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Discussions

Using geochemical tracers to distinguish groundwater and parafluvial inflows in rivers (the Avon Catchment, SE Australia)

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Abstract

Understanding the location and magnitude of groundwater inflows to rivers is important for the protection of riverine ecosystems and the management of connected groundwater and surface water systems. Downstream trends in ^{222}Rn activities and Cl concentrations in the Avon River, southeast Australia, implies that it contains alternating gaining and losing reaches. ^{222}Rn activities of up to 3690 Bq m^{-3} imply that inflows are locally substantial (up to 3.1 m^3 m^{-1} day^{-1}). However, if it assumed that these inflows are solely from groundwater, the net groundwater inflows during low-flow periods exceed the measured increase in streamflow along the Avon River by up to 490 %. Uncertainties in the ^{222}Rn activities of groundwater, the gas transfer coefficient, and the degree of hyporheic exchange cannot explain this discrepancy. It is proposed that a significant volume of the total calculated inflows into the Avon River represents water that exfiltrates from the river, flows through parafluvial sediments, and subsequently re-enters the river in the gaining reaches. This returning parafluvial flow has high ^{222}Rn activities due to ^{222}Rn emanations from the alluvial sediments. The riffle sections of the Avon River commonly have steep longitudinal gradients and may transition from losing at their upstream end to gaining at the downstream end and parafluvial flow through the sediment banks on meanders and point bars may also occur. Parafluvial flow is likely to be important in rivers with coarse-grained alluvial sediments on their floodplains and failure to quantify the input of ^{222}Rn from parafluvial flow will result in overestimating groundwater inflows to rivers.

1 Introduction

Quantifying groundwater inflows to streams and rivers is critical to understanding hydrogeological systems, protecting riverine ecosystems, and managing water resources (e.g., Winter, 1999; Sophocleous, 2002; Brodie et al., 2007). Groundwater inflows may form the majority of water in gaining rivers during periods of low streamflow, and river-

ine ecosystems are commonly sustained by groundwater inflows at those times (Kløve et al., 2011; Barron et al., 2012; Cartwright and Gilfedder, 2015). Thus, understanding the distribution and magnitude of groundwater inflows is important for managing and protecting these commonly vulnerable ecosystems. Failure to understand groundwater contributions to rivers may result in double allocation of water resources (i.e., the surface water and groundwater allocations might represent the same water). Documenting the distribution and quantity of groundwater inflows to rivers is also required for flood forecasting, understanding the impacts of contaminants on rivers, and understanding the potential impacts of climate or landuse changes on river systems.

There are many methods to assess the distribution and magnitude of groundwater inflows to rivers (e.g., Brodie et al., 2007). Differential gauging may be used to determine both groundwater inflows and outflows. In many catchments, however, the distribution of river gauges is insufficient to allow anything other than a large-scale categorisation of gaining and losing behaviour. Numerical techniques based on river hydrographs (e.g., Nathan and McMahon, 1990; Askoy et al., 2009) provide a straightforward method of estimating baseflow. However, these are of limited use in highly-regulated rivers and may aggregate several stores of water including regional groundwater, bank return flows, and interflow into the baseflow component (McCallum et al., 2012; Cartwright et al., 2014a). Groundwater flow models and water balance models may also be used to calculate groundwater inflows but their applicability requires a detailed knowledge of hydrological parameters such as hydraulic conductivity, groundwater elevations, evapotranspiration rates, and runoff.

Providing that groundwater and surface water have different concentrations of a given geochemical component, changes in the geochemistry of the river may be used to estimate groundwater inflows into individual reaches (e.g., Cook, 2013). Tracers such as major ions, stable isotopes, radioactive isotopes, and chlorofluorocarbons have been used to quantify groundwater inflows to rivers (e.g., Ellins et al., 1990; Genereux and Hemond, 1992; Négrel et al., 2001; Stellato et al., 2008; Cartwright et al., 2011; Cook, 2013; Bourke et al., 2014a, b). Geochemical tracers only quantify

groundwater inflows, and while they are commonly used to determine the distribution of gaining and losing reaches, they do not quantify the magnitude of any groundwater outflows. Thus, if rivers have significant losing sections, the calculated groundwater inflows from geochemical tracers may exceed the total increase in streamflow.

