



Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers

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Abstract

Measurements of ²²²Rn, CFC-11, CFC-12, major ions and temperature of river water and springs are used to quantify rates of groundwater inflow to a tropical lowland river in the Northern Territory of Australia. Groundwater inflow results in increases in ²²²Rn concentrations within the river, but decreases in concentrations of CFC-11 and CFC-12, because the inflowing groundwater is relatively old. ²²²Rn, CFC-11 and CFC-12 concentrations are affected by gas exchange with the atmosphere, while ion concentrations are not. Additionally, CFC concentrations in the river appear to have been increased by air entrapment and dissolution during turbulent flow at river rapids. Because the regional groundwater is old, CFC concentrations in groundwater inflow are zero. In contrast, ²²²Rn and ion concentrations in the river are very sensitive to concentrations of these tracers in groundwater inflow. Numerical simulation of ²²²Rn, CFC-11 and CFC-12 stream concentrations allows the groundwater inflow rate, gas transfer velocity and air entrapment coefficient to be reasonably accurately constrained.

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1. Introduction

Measurement of groundwater discharge to rivers is important for calculation of groundwater balances, for determining sustainable limits of groundwater extraction and for protecting environmental flows of rivers. Environmental tracer methods have been used for this purpose for the past few decades. They offer advantages over physically-based methods (seepage meters, river flow gauging) in that they can potentially

provide more accurate information on the spatial distribution of groundwater inflows with a much lower investment of resources. An environmental tracer will be useful for estimating groundwater inflows to rivers when the concentration of the tracer in groundwater is relatively uniform and significantly different to that in the river. One of the most powerful tracers for this purpose is radon (²²²Rn). With a half-life of 3.8 days, radon is produced in the subsurface by the radioactive decay of uranium-series isotopes. After groundwater containing radon discharges to surface water bodies, radon concentrations decrease due to gas exchange with the atmosphere and

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radioactive decay. High radon concentrations are, therefore, present in surface waters only in the immediately vicinity of points of groundwater inflow, and for relatively short distances downstream of such locations. Of course, if only a single tracer is used, accurate estimation of groundwater inflow will be heavily dependent on accurate determination of the end-member concentrations, and on accurate estimation of the gas exchange rate. While ionic tracers are not subject to decay or gas exchange, changes in groundwater inflow rates will not necessarily cause changes in streamflow concentrations. Moreover, biogeochemical reactions can modify concentrations of most ions. Changes in temperature provide a useful qualitative indicator, but quantification of inflows from temperature changes usually requires sophisticated modelling of river heat budgets (Evans et al., 1998).

In this paper, we show that variations in chlorofluorocarbon (CFC) concentrations within streams can also be used to quantify rates of groundwater inflow. CFCs are man-made organic compounds whose concentration in the atmosphere increased rapidly between the 1950s and 1990s. Because they are soluble in water, concentrations of CFCs in groundwater samples have been used to obtain estimates of groundwater age (Busenberg and Plummer, 1992). Provided that the groundwater is more than 10 years old, then the concentration of CFCs in the groundwater will be significantly less than that of water in equilibrium with the atmosphere. Concentrations of ^{222}Rn , CFC-11, CFC-12, major ions and temperature have been measured on the Daly River, Northern Territory, Australia, and on springs and small streams discharging to the river. Measurements have been made on three occasions over a period of 13 months, and these have been analysed using a numerical flow model that simulates longitudinal chemistry profiles as a function of groundwater inflow, evaporation, exchange of dissolved gases with the atmosphere, bubble entrapment during turbulent flow at river rapids, and radioactive decay. River flow data have been collected and used to help constrain the geochemical interpretations. The combination of ^{222}Rn , CFC-11, CFC-12 and river gauging data allows model parameters to be tightly constrained.

2. Theory

Changes in solute load within a stream receiving groundwater inflow can be expressed

$$\frac{\partial Qc}{\partial x} = Ic_i + kw(Sc_a - c) - \lambda dwc \quad (1)$$

where c is the concentration within the stream, c_i is the concentration in groundwater inflow, c_a is the atmospheric mixing ratio in the case of gaseous tracers (cm^3/cm^3), S is the tracer solubility, Q is the stream flow rate (m^3/day), I is the groundwater inflow rate per unit of stream length ($\text{m}^3/\text{m}/\text{day}$), k is the gas transfer velocity across the water surface (m/day) (zero for tracers that do not exchange with the gas phase), λ is the radioactive decay constant ($1/\text{day}$), w is the width of the river surface (m), d is the mean stream depth (m), and x is distance in the direction of flow. (Sc_a is the concentration of the tracer that would occur in equilibrium with the atmosphere. The units for S will be determined by the choice of units for c). (Surface water inflows can also be considered with this same equation, with I and c_i becoming surface water inflows and concentrations, respectively).

In the case of turbulent streams, gas exchange can also occur through the direct entrainment of air bubbles (Cirpka et al., 1993). In the simplest case, we assume that the entrapped air bubbles are completely dissolved, and contained atmospheric gases are incorporated into the stream. This process can be represented by inclusion of an additional term in Eq. (1). The change in concentration due to air entrapment and dissolution can be expressed

$$\frac{\partial Qc}{\partial x} = +k'w\rho c_a \quad (2)$$

where k' is the air entrapment coefficient ($\text{cm}^3/\text{cm}^2/\text{day}$) and ρ is the gas density (g/cm^3). In the present study, this additional term is only significant for CFC-11 and CFC-12, as ^{222}Rn has a negligible atmospheric concentration.

Change in flow with distance is simply given by

$$\frac{\partial Q}{\partial x} = I - Ew \quad (3)$$

where E is the evaporation rate (m/day), so that the equation for concentration with distance becomes

$$Q \frac{\partial c}{\partial x} = I(c_i - c) + wEc + kw(Sc_a - c) + k'wpc_a - dw\lambda c \quad (4)$$

The gas exchange process is usually modelled as a diffusion process through a surface water film. Gas transfer velocities for different tracers (a and b) are related by

$$\frac{k_a}{k_b} = \left(\frac{D_a}{D_b} \right)^n \quad (5)$$

where D is the tracer aqueous diffusion coefficient and n is a constant. Where the water surface is rough, a value of $n = 0.5$ is usually adopted (Clark et al., 1995).

3. Site description

The Daly River, located in the Northern Territory of Australia, drains an area of approximately 52,000 km². Its catchment comprises metamorphic and igneous rocks (granite, basalt) and fractured sedimentary rocks (sandstone, limestone, dolomite), mostly of Proterozoic and Paleozoic ages. The landscape is characterised by broad undulating landsurfaces of low relief, mostly inherited from long-term deep weathering (Chappell, 1993). In the study area (Fig. 1), the Daly River is deeply incised in the landscape, between 25 and 55 m Australian Height Datum (AHD), compared to altitudes of the order of 100–200 m AHD a few kilometres from the river. River chemistry is dominated by calcium carbonates and magnesium carbonates, produced by weathering of limestones and dolomites. The climate of the basin ranges from semiarid in the south (600 mm/year rainfall) to monsoonal at the mouth of the river (1500 mm/year rainfall). Within the study area, mean annual rainfall is approximately 1000 mm, with 90% of the annual rainfall occurring during the wet season (November–March). Mean annual air temperature is approximately 29 °C, and pan evaporation is 2900 mm/year.

