^4\text{He}_{\text{terr}}$ converges to the major spring zone (Fig. 8d). This location is coincident with the upper portion of the Ooloolo Dolostone that outcrops with the Daly River (Fig. 8a). Downstream of the spring zone a decrease in elevated $^4\text{He}_{\text{terr}}$ was observed in springs and groundwater, clearly indicating that regional-scale groundwater discharge from the Ooloolo Dolostone is a major source of baseflow to the Daly River.

When our findings are compared with those of Cook et al. (2003) for the same segment of the Daly River, the current study found a similar spatial pattern but slightly lower rates for groundwater discharge (Fig. 7). In the current study, we have attempted to constrain the concentration of groundwater inflow by sampling groundwater at various points along the end of the groundwater flow system (Fig. 8b–d), and including a hyporeic zone in the discharge modelling. These refinements have resulted in a slightly lower modelled groundwater discharge rate, as expected. The modelled groundwater discharge rates depend on synoptic in-river sampling, which in-turn requires consideration of the length scale. Cook et al. (2006) describe the length scale as an acceptable distance between tracer input to a river and subsequent equilibration with the atmosphere occurring downstream, with the following definition:

$$\frac{Q}{x \times \frac{1}{\text{km}}} \quad \delta^5\text{P}_{\text{kw}} \text{ p dwk}$$

Upstream of the major spring zone in this study, the length scale for ^{222}Rn and ^4He were 27.2 and 14.8 km, respectively. Downstream of the major spring zone, the length scales increased to 40.7 and 22.2 km for ^{222}Rn and ^4He because of higher flow of the Daly River caused by groundwater discharge. This study benefited from previous groundwater discharge modelling by Cook et al. (2003) and a priori knowledge of the groundwater discharge zone location. Downstream of the major spring

zone, the in-river sample spacing was approximately 15 km, which is less than the length scale; however it should be noted that additional in-river sampling would be required to identify location of groundwater discharge without a priori knowledge.

Detection of a regional-scale source of baseflow may have implications for use of other environmental tracers. Well defined

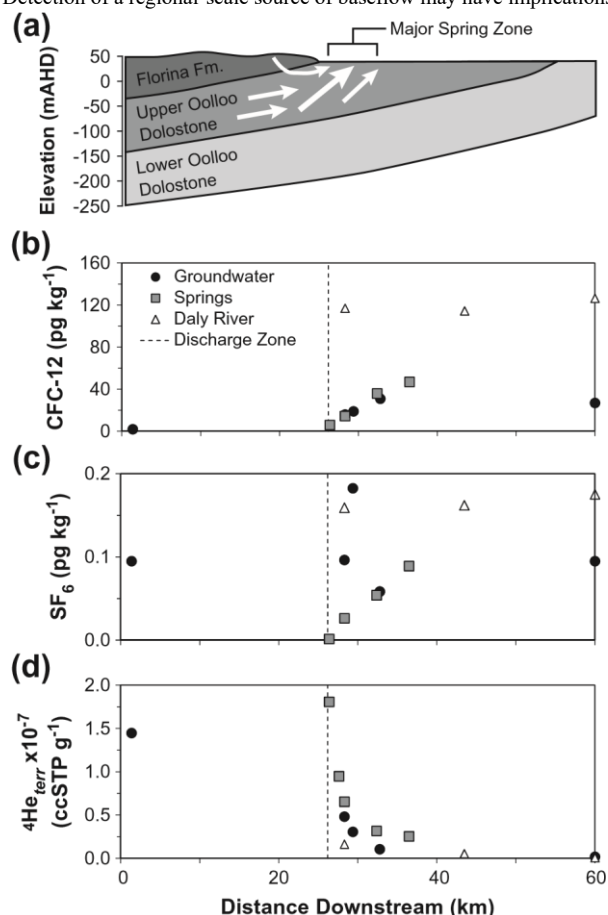


Fig. 8. (a) Illustrative cross section of the major spring zone and uppermost aquifers of the Daly Basin shown with concentrations of environmental tracers (b–d) in groundwater, springs, and the Daly River.