1.1 ^{222}Rn as a tracer of groundwater inflows

^{222}Rn, which is an intermediate isotope in the ^{238}U to ^{206}Pb decay series, is an important tracer for quantifying groundwater inflows to rivers. ^{222}Rn has a half-life of 3.8 days and the activity of ^{222}Rn reaches secular equilibrium with its parent isotope ^{226}Ra over 3 to 4 weeks (approximately 5 half-lives) (Cecil and Green, 2000). Because the concentrations of Ra in minerals are several orders of magnitude higher than dissolved Ra concentrations in surface water, groundwater ^{222}Rn activities are commonly two or three orders of magnitude higher than those of surface water (Cecil and Green, 2000). This makes ^{222}Rn a valuable tracer in catchments where the groundwater has similar major ion concentrations and stable isotope ratios to the river water. As ^{222}Rn activities in rivers decline downstream from regions of groundwater inflow due to radioactive decay and degassing to the atmosphere (Ellins et al., 1990; Genereux and Hemond, 1992), ^{222}Rn is also useful in determining locations of groundwater inflow, even if the inflows are not quantified.

Assuming that the atmosphere contains negligible radon, the change in ^{222}Rn activities along a river may be estimated by mass balance:

$$Q\frac{\mathrm{d}c_\mathrm{r}}{\mathrm{d}x} = I\left(c_\mathrm{gw} - c_\mathrm{r}\right) + wEc_\mathrm{r} + F_\mathrm{h} + F_\mathrm{p} - kdwc_\mathrm{r} - \lambda dwc_\mathrm{r} \quad (1)$$

(modifed from Mullinger et al., 2007; Cartwright et al., 2011; and Cook, 2013). In Eq. (1): Q is streamflow ($\mathrm{m^3\,day^{-1}}$); I is the groundwater inflow ($\mathrm{m^3\,m^{-1}\,day^{-1}}$); c_r and c_gw are the ^{222}Rn activities ($\mathrm{Bq\,m^{-3}}$) in the river and groundwater, respectively; E is the evaporation rate ($\mathrm{m\,day^{-1}}$); x is longitudinal distance (m); w is river width (m); d is river depth (m); F_h and F_p are the fluxes of ^{222}Rn ($\mathrm{Bq\,m^{-1}\,day^{-1}}$) from the hyporheic

zone and the broader parafluvial zone, respectively; k is the gas-transfer coefficient (day^{-1}); and λ is the decay constant (0.181 day^{-1}) (Table 1). Unlike most applications of ^{222}Rn mass balance, F_h and F_p have been separated which allows both small-scale (hyporheic) and larger-scale (parafluvial) flow through the near-river sediments to be considered (c.f., Bourke et al., 2014a). Equation (1) can also be used to estimate the changes in composition of major ion tracers. Since the concentration of a conservative tracer such as Cl is controlled only by groundwater inflows and evaporation, only the first two terms on the right-hand-side of Eq. (1) are relevant. If the river is solely fed by groundwater the increase in streamflow downstream is:

$$\frac{dQ}{dx} = I - Ew. \quad (2)$$

Uncertainties in the parameters in Eq. (1) can result in significant uncertainties in calculated groundwater inflows. The evaporation term is generally much smaller than the other terms in Eq. (1), and thus uncertainties in evaporation rates have little impact on the calculations (Cartwright et al., 2011; Cook, 2013). By contrast, heterogeneous ^{222}Rn activities in groundwater may result in substantial uncertainties in calculated groundwater inflows (Cook et al., 2006; Mullinger et al., 2007; Unland et al., 2013; Yu et al., 2013; Cartwright et al., 2011; Atkinson et al., 2015); groundwater Cl concentrations are also commonly heterogeneous (Cook, 2013; Cartwright, 2014b) and this leads to similar uncertainties when using Cl to estimate groundwater inflows. Additionally, while it is well established that the rate of Rn degassing increases with increasing river turbulence and decreasing river depth, different empirical formulations that predict k from river widths, depths, and velocities can yield disparate k values (Genereux and Hemond, 1992), which can also lead to significant uncertainties in calculated groundwater inflows.