The studied section of river is 117 km in length, and extends from the gauging station at Dorisvale to the Douglas River junction (Fig. 1). In this part of the watercourse, the Daly River has a gentle

meandering channel with small rapids, and a mean channel gradient of approximately 0.25 m per km. The monsoon climate results in high seasonal fluctuations in river flow (Fig. 2). Between January 2000 and December 2001, daily flow rates at Dorisvale varied between 8 and 6000 m³/s (Jolly, 2001). At the end of the dry season (September/October), the river width varies between 25 and 75 m, and the depth is mostly between a few centimeters and 3 m. The river would be entirely sustained by groundwater inflows at this time.

Within the studied section of the river, warm springs with a temperature of 35–36 °C occur as discrete seepage points from limestone aquifers to the river. Based on a mean annual air temperature of 29 °C and a mean regional geothermal gradient of 0.025–0.030 °C/m (Cull and Conley, 1983), spring waters may come from a depth of the order of 200–300 m. This is consistent with temperatures of 38 and 47 °C measured in nearby boreholes drilled to depths of 315 and 520 m, respectively. Elsewhere, spring water temperatures are lower and may reflect shallow groundwater inflow or return of bank storage that was recharged the previous wet season (Seasonal fluctuations in river flow can result in a rise of the river level of up to 20 m during the wet season; Jolly, 2001). Three small creeks enter the Daly River between Dorisvale gauging station and the Douglas River: Bradshaw Creek, Stray Creek, and Jinduckin Creek (Fig. 1). Although these creeks have not been gauged, their contribution to the Daly River at the end of the dry season is considerably less than that due to groundwater inflow.

4. Methods

Samples were collected for geochemical analysis during three sampling periods spanning a period of 13 months (19–21/09/2000, 4–6/09/2001 and 14–18/10/2001). Sampling was timed to coincide with the end of the dry season, when river flows were lowest. Most of the samples were collected from near the middle of the river using a small dinghy and submersible pump located ~0.5 m below the water surface. Measurements of dissolved oxygen, pH and electrical conductivity (EC) were made using a WTW Multiline P4 Universal Meter. Diurnal variations in

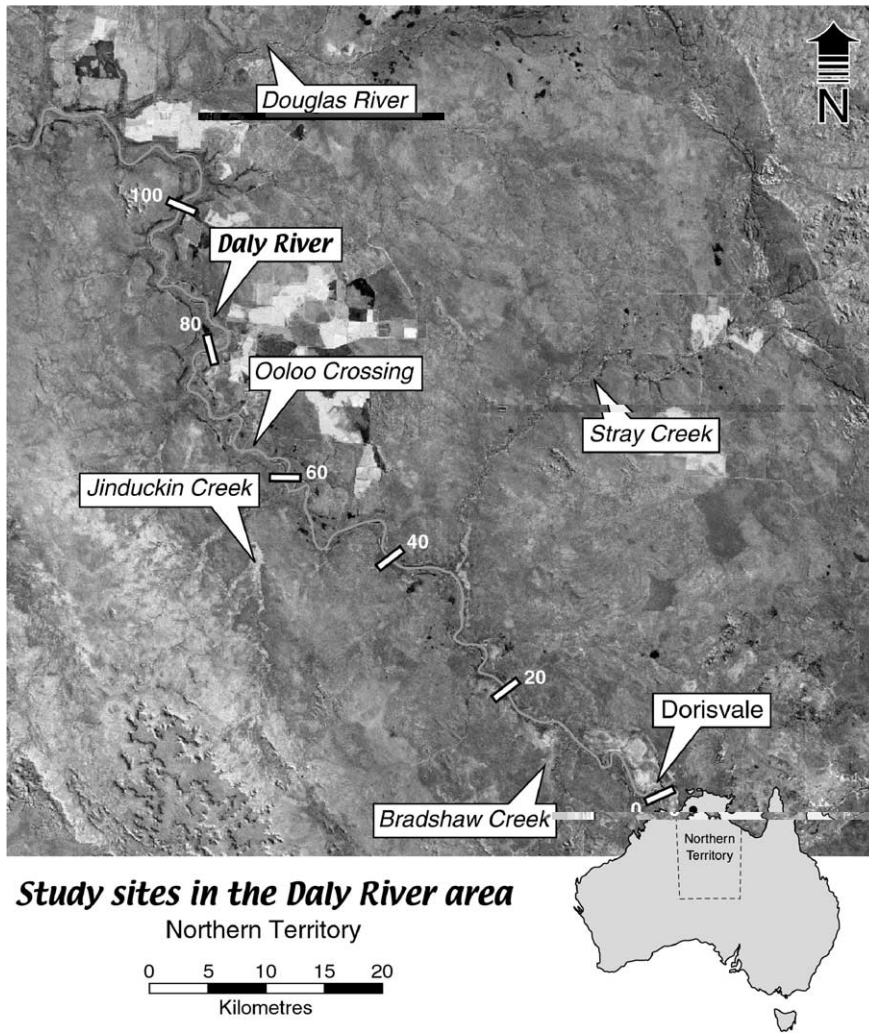


Fig. 1. Location map. Numerals denote river distances downstream of Dorisvale gauging station.

river temperature were measured over a 4 day period in October 2001, using DATAFLOW EC and temperature loggers. The exact location on the river was measured at the time of sampling with a GPS, and converted to the river distance by comparison with data from the second downstream trip when automatic recording of river coordinates was done at approximately 20 m intervals (River distance is determined along straightline distances between these measured coordinates). In this paper, all river distances are expressed downstream of the Dorisvale gauging station (Fig. 1).

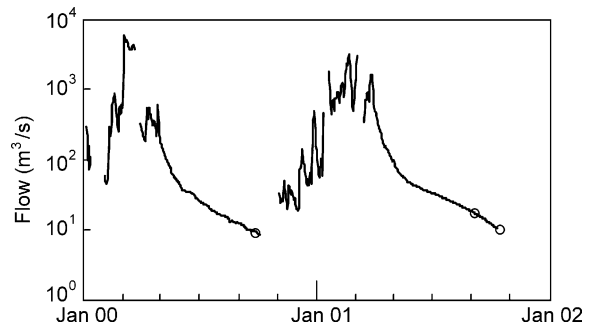


Fig. 2. Mean daily river flow for Dorisvale gauging station for calendar years 2000 and 2001. Circles denote river sampling times.

River samples were collected for analyses of EC, major ions, ^{222}Rn , CFC-11 and CFC-12. Major ion analysis was carried out on samples that had been filtered through a $0.45\ \mu\text{m}$ membrane filter. Cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and dissolved silica were analysed by ICP-ES while Cl^- and SO_4^{2-} were analysed by ion chromatography. Only Mg and Cl data is presented in this paper. Water samples for CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) analyses were collected during the third sampling trip, in October 2001. CFC samples were collected in copper tubes with an internal volume of $22\ \text{cm}^3$, sealed with metal pinch-off clamps. Analyses were performed by gas chromatography, using an electron capture detector (Busenberg and Plummer, 1992). For radon analyses, 950 ml water samples were collected in 11 teflon-coated separatory funnels, to which was added 20 ml of Packard NEN mineral oil cocktail from a 22 ml pre-weighed scintillation vial. The flask was shaken for 3 min to degas the radon and equilibrate it between the water–gas–scintillant phases. After allowing the scintillant to settle to the top of the inverted flask (about 1 min), the scintillant was returned to the vial, sealed and the time recorded. The vials were returned to Adelaide by courier for counting within 3 days of sample collection, and counted 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). Efficiency of radon extraction and counting was $49 \pm 2\%$. Radon concentrations are expressed in Becquerels of radioactivity per litre of water (Bq/l).