time varying concentrations in the atmosphere have made CFCs an ideal transient environmental tracer in hydrology (Busenberg and Plummer 1992; Cook et al., 1995) that have been used when determining groundwater interaction with rivers. However, several studies have found that subsurface conditions may promote degradation, which restricts CFC use for age determination and in mixing models. Degradation of CFCs in anaerobic conditions can occur naturally (Lovely and Woodward, 1992; Semprini et al., 1992) and will either limit the applicability of use as a tracer or worse, complicate interpretation if degradation is not considered. Cook et al. (1995), Oster et al. (1996), and Horneman et al. (2008) demonstrate the effects of degradation on assessment of dating modern groundwater in a variety of geologic environments and climate regions. In the current study we observe that CFC degradation appears to be occurring within 1 km of the Daly River. When compared with SF₆, there is a discrepancy observed for CFC-12 in the groundwater samples that is not observed for water samples collected from the springs (Fig. 4a). When CFC concentrations are compared to Fe²⁺, a correlation is apparent between low CFC concentrations and elevated Fe²⁺ (Fig. 5), as suggested by Oster et al. (1996). These findings are similar to those of Happell et al. (2003), who found that CFC degradation could occur at the interface of surface water and groundwater. At this interface, bacteria may be present to promote reducing conditions; however, in the current study there is insufficient evidence to indicate exactly which reduction process is occurring. However, CFC degradation appears to have occurred, which would lead to a misinterpretation in the absence of other environmental tracers.

For suspected anaerobic conditions, Hinsby et al. (2007) advocated use of multiple tracers in groundwater age studies. On a plot with hypothetical mixing models (Fig. 4a), there is apparent agreement between SF₆ and CFC-12 for samples collected from the springs when a BMM is considered. Agreement of SF₆ and CFC-12 can often be found for one of the hypothetical mixing models (e.g., Gooddy et al., 2006; Solomon et al., 2010). However, we found that groundwater samples with low CFC-12 concentrations and relatively higher Fe²⁺ appeared to have SF₆ concentrations that could not be explained by any of the hypothetical mixing models. Combined with other results of the current study, this suggests that a mixing process is occurring in conjunction with reducing conditions in close proximity to the Daly River. The major springs are a terminus for a regional-scale groundwater flow system in the Ooloo Dolostone. Baseflow sourced from the regional-scale groundwater is composed of almost entirely of old water, with elevated ⁴He concentrations. Subsequent springs in the downstream direction are located within the terminus for regional-scale flow but also contain a small fraction of younger water. The remainder of the study reach has a minor amount of baseflow that originates from local-scale groundwater. These sources of baseflow for the Daly River are composed of waters with varying travel times, similar to the findings of Solomon et al. (2010) for a river in Costa Rica. However, additional investigation of groundwater conditions in the current study reveals that the local-scale groundwater appears to have a redox fence near the river, where reducing conditions are present within 1 km of the river and diminish use of CFCs for quantifying the young water. These factors demonstrate that multiple-tracer studies contribute to a better understanding of baseflow sources and the mixing between local- and regional-scale groundwater.

6. Summary and conclusion

A suite of environmental tracers (^{222}Rn , CFCs, SF_6 , and ^4He) was used to identify the sources of baseflow for a perennial river in a tropical savanna climate region. The presence of a redox fence within 1 km of the river complicates interpretation of the CFC results because CFC degradation may occur in this zone. Waters sampled directly from the springs do not appear to have been affected by CFC degradation, suggesting that the source is different than waters entering the river by diffuse seepage. Baseflow contribution from diffuse seepage is hypothesized to have undergone a CFC degradation process that may be related to iron reduction in the riparian zone. Detection of elevated ^4He from a deep portion of the geologic basin and in waters discharging from a group of springs clearly indicates a regional-scale groundwater source. Elevated ^4He

He concentrations that were measured at the terminus of an extensive dolostone aquifer are indicative of relatively long travel times, on the order of 10,000 year. Upstream and downstream of the springs, the source of baseflow is composed of waters containing SF_6 and CFCs, indicating a younger, local-scale groundwater source that can mix with the regional-scale source. Over the entire 60 km segment of river studied, we conclude that 45% of baseflow originated from a regional-scale source. Multiple sources of baseflow, having different residence times provides important information for characterizing and managing catchment water resources. In order to identify multiple sources of baseflow and waters having different residence times, multiple tracers are needed to develop a conceptual understanding of water cycling in a catchment. The multiple tracer method demonstrated for part of a catchment in this study has the potential for application across different regions and for catchments of different scales. The approach provides a means to quantify groundwater discharge occurring at different spatial scales through sampling of environmental tracers, which will respond to changes within a catchment at differing timeframes.

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