1.2 Hyporheic and parafluvial flow

In most rivers, there is likely to be a contribution of ^{222}Rn resulting from water flowing through the hyporheic zone (the zone immediately below the river bed through which water flows driven by irregularities in the river bed) and the broader parafluvial zone, which includes features such as point bars and gravel banks (Boulton et al., 1998; Edwardson et al., 2003). Both hyporheic and parafluvial flow represent water that exfiltrates the river and subsequently re-infiltrates at some point downstream. The ^{222}Rn activity in water flowing through the hyporheic and parafluvial zones increases over time due to ^{222}Rn emanation from the sediments and the contribution of ^{222}Rn from these sources needs to be estimated when calculating groundwater inflows (Cook, 2013). While the contribution of ^{222}Rn derived from the hyporheic zone is commonly considered, few studies have considered the contribution of ^{222}Rn from the parafluvial zone (c.f. Bourke et al., 2014a; Cartwright et al., 2014b); however, in rivers with coarse-grained sediments on the floodplain the input of ^{222}Rn from the parafluvial zone may be significant.

The ^{222}Rn activity in the hyporheic or parafluvial zone waters (c_h or c_p) is governed by the ^{222}Rn activity of the water flowing into the hyporheic zone (c_{in}), the ^{222}Rn emanation rate (γ in Bq m^{-3} day^{-1}), and the residence time (t_h or t_p, in days):

$$c_h = \left(\frac{\gamma}{\lambda} - c_{in}\right)\left(1 - e^{-\lambda t_h}\right) + c_{in} \quad (3)$$

(Hoehn et al., 1992; Hoehn and Cirpka, 2006) (Fig. 1a). c_h increases with residence time (t_h) and at steady state (i.e., as t_h in Eq. 3 $\rightarrow \infty$), $c_h = \gamma/\lambda$. In a losing or neutral (i.e. neither gaining nor losing) river $c_{in} = c_r$. In a gaining river, water derived from the river will mix in the alluvial sediments with upwelling regional groundwater that has high ^{222}Rn activities and Cartwright et al. (2014b) discussed using the concentration of a conservative ion such as Cl to estimate the degree of mixing within the alluvial sediments to estimate c_{in}. Assuming that all the water entering the hyporheic zone

subsequently re-enters the river, the ^{222}Rn flux from the hyporheic zone (F_h) is given by:

$$F_h = \frac{\gamma A_h \phi}{1 + \lambda t_h} - \frac{\lambda A_h \phi}{1 + \lambda t_h} c_{in}, \quad (4)$$

where A_h is the cross-sectional area of the hyporheic zone and ϕ is the porosity (Lamontagne and Cook, 2007). Equation (4) treats the hyporheic zone as a homogeneous region adjacent to the river in which river water resides for a certain period of time and then re-enters the river. While recognising that this is an oversimplification, it does provide a means of calculating the changes in ^{222}Rn in the hyporheic zone from estimates of emanation rates and the dimensions of the hyporheic zone.

Equation (4) can also be applied to parafluvial exchange (e.g., Cartwright et al., 2014b). However, where parafluvial flow involves long flow paths through alluvial sediments, an alternative conceptualisation is to consider the flux of ^{222}Rn into the river at the end of discrete flow paths through the parafluvial zone (Hoehn and Von Gunten, 1989; Hoehn and Cirpka, 2006; Bourke et al., 2014a). In this case, F_p may be defined in a similar way to the groundwater inflow term in Eq. (1):