In addition to the permanent gauging station at Dorisvale (which records stage height, and calculates flow using a rating curve), a series of river gaugings have been made along the river using an impeller flowmeter. Fourteen gaugings were made between 3 and 19 October 2000, and a further four between 17 and 18 October 2001.

5. Results

5.1. Temperature

Diurnal variations in river temperature were measured at three locations over a 4 day period in October 2001 (Fig. 3). At two sites (river distance

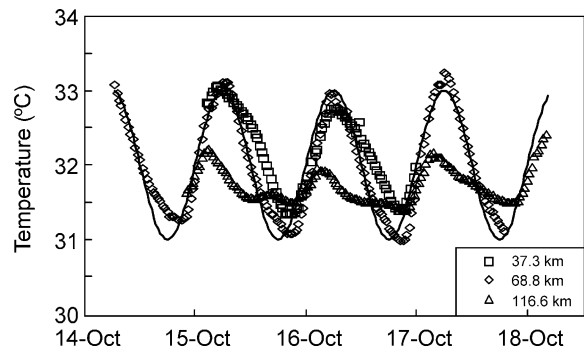


Fig. 3. Diurnal temperature variations of the river measured at three locations in October 2001 (The ticks on the x -axis denote 12:00 midday). The solid line depicts a sine-wave approximation to the 37.3 and 68.8 km data.

37.3 and 68.8 km), an approximate $2\ ^\circ\text{C}$ daily variation is apparent, with the maximum temperature recorded at approximately 6:00 p.m. each day. At 116.6 km (approximately 100 m upstream of the confluence with the Douglas River) much smaller temperature variations were observed, which is consistent with an increased river depth in this location (Tickell, 2002). The upstream data are more representative of the rest of the river.

Temperatures of springs and streams flowing into the Daly River are depicted in Fig. 4a. Spring temperatures are mostly between 25 and $31\ ^\circ\text{C}$, except for an area of warm springs with temperatures up to $36\ ^\circ\text{C}$ at 27–30 km. Fig. 5a shows longitudinal stream temperature measurements normalised to 12:00 midday temperatures using a sine-curve model fitted to the daily temperature data. Using this model, measured temperatures at 6:00 p.m. were reduced by $1\ ^\circ\text{C}$, measured temperatures at 3:00 p.m. were reduced by $0.7\ ^\circ\text{C}$, and measured temperatures at 9:00 a.m. were increased by $0.7\ ^\circ\text{C}$. Changes in normalised river temperature should primarily reflect groundwater inputs. A marked increase in stream temperature is apparent between 27 and 30 km on each sampling time. (The increase in temperature in October 2001 is less apparent than on other sampling times, because the river was warmer on this occasion, and hence the temperature contrast between the river and the springs was less). A decrease in stream temperature of 1 – $2\ ^\circ\text{C}$ is also apparent in September 2001 and October 2001 at approximately 68 km river distance.

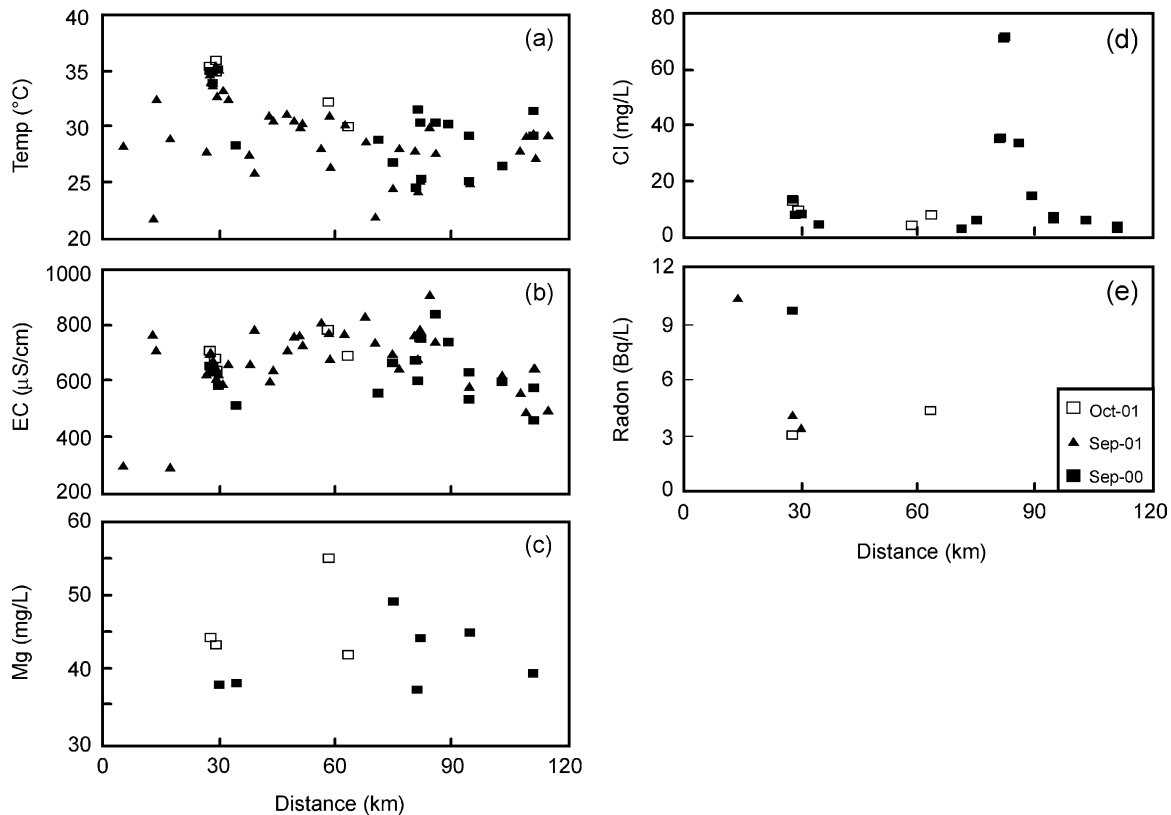


Fig. 4. Temperature, EC, magnesium, chloride and ^{222}Rn concentrations in springs flowing into the Daly River.

5.2. Electrical conductivity and ion chemistry

The EC of springs discharging into the Daly River ranges between 300 and 950 $\mu\text{S/cm}$ (Fig. 4b). Some spatial trends in spring EC are apparent, with lower values occurring downstream of 90 km. The EC of warm springs located between 27 and 30 km ranges between 583 and 708 $\mu\text{S/cm}$. The EC of river water increases downstream, with the most noticeable increase coinciding with the location of the warm springs (Fig. 5b). However, while the pattern of EC variation is similar at the three sampling times, the values show significant variation. Mg concentrations show a similar pattern of variation to EC.