$$F_p = I_p(c_p - c_r), \quad (5)$$

where c_p is the activity of ^{222}Rn in the parafluvial zone waters and I_p is the volume of water derived from the parafluvial zone per unit length of river ($m^3\,m^{-1}\,day^{-1}$). c_p is given by Eq. (3) and the minimum value of I_p required to produce a given F_p is achieved when c_p approaches steady state (Fig. 1b), which requires t_h to be at least several days (c_p is ~ 95 % of the steady state activity after 16 days: Fig. 1a). The volume of sediments with which the water has interacted during flow through the parafluvial zone (V_p in $m^3\,m^{-1}$ length of river) is governed by I_p, t_p and ϕ. If the distribution of flow paths through the parafluvial zone is regular V_p will be the cross-sectional area of the

parafluvial zone through which the water from the river flows (A_p):

$$V_p = A_p = \frac{t_p I_p}{\phi} \quad (6)$$

(Bourke et al., 2014a). For the same input parameters, Eqs. (4) and (5) yield closely similar estimates of F_h or F_p (as noted by Bourke et al., 2014a) and the least well-known parameters are the same in both cases (A_h or A_p and t_h or t_p). The choice between the two approaches largely depends on how the system is conceptualised; in the case of hyporheic exchange it is more convenient to consider the exchange between the hyporheic zone and the river whereas parafluvial flow may be better conceptualised as discrete flow paths.

The successful application of ^{222}Rn to determine groundwater inflows thus requires careful consideration of several processes. While this complicates the application of ^{222}Rn as a tracer, it also allows characterisation of processes such as degassing and hyporheic or parafluvial flow that may be difficult to achieve using other chemical tracers. As has been outlined in several studies, comparison of the calculated groundwater inflows from ^{222}Rn with those made from other geochemical tracers or with streamflow measurements is a crucial test of the veracity of the calculations (Cook et al., 2003; Mullinger et al., 2007, 2009; Cartwright et al., 2011, 2014b; Unland et al., 2013).

1.3 Objectives

This paper examines groundwater-river interaction in the Avon River, southeast Australia, primarily using ^{222}Rn. Specifically, we test the following hypothesis: (1) that large-scale parafluvial flow is an important contributor of ^{222}Rn to the river; and (2) that major flooding events which alter the geometry of the floodplain result in changing locations of groundwater inflows. Being able to separate groundwater and parafluvial inflows and understand how the locations of groundwater inflows change following major flood events are important to studies of groundwater-river interactions elsewhere.

2 Local geology and hydrogeology

The Avon River occurs within the Gippsland Basin in southeast Australia (Fig. 2) and has a total catchment area of $\sim 1830\,km^2$ (Cochrane et al., 1991; Department of Environment and Primary Industries, 2015). The Avon River is unregulated and drains the southern slopes of the Victorian Alps (maximum elevation in the catchment is 1634 m), and discharges into Lake Wellington, which is a coastal saline lake connected to the Southern Ocean. The upper slopes represent ~ 30 % of the Avon catchment and are dominated by temperate native eucalyptus forest while the majority of the plains representing ~ 70 % of the catchment have been cleared for agriculture, including dairying, sheep grazing, and vegetable production. The estimated population of the Avon catchment is ~ 4000 with Stratford being the largest town (population ~ 2000).

The highlands of the Victorian Alps comprise indurated Palaeozoic and Mesozoic igneous rocks and metasediments that only host groundwater flow in fractures or in near-surface weathered zones (Walker and Mollica, 1990; Cochrane et al., 1991). These rocks form the basement to the Tertiary and Quaternary sediments of the Gippsland Basin (Fig. 2). The shallowest regional aquifer within the Avon Catchment is the Pliocene to Pleistocene Haunted Hill Formation which comprises up to 40 m of interbedded alluvial sands and clays that have hydraulic conductivities between 10^{-7} and $10^{-5}\,m\,s^{-1}$ (Brumley et al., 1981; Walker and Mollica, 1990). Quaternary sediments that consist of coarse-grained sand and gravels interbedded with finer-grained silts occur mainly within the river valleys and have hydraulic conductivities of 10^{-5} and $10^{-2}\,m\,s^{-1}$ (Brumley et al., 1981; Walker and Mollica, 1990).