Chloride represents a relatively small fraction of the total dissolved solids in waters within the study area (typically less than 6% of total anions). Chloride concentrations of springs and small streams entering the Daly River are less than

20 mg/l, except for a few small streams that enter the river between 80 and 86 km, which drain swampy ground, and show higher concentrations reflecting evaporative enrichment (Fig. 4d). River concentrations vary between 9 and 12.5 mg/l, and display a very different pattern of variation than EC or Mg (Fig. 5d). A marked decrease in concentration from 12.5 to 9.5 mg/l occurs between 26 and 32 km. An increase in concentration of ~ 2 mg/l between 80 and 88 km coincides with the area, where streams with high chloride concentrations enter the river.

5.3. Radon and chlorofluorocarbons

Radon concentrations measured in spring water range between 3 and 10 Bq/l (Fig. 4e). The increase in EC of the river between 27 and 30 km also coincides with an increase in ^{222}Rn (Fig. 5e). The ^{222}Rn concentration decreases rapidly after 30 km, due to

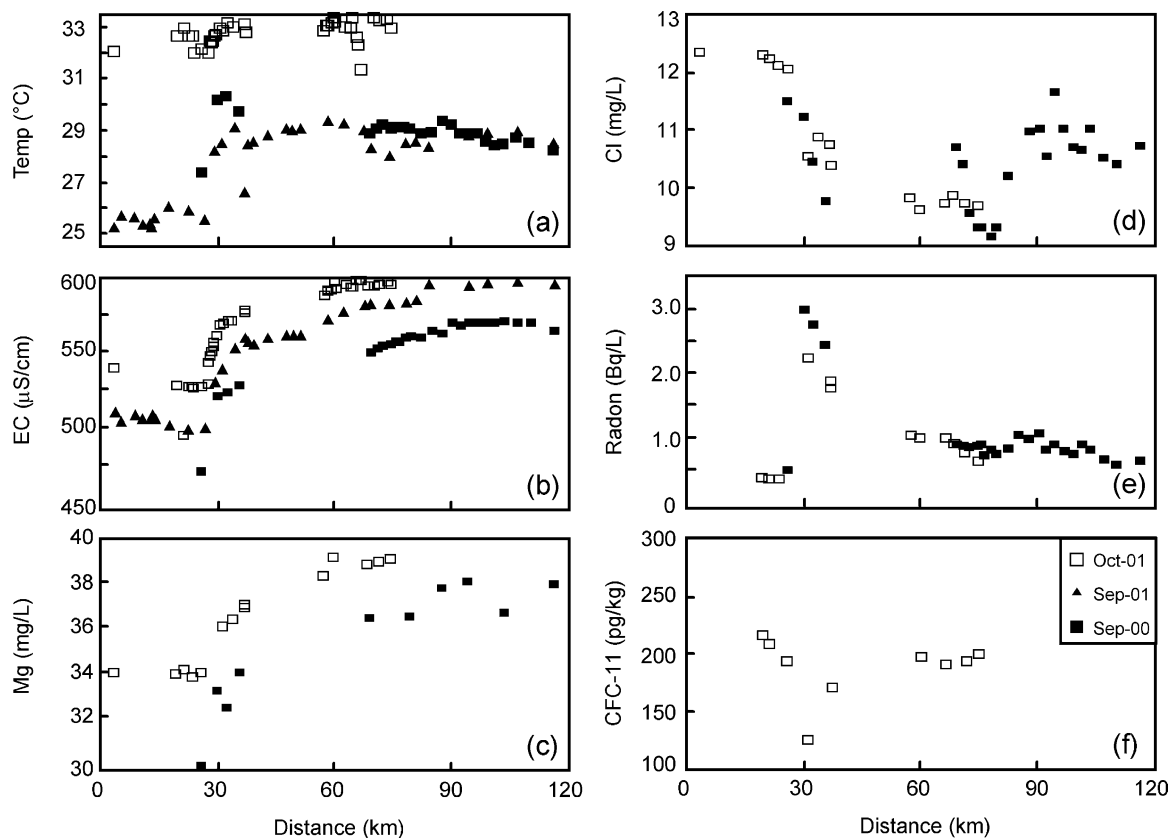


Fig. 5. Normalised stream temperature, EC, magnesium, chloride, radon and CFC-11 concentrations. Closed squares denote samples collected in September 2000, triangles denote September 2001, and open squares denote October 2001.

a combination of radioactive decay and exchange with the atmosphere. Downstream of 60 km, the ^{222}Rn concentration ranges between 0.6 and 1.1 Bq/l.

CFC concentrations were measured on nine stream samples collected in October 2001, although no reliable measurements of CFC concentrations on spring samples were obtained (At many of the small springs, the pool of water was not sufficiently deep to obtain samples free of atmospheric concentration. Two samples collected from larger springs were broken in transit). Fig. 6 shows CFC-11 versus CFC-12 concentrations for these samples, where they are also compared with the air-equilibration curve at a temperature of 30 °C. Atmospheric concentrations of CFC-11 and CFC-12 increased between 1950 and the mid 1990s. Since 1995, the atmospheric CFC-11 concentration has decreased slightly. The air-equilibration curve shows the evolution of CFC-11 and

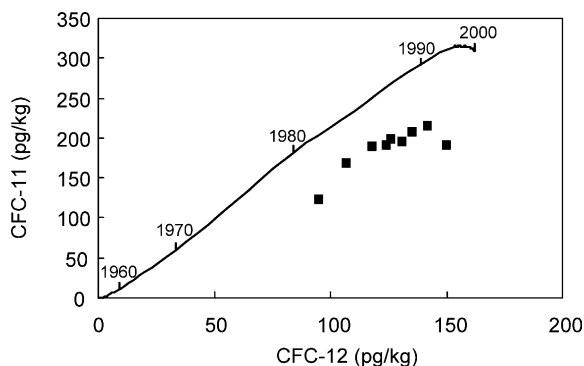


Fig. 6. CFC-12 versus CFC-11 concentrations for streamwater samples collected in October 2001. The solid line indicates the relationship between CFC-11 and CFC-12 concentrations that should occur for samples in equilibrium with the atmosphere, at a temperature of 30 °C.

CFC-12 concentrations of water in equilibrium with the atmosphere over this time. All of the samples fall to the right of this line, indicating either preferential addition of CFC-12 or loss of CFC-11. In our situation, loss of CFC-11, which can occur through microbial degradation, is unlikely because the river is well-oxygenated (6–8 mg/l dissolved oxygen). In groundwater samples, preferential enrichment of CFC-12 has been explained in terms air bubbles trapped during groundwater recharge and subsequently dissolved (excess air, Heaton and Vogel, 1981). In our case, it is thought to be due to entrapment of bubbles during turbulent transport within the stream. Because CFC-12 has a lower solubility than CFC-11, dissolution of air bubbles will preferentially enrich CFC-12.

Fig. 5f shows CFC-11 concentrations versus distance downstream. A significant decrease in

concentration is apparent between samples collected at 26 and 31 km, coincident with increases in EC and in concentrations of Mg and ^{222}Rn . The decrease in CFC-11 concentration (which is accompanied by a similar decrease in CFC-12 concentration) is consistent with inflow of groundwater of low CFC concentration in this reach. Although spring concentrations were not measured, the warm springs in this area would contain groundwater in excess of 50 years old, and hence with negligible CFC concentrations.