Average rainfall within the Avon catchment ranges from $\sim 1.5\,m\,yr^{-1}$ in the highlands to $\sim 0.9\,m\,yr^{-1}$ on the plains and most precipitation occurs in the austral winter (June to September) (Bureau of Meteorology, 2015). The Avon River displays strong seasonal flows with ~ 80 % of annual streamflow occurring during winter (Department of Environment and Primary Industries, 2015). This study focusses on the reaches of the Avon River located on the plains formed by the Gippsland Basin sediments that are

upstream of tidal influence. Streamflow is measured at three sites (The Channel, Stratford, and Chinns Bridge: Fig. 2). Total annual streamflow at Stratford (Fig. 2) between 1977 and 2014 ranged from 1.3×10^{7} to $9.02\times10^{8}\,m^3\,yr^{-1}$ (median = $3.04\times10^{8}\,m^3\,yr^{-1}$) and varies with total annual rainfall (Department of Environment and Primary Industries, 2015). The Avon River only ceases to flow during the summers of severe drought years (e.g., 1983) and experiences periodic floods during high rainfall periods (Fig. 3). Streamflow generally increases downstream at all flow conditions, except at very low flows when streamflow decreases between Stratford and Chinns Bridge. Valencia Creek and Freestone Creek are the main tributaries; both are have streamflow measurements and both enter the Avon in the upper reaches of the studied section.

The Avon River has incised through the Haunted Hill Formation and Quaternary sediments to create terraces that are up to 30 m high with a lower floodplain that is up to 500 m wide. Where it crosses the sedimentary plains, the Avon River comprises a sequence of slow-flowing pools that are typically 10 to 30 m wide, up to 2 m deep at low flows, and up to 2 km long. These pools are connected by shorter (typically 10's to 100's m) and narrow (typically < 5 m) faster-flowing riffle sections that commonly have steep longitudinal gradients.

The floodplain of the Avon River comprises numerous gravel banks and point bars of coarse-gained unconsolidated sediments with clasts of up to 50 cm in diameter. The coarse-grained alluvial sediments are most common between Browns and Redbank (Fig. 2); downstream of Redbank, the Avon River occupies an incised channel with steep banks of finer-grained (clay to sand sized) sediments. The alluvial sediments are sparsely vegetated and the geometry of the floodplain changes markedly following flood events, such as those in 2011, 2012, and 2013 (Fig. 3). These changes include the downstream migration of pools (often by several tens of metres), scouring of the alluvial sediments, and changes to the size and location of the sediment banks. In regions where the river is incised, there are seeps of water at the base of the slope and permanent patches of vegetation such as Juncus that commonly colonise waterlogged soils in Australia.

Groundwater flows from the Victorian Alps to the coast (Hofmann and Cartwright, 2013: Fig. 2); however, there are few groundwater monitoring bores in the Avon catchment that can be used to construct detailed groundwater flow paths or define the relationship of the Avon River to the groundwater. Both the Avon River and shallow groundwater from the Haunted Hills and Quaternary aquifers are used for irrigation and stock use, and groundwater is also used for water supply for Briagolong (population ~ 950) (Gippsland Water, 2012). Current annual groundwater allocations are 1.4×10^7 m^3, although these are not fully utilised at present (Gippsland Water, 2012). Use of water from the Avon River and its tributaries for irrigation is up to 8×10^6 m^3 yr^{-1} (~ 2.6 % of the annual median streamflow at Stratford); however, this is seasonally adjusted with a prohibition on river water use when the streamflow at Stratford is $< 10^4$ m^3 day^{-1}.

The incised nature of the Avon River and the fact that it rarely ceases to flow has led to an assumption that it receives significant groundwater inflows (Gippsland Water, 2012); however, there has been little attempt to quantify the inflows or determine their distribution. Such information is required to protect and manage the Avon River, especially in assessing the potential impacts of increased groundwater or surface water use.

3 Methods

Sampling took place between February 2009 and February 2015 in six sampling campaigns. The sampling periods (Fig. 3a) include periods of very low streamflow (February 2009 and March 2014), periods of low to moderate streamflow (April 2010 and February 2015), and periods of higher streamflow (September 2010, and July 2014). Major flood events between 2011 and 2013 caused redistribution of the pools and sediment banks in the river. Each sampling campaign involved sampling the river sites (Table S1, Fig. 2) over a two to three day period, with the February 2015 sampling campaign involving additional sites to the others. Streamflow data is from gauging stations at The Channel, Stratford, and Chinns Bridge on the Avon River and from gauges

on the Valencia Creek and Freestone Creek tributaries (Department of Environment and Primary Industries, 2015: Fig. 2). Distances are measured relative to the first site at Browns (Fig. 1)

Sampling and analytical techniques were similar to those in other studies (e.g. Unland et al., 2013; Yu et al., 2013; Cartwright et al., 2014b). River samples were collected from 0.5–1 m below the river surface using a manual collector mounted on a pole. Groundwater was sampled from bores installed on the river bank and floodplain at Stratford and Pearces Lane (Fig. 2) that have 1 to 3 m long screens. Water was extracted using an impeller pump set at the screened interval and at least 3 bore volumes of water were purged before sampling. Cations (Tables S1 and S2) were analysed on samples that had been filtered through 0.45 µm cellulose nitrate filters and acidified to pH < 2 using a ThermoFinnigan quadropole ICP-MS at Monash University. Anions (Tables S1 and S2) were analysed on filtered unacidified samples using a Metrohm ion chromatograph at Monash University. The precision of major ion concentrations based on replicate analyses is 2–5 %. A suite of anions and cations were measured; however, only Cl and Na are discussed in this study. ^{222}Rn activities in groundwater (Table S2) and surface water (Table S1) were determined using a portable radon-in-air monitor (RAD-7, Durridge Co.) following methods described by (Burnett and Dulaiova, 2006) and are expressed in Bq m^{-3}. 0.5 L of sample was collected by bottom-filling a glass flask and ^{222}Rn was subsequently degassed for 5 min into a closed air loop of known volume. Counting times were 1–2 h for surface water and 20 min for groundwater. Typical relative precision is < 3 % at 10 000 Bq m^{-3} and ~ 10 % at 100 Bq m^{-3}.

Forty four samples of river bed sediments from sites along the Avon River were collected in order to determine ^{222}Rn production in the hyporheic and parafluvial zones and to further constrain groundwater ^{222}Rn activities. ^{222}Rn emanation rates (γ in Bq m^{-3} day^{-1}) (Table 2) were calculated by sealing a known dry weight of sediment in airtight containers with water and allowing ^{222}Rn to accumulate. Following 4–5 weeks incubation, by which time the rate of ^{222}Rn production and decay will have reached steady state, 20 to 40 mL of pore water was extracted and analysed for ^{222}Rn activities

using the same method as above but with counting times of 6 to 12 h. γ is related to the ^{222}Rn produced per unit mass of sediment E_m (Bq kg^{-1} of sediment), sediment density ρ_s (kg m^{-3}), and porosity ϕ by

$$\gamma = \frac{E_m(1-\phi)\rho_s\lambda}{\phi} \quad (7)$$

(Lamontagne and Cook, 2007).