6. Modelling

In Fig. 7, measured concentrations of ^{222}Rn , CFC-11, CFC-12 and Mg are compared with those obtained from numerical solution to Eq. (4). (Chloride was not modelled due to large variations in spring

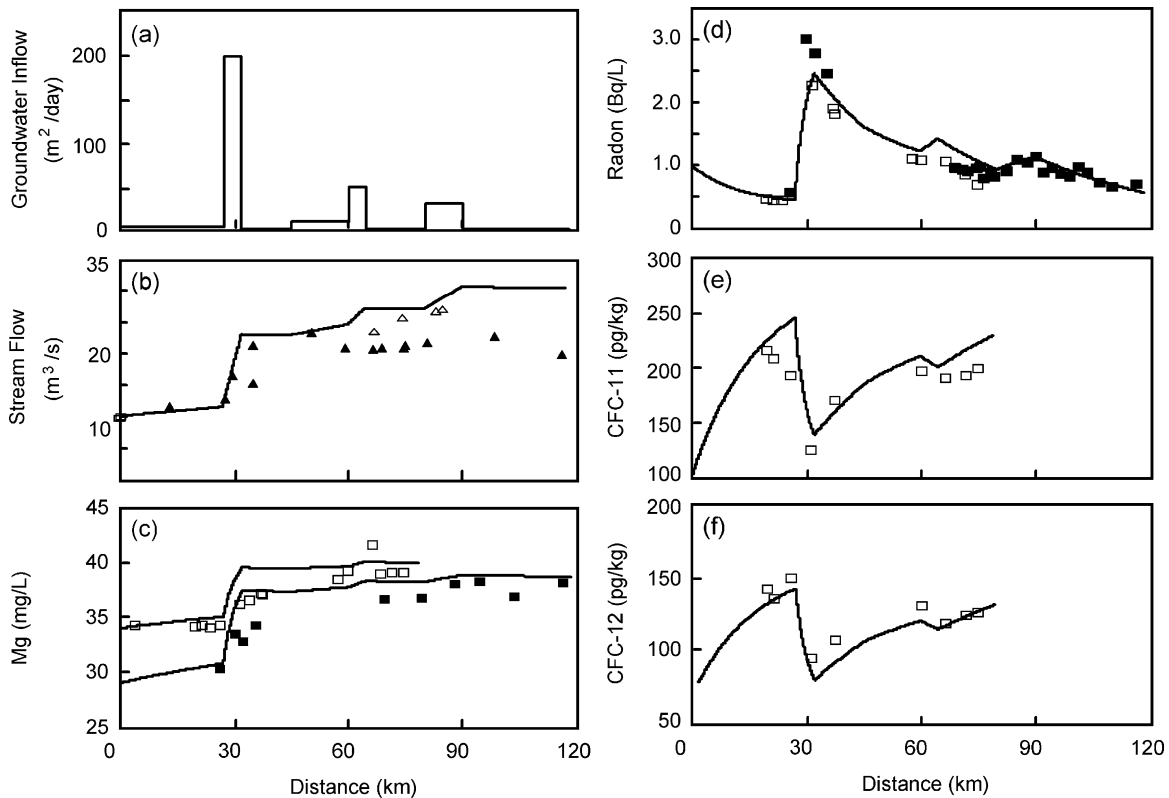


Fig. 7. Comparison of modelling results and field measurements. Open squares denote samples from October 2001, and closed symbols denote September 2000. (a) Inferred groundwater inflows; (b) Comparison of inferred total streamflow and river gauging data. Square at $x = 0$ denotes Dorisvale gauging station, triangles denote gaugings based on impeller flowmeter measurements (closed triangles denote October 2000, and open triangles denote October 2001); (c) Mg; (d) ^{222}Rn ; (e) CFC-11; (f) CFC-12.

concentrations and the resulting uncertainty of groundwater inflow concentrations). Flow rates used in the model are also compared with gauged river flows. The only parameter that was allowed to vary with distance was the groundwater inflow (I). Concentrations of all tracers in groundwater inflow were assumed to be constant, and gas transfer velocity and air entrapment coefficient were also assumed to be invariant with distance. The relative gas transfer velocities for the different tracers were determined according to Eq. (5) (with $n = 0.5$), using published diffusion coefficients at 25 °C (Cook and Herczeg, 2000), with the gas transfer velocity for ^{222}Rn as the reference (see below).

Initial concentrations (at distance zero) were chosen so that initial measured concentrations matched those of the model. As discussed above (and shown in Fig. 4), there is considerable uncertainty in groundwater inflow concentrations for many of the chemical parameters. In the modelling we used groundwater inflow concentrations of 5.0 Bq/l for ^{222}Rn and 44 mg/l for Mg (Table 1). Zero concentrations were used for CFC-11 and CFC-12. Despite the uncertainty concerning ^{222}Rn and Mg concentrations, the zero concentration for CFC-11 and CFC-12 is reasonably certain, at least in the region of the warm springs. Atmospheric concentrations of CFC-11 and CFC-12 were fixed at 260 and 510 pptv, respectively, based on measured values at Cape Grimm, Tasmania. An atmospheric concentration of zero was used for ^{222}Rn . Equilibrium values for CFC-11 and CFC-12 (Sc_a) are determined from the atmospheric concentrations by multiplying by their solubility in fresh water at 30 °C (Warner and Weiss, 1985). The river depth was held constant at 1.5 m, and the width at 50 m. The initial river flow rate was specified to be that measured at the Dorisvale gauging station at the time of sampling. Other river gauging data were not directly used for model calibration. Other than groundwater inflow rates, the only parameters that were varied in the model-fitting exercise were the gas transfer velocity for ^{222}Rn (those of other tracers were then determined from this) and the air entrapment coefficient.

The best-fit simulations for September 2000 and October 2001 were determined by trial and error, and are shown in Fig. 7. They were achieved using a radon gas transfer velocity of $k = 1.0$ m/day, and an air

Table 1
Parameters used in numerical simulations

Parameter	Symbol	Units	Value
Initial upstream flow		m ³ /sec	10
Initial radon concentration		Bq/l	1.0
Initial Mg concentration		mg/l	29/34
Initial CFC-12 concentration		pg/kg	70
Initial CFC-11 concentration		pg/kg	100
Radon gas transfer velocity	k	m/day	1.0
CFC-12 gas transfer velocity	k	m/day	0.90
CFC-11 gas transfer velocity	k	m/day	0.87
Inflow radon concentration	c_1	Bq/l	5.0
Inflow Mg concentration	c_1	mg/l	44
Inflow CFC-12 concentration	c_1	pg/kg	0.0
Inflow CFC-11 concentration	c_1	pg/kg	0.0
Atmospheric radon concentration	c_a	Bq/cm ³	0.0
Atmospheric CFC-12 concentration	c_a	pptv	510
Atmospheric CFC-11 concentration	c_a	pptv	260
Equil radon concentration	Sc_a	Bq/l	0.0
Equil CFC-12 concentration	Sc_a	pg/kg	156
Equil CFC-11 concentration	Sc_a	pg/kg	310
Width	w	m	50
Depth	d	m	1.5
Evaporation	E	m/day	7×10^{-3}
Radon decay constant	λ	day ⁻¹	0.181
Air entrapment coefficient	k'	cm ³ /cm ² /day	100

entrapment coefficient of $k' = 100$ cm³/cm²/day. (Based on the river geometry and flow rate, this air entrapment coefficient is equivalent to dissolving 30 cm³ of air/m³ of water/m of river travel distance). Actual river flows were very similar at these two sampling times (9.8 and 10.3 m³/s at Dorisvale on 18/09/00 and 10/10/01, respectively), and the same model parameters can be used for simulation of the two sampling times (The only parameter that had to be changed between the different times was the initial Mg concentration of the river, which was set to be 29 mg/l in September 2000 and 34 mg/l in October 2001). Most model parameters were reasonably well-constrained by the observations. In particular, even though it was not accurately determined (and appeared to be somewhat variable), the concentration of ^{222}Rn in groundwater inflow was reasonably well constrained. For example, if the concentration of ^{222}Rn in groundwater inflow was much less than 5 Bq/l, this would require a much greater volume of

groundwater inflow to produce the observed increase in stream concentration below 27 km. However, a much greater volume of inflow would result in simulated concentrations of CFC-11 and CFC-12 that were much less than those observed, and Mg concentrations that were much greater than those observed (The values used in the model can be considered to be mean values for groundwater inflow concentrations, and do not prohibit variations between different springs). The resultant groundwater inflows were 5.0 m²/day from 0 to 27 km, 200 m²/day from 27 to 32.0 km, 0.0 m²/day from 32 to 45 km, 10 m²/day from 45 to 60 km, 50 m²/day from 60 to 64.5 km, 0.0 m²/day from 64.5 to 80 km, 30 m²/day from 80 to 90 km, and zero inflow downstream of 90 km (Fig. 7a). Fig. 7b compares the resultant streamflow curve versus results of stream gaugings. A flowrate of 10.3 m³/s was measured at Dorisvale gauging station on 10 October 2001 (river distance of zero), and flows of between 23.6 and 27.2 m³/s were measured at four gaugings between 66.6 and 84.7 km measured between 17 and 18 October 2001. The calibrated model results compare well with this data. River gauging data downstream of 55 km for October 2000 are significantly lower than those for October 2001, and also lower than the model results. However, these gaugings were affected by a surface water runoff event during the week the gaugings took place. Gaugings downstream of 55 km were pre-event, and upstream gaugings were post-event. Unfortunately, the Dorisvale recorder malfunctioned during the period. However, a recorder located approximately 30 km downstream of the Douglas River confluence clearly shows that pre-event flows in October 2000 (34.3 m³/s on 9/10/00) were lower than when sampling occurred in September 2000 and October 2001 (38.9 m³/s on both 18/9/00 and 10/10/01), while post-event flows (43.6 m³/s on 19/10/00) were greater.

6.1. Sensitivity analysis

Figs. 8 and 9 show results of sensitivity analyses for the numerical modelling of ²²²Rn and CFC-12 concentrations. Model parameters were varied by ±50%, to determine the effect on simulated concentrations. As can be seen in Fig. 8b, ²²²Rn concentrations are relatively insensitive to the stream depth. CFC-12 concentrations are completely independent of

stream depth (not shown) as this parameter only appears in the term for radioactive decay in Eq. (4). While this may appear counter-intuitive, it occurs because when initial flow rate and groundwater inflow rate are held constant, decreases in stream depth cause a proportional increase in flow velocity. The insensitivity to depth arises because concentrations are plotted against distance, and not against travel time.

²²²Rn concentrations are completely independent of air entrapment (Fig. 8e), while CFC-12 concentrations have a reasonably low sensitivity to this parameter (Fig. 9c) (CFC-11 has lower sensitivity to air entrapment than CFC-12, due to its higher solubility). Stream concentrations of both tracers are extremely insensitive to evaporation rate (not shown), because the water loss during the transit time is small. (The transit time for the 117 km flow distance is estimated to be approximately 5 days). Concentrations of both tracers are most sensitive to stream width, groundwater inflow rate and gas transfer velocity. ²²²Rn concentrations are also highly sensitive to concentration in groundwater inflow, whereas for CFC-11 and CFC-12 this concentration is zero. Because equilibrium concentrations of CFC-12 are greater than concentrations in groundwater inflow, river concentrations increase with increases in stream width, increases in gas transfer velocity and decreases in groundwater inflow. For ²²²Rn, equilibrium concentrations are zero while groundwater concentrations are high, and so this sensitivity is reversed.

Fig. 10 shows the change in inflow which produces the same change in concentration as a 10% change in river width, gas transfer velocity, air entrapment coefficient (for CFC-12) and inflow concentration (for ²²²Rn). This plot might be considered to represent the absolute error of the estimated inflows if we had not had access to river gauging data for calibration (The river flow data provides an additional constraint on groundwater inflows). For example, a 10% change in gas transfer velocity for CFC-12 at 27 km causes the same change in concentration as a 0.4 m³/m/day change in groundwater flow, while a 10% change in gas transfer velocity at 32 km is equivalent to a 4.3 m³/m/day change in inflow. The relative error of the inflows can be determined by dividing these values by the estimated inflows (Fig. 7a). The relative errors for CFC-12 are least at 27 km (<5% change in inflow for a 10% change in k and k').

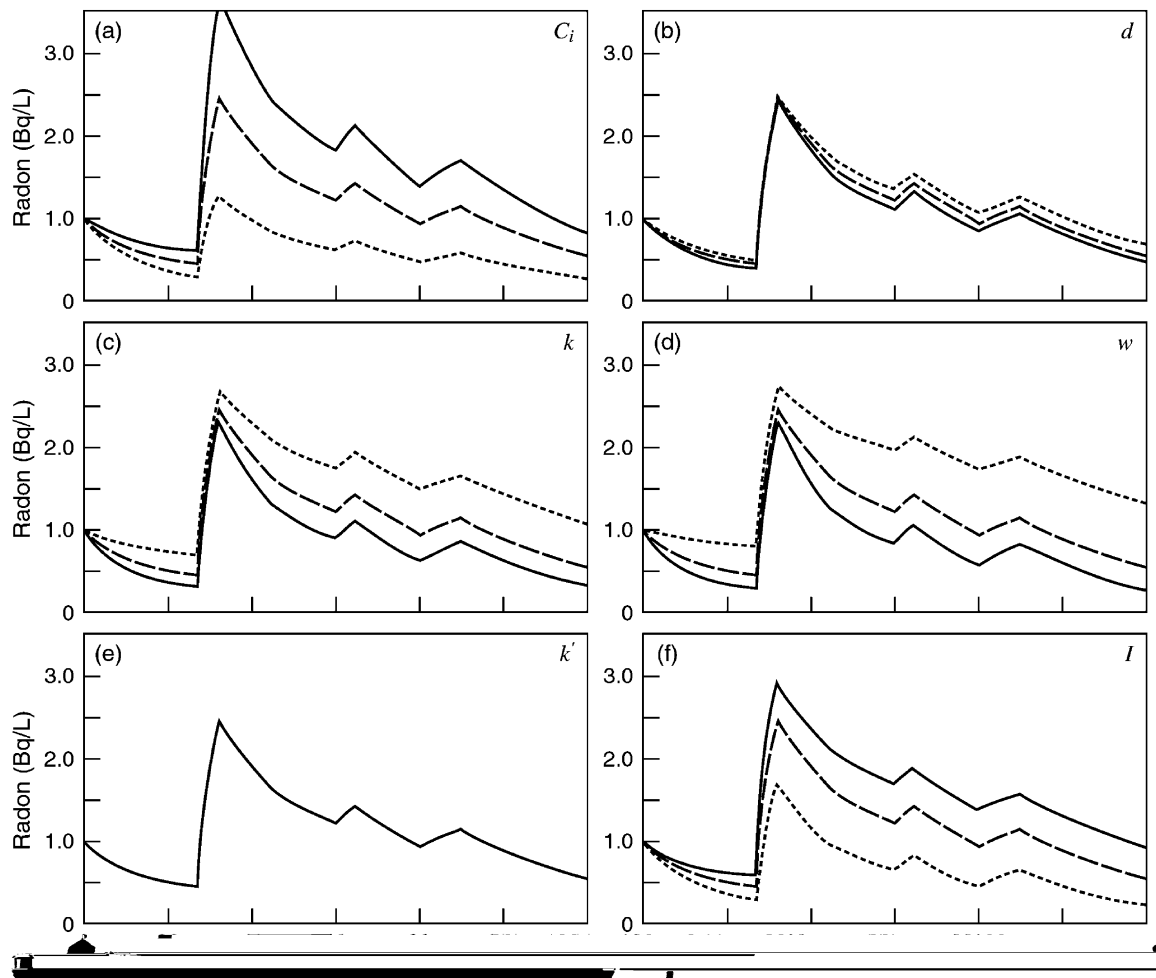


Fig. 8. Sensitivity analyses for ^{222}Rn concentrations. Base case simulations (broken line) are as shown in Fig. 7d. Results for variations in parameters of +50% (solid line) and –50% (dotted line) are compared. (a) concentration in groundwater inflow; (b) stream depth; (c) gas transfer velocity; (d) stream width; (e) air entrapment coefficient; (f) groundwater inflow rate. Radon concentrations are totally insensitive to air entrapment, and also to evaporation rate (not shown).

It is possible to provide satisfactory fit to all of the chemical data using greater values for groundwater inflows, if the concentrations in groundwater inflow are reduced proportionally. For example, it is possible to obtain a satisfactory fit to the chemistry data with double the volume of groundwater inflow along the entire length of the river, if inflow concentrations are reduced to 3.5 Bq/l and 41 mg/l for ^{222}Rn and Mg, and increased to 40 and 50 pg/kg for CFC-11 and CFC-12, respectively, and the gas transfer velocity for ^{222}Rn is increased to 1.5 m/day (with other gas

transfer velocities increased proportionally). All of these inflow concentrations are within the range of the measured values (Although no values for CFC concentrations in groundwater inflow were obtained, it is unlikely that measurable concentrations exist in the warm spring area, because the water has originated from great depth and would be more than 50 years old. However, non-zero CFC concentrations could occur in other areas, where springs may contain water from shallower depths). Satisfactory simulation of the ^{222}Rn and Mg data can also be achieved using

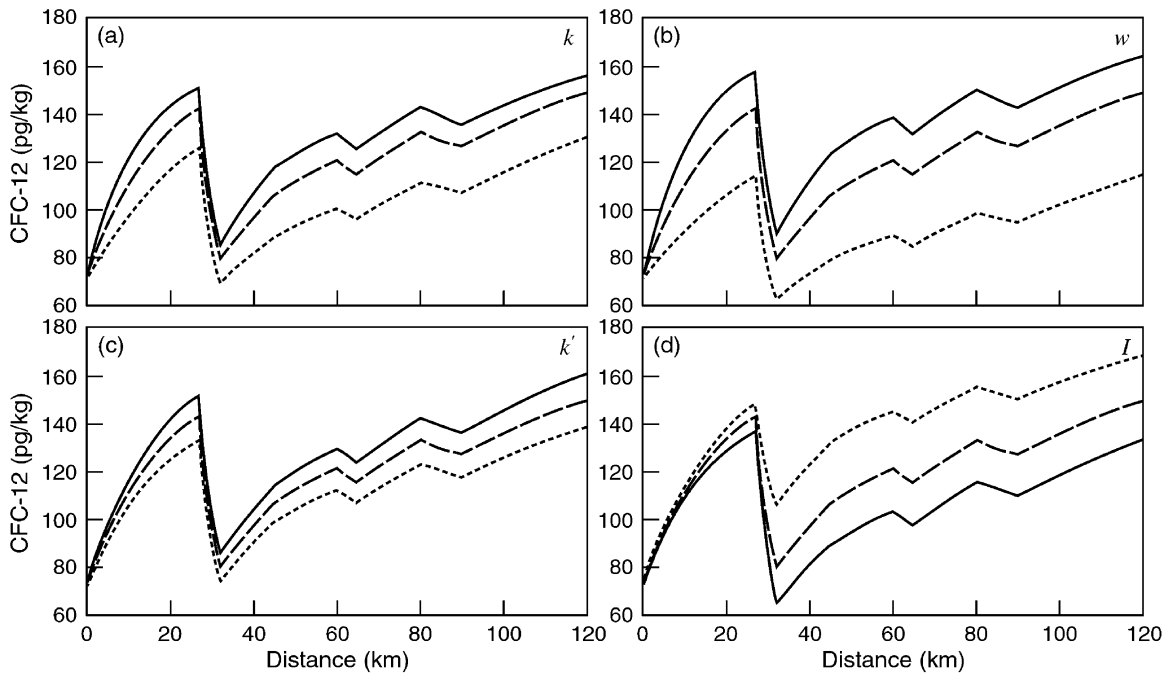


Fig. 9. Sensitivity analyses for CFC-12 concentrations. Base case simulations (broken line) are as shown in Fig. 7f. Results for variations in parameters of +50% (solid line) and -50% (broken line) are compared. (a) gas transfer velocity; (b) stream width; (c) air entrapment coefficient; (d) groundwater inflow rate.

lesser volumes of groundwater inflow and greater values for inflow concentrations. For example using groundwater inflow concentrations of 47 mg/l for Mg (rather than 44 mg/l) and 8 Bq/l for ^{222}Rn (rather than 5 Bq/l), and halving volumes of groundwater inflow over the entire length of the river, provides excellent

fit to the observed ^{222}Rn and Mg data. However, it is not possible to simulate CFC data with significantly lower inflow rates than those shown in Fig. 7. However, none of these alternative parameter sets also provided a satisfactory fit to the river flow data. Because variations in gas transfer velocity and air

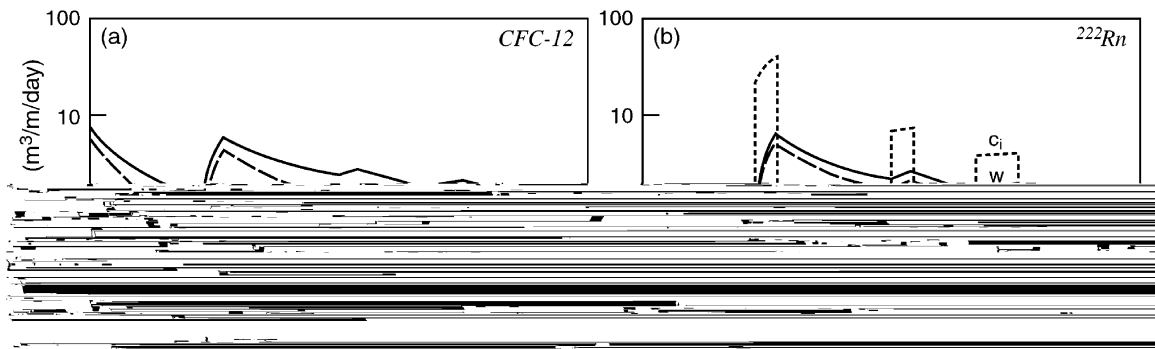


Fig. 10. Sensitivity of groundwater inflows to changes in model parameters (P). The plot indicates the change in groundwater inflow that will result in the same change in concentration as a 10% change in river width, gas transfer velocity, air entrapment coefficient (for CFC-12) and groundwater inflow concentration (for ^{222}Rn).

entrapment coefficient affect ^{222}Rn , CFC-11 and CFC-12 concentrations differently, these parameters are relatively tightly constrained by the stream chemistry data (It is actually the parameters kw and $k'w$ that are constrained by the model, although the stream width, w , can be reasonably accurately determined by direct measurement).

7. Discussion

A number of authors (Ellins et al., 1990; Genereux and Pringle, 1997) have used a simple tracer mass balance approach for determining rates of groundwater inflow, particularly, where the inflow is concentrated in discrete reaches of the river. Their mass balance approach can be expressed

$$\frac{I(x_2 - x_1)}{Q_2} = \frac{c_2 - c_1}{c_1 - c_1} \quad (6)$$

where c_1 is the concentration of the tracer in streamflow at an upstream point x_1 , Q_2 is the rate of streamflow downstream of the groundwater inflow (at x_2) and c_2 is the concentration of the tracer downstream (Other parameters are as previously defined). Eq. (6) defines the ratio of groundwater inflow to the total streamflow, and can be determined from Eqs. (1) and (3) by assuming that evaporation, gas exchange and radioactive decay are negligible ($E = k = \lambda = 0$). However, while this simple approach has been more widely used than the modelling approach adopted in this paper, it will only be accurate if solute inflow from groundwater dominates other processes over this stretch. This assumption is rarely tested.

The use of Eq. (6) requires inflow concentrations of tracers to be accurately defined. We can apply this simple mass balance to each of the chemical parameters measured in this study, to quantify the volume of groundwater inflow that occurs to the Daly River between 27 and 32 km. In September 2000 the normalised river temperature increases from $c_1 = 26.9^\circ\text{C}$ to $c_2 = 29.7^\circ\text{C}$ in this region. Based on a spring temperature of 35.0°C , the relative groundwater inflow is estimated to be 35%. Similarly, relative groundwater inflows in this reach of the river are estimated to be 29–31% in September 2001 and 21–24% in October 2001. In October 2001, Mg concentrations increase from 34.2 to 36.2 mg/l

between 26.1 and 33.5 km, and the Mg concentration of the warm springs was measured to be 43.5–44.4 mg/l. Based on this data, Eq. (6) estimates a relative groundwater inflow of 20%. In September 2000 the inflow fraction is estimated to be 27%. While CFC-11 and CFC-12 concentrations were not measured on the inflow, these concentrations can be assumed to be zero, and so it might be argued that they are known with greatest accuracy. The relative groundwater inflow is calculated to be 35 and 38% using CFC-11 and CFC-12, respectively. Although the ^{222}Rn concentration in groundwater inflow was not accurately measured, using the same value as used for the numerical model (5 Bq/l), would give a mean groundwater inflow fraction for September 2000 and October 2001 of 48%. Using the numerical model, we determine a relative groundwater inflow for the same reach of the river of 50%. This is higher than that obtained using the simple mass balance approach, because the latter neglects a number of important processes.

Fig. 10 can be used to estimate the effect of not including any particular parameter in the model. Multiplying the values by 10, gives the impact of changing k or k' by 100%. Fig. 10 shows that neglecting both k and k' would require a change in groundwater inflow between 27 and 32 km of between 5 and 58 $\text{m}^3/\text{m/day}$ (between 2.5 and 29%). Hence for the area of highest inflow, parameters other than groundwater inflow are responsible for between 2 and 29% of the change in concentration, and so the simple mass balance will underestimate the true inflow by this amount. Where groundwater inflows are lower, the gas exchange parameters become even more important.

The parameters in our model include gas transfer velocities and groundwater inflow concentrations for the various tracers, as well as the air entrapment coefficient, stream width, depth, and evaporation rate. In practice, all of these parameters may vary along the length of the stream, although we have been able to calibrate our model using constant values of all of these parameters. Accurate calibration of such models is improved by the use of multiple tracers, with different sensitivities to the different model parameters. Measurements of river flow rate can greatly assist in model calibration, particularly, where groundwater inflow concentrations are not well-defined. Upstream and downstream flow rates will

usually be sufficient to constrain the model, and stream chemistry between these gauging stations can then be used to determine the distribution of groundwater inflow.

The model parameter that is most difficult to measure, and that the model is most sensitive to, is the gas transfer velocity. Often, studies using ^{222}Rn to estimate groundwater inflows rely on literature values for this parameter. These literature values are often obtained from artificial tracer tests in which dissolved gaseous tracers are added to streams and their rate of dissipation is monitored (Genereux and Hemond, 1992). In our study, the gas transfer velocity was determined in the model fitting exercise. The value obtained (1.0 m/day for ^{222}Rn) is similar to that obtained in other studies of low gradient rivers (Raymond and Cole, 2001). The inclusion of the air entrapment coefficient was necessary to explain the difference between CFC-11 and CFC-12 concentrations, and represents a simplification of the bubble entrapment process that occurs at river cascades (Cirpka et al., 1993). The sensitivity of our model to this parameter is relatively low. For higher-gradient rivers, with a greater frequency of cascades, it may be necessary to model this process in more detail.

This study did not include any measurements of CFC concentration in springs or in the groundwater. In the area of the warm springs, this was not a serious omission because the groundwater was certain to be in excess of 50 years old, and hence to contain negligible CFCs. However, we were able to accurately simulate stream concentrations with inflow concentrations of zero throughout the length of the river, suggesting that over the entire river, the groundwater discharging to the river is in excess of 50 years old. In our study, samples were collected towards the end of the dry season. Earlier in the dry season, it is likely that a fraction of groundwater inflow to the river would be from bank storage, which entered the aquifer during high river stages during the wet season. At this time, locations and volumes of groundwater inflows might be able to be determined using ^{222}Rn , but CFC concentrations might allow differentiation of bank storage versus regional groundwater (Bank storage would acquire the ^{222}Rn signature of

the aquifer after a residence time of only a few weeks, but would retain a modern CFC signal).

It should be noted that in small catchments, where travel times from recharge to discharge is less than a few years, CFCs are unlikely to be useful as tracers of groundwater inflow because groundwater concentrations would not be sufficiently distinct from those in equilibrium with the atmosphere ($c_i \approx Sc_a$). However, for larger river systems groundwater inflow will usually be greater than 10 years old and often greater than 50 years old. In such cases, CFCs should prove to be a valuable tracer of groundwater inflow.

8. Conclusions

For several decades, concentrations of dissolved ^{222}Rn and major ion chemistry of river water have been used to infer rates of groundwater discharge to streams. In this paper, we have shown that CFC-11 and CFC-12 can also be used for this purpose. The use of a numerical model to simultaneously simulate concentrations of a number of different tracers allows most parameters to be constrained. This is despite poor definition of groundwater inflow concentrations of some tracers, and without gas transfer velocity and air entrapment coefficients having been independently estimated. The availability of flow gauging data at the upper and lower ends of the stream reach being studied greatly assists in constraining the model.

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