4 Results

4.1 Streamflow

Streamflow at Stratford between January 2000 and February 2015 varied between 500 and 1.38×10^8 m^3 day^{-1} (Department of Environment and Primary Industries, 2015). Despite this period including years with well below average rainfall, for example 2006 when rainfall was ~ 50 % of the long-term average (Bureau of Meteorology, 2015), there are no periods of zero streamflow. Mean daily streamflow at Stratford during the two low flow sampling rounds were 10 700 m^3 day^{-1} in February 2009 and 16 200 m^3 day^{-1} in March 2014 (Fig. 3a); these represent the 89.9 and 83.0 percentiles of streamflow, respectively (Fig. 3b). Mean daily streamflow in the other sampling rounds were 23 100 m^3 day^{-1} in February 2015, 24 300 m^3 day^{-1} in April 2010, 84 100 m^3 day^{-1} in July 2014, and 88 800 m^3 day^{-1} in September 2010, which represent the 73.5, 74.9, 41.0, and 39.5 percentiles of streamflow, respectively (Fig. 3b). In February 2015, which is the sampling round discussed in most detail below, the mean daily streamflow was 12 500 m^3 day^{-1} at The Channel and 25 800 m^3 day^{-1} at Chinns Bridge with inflows of 2410 m^3 day^{-1} from Valencia Creek and 600 m^3 day^{-1} from Freestone Creek (Department of Environment and Primary Industries, 2015).

4.2 River geochemistry

Figure 4a shows the ^{222}Rn variation in the Avon River for the six sampling campaigns. There are several distinct zones of elevated ^{222}Rn activities notably at Wombat Flat (^{222}Rn activities up to 2040 Bq m^{-3}) and between Bushy Park and School Lane (^{222}Rn activities up to 3690 Bq m^{-3}). ^{222}Rn activities are lowest in the upper reaches at Smyths Road (^{222}Rn activities between 226 and 460 Bq m^{-3}) and in the reaches between Stewarts Lane and Stratford (^{222}Rn activities generally between 270 and 800 Bq m^{-3}). The downstream river reaches between Knobs Reserve and Chinns Bridge also have low ^{222}Rn activities of between 74 and 750 Bq m^{-3} that generally decline downstream. The position of the highest ^{222}Rn activities in March 2014 and February 2015 (i.e., post the 2011 to 2013 floods) was at Bushy Park, while this site had relatively low ^{222}Rn activities in February 2009 and April 2010 (highest ^{222}Rn activities in these sampling periods was at Pearces Lane). The distribution of ^{222}Rn activities in the detailed sampling campaign in February 2015 is similar to that at other periods of low to moderate streamflow (e.g. March 2014). The lowest overall ^{222}Rn activities were recorded during the two highest flow sampling campaigns (September 2010 and July 2014).

Cl concentrations generally increase downstream from 4 to 10 mg L^{-1} at Browns to as high as 98 mg L^{-1} at Chinns Bridge (Fig. 4b). Cl concentrations in March 2014 were generally higher (up to 98 mg L^{-1}) than in the other sampling campaigns, while Cl concentrations during the highest streamflows in September 2010 are < 20 mg L^{-1}. A major increase in Cl concentrations occurs downstream of Smyths Road in the reaches over which ^{222}Rn activities are highest at low streamflow. The concentrations of other major ions (e.g., Na) increase downstream in a similar manner (Table S1).

4.3 Groundwater geochemistry

Groundwater from the near-river bores at Pearces Lane and Stratford has ^{222}Rn activities that vary from 480 to 28 980 Bq m^{-3} (Table S2). There is some variation in ^{222}Rn activities in individual bores between the sampling rounds with relative standard de-

viations varying from 6 to 34 %. The mean value of all groundwater ^{222}Rn activities (n = 26) is 12 890 Bq m^{-3}. Bore 5 at Pearces Lane is immediately adjacent to the Avon River and possibly samples water from the parafluvial zone rather than groundwater. Excluding data from that bore, the mean value of ^{222}Rn activities is 13 830 Bq m^{-3} (n = 24) with a standard error of 1273 Bq m^{-3} and a 95 % confidence interval (calculated using the Descriptive Statistics tool in Excel 2010 which assumes that the data follows a t-distribution) of 2634 Bq m^{-3}. EC values of groundwater from the bores at Pearces Land and Stratford are between 100 and 680 µS cm^{-1} and Cl concentrations range from 46 to 147 mg L^{-1} with a mean value of 79 ± 34 mg L^{-1} (n = 16) (Table S2). If Bore 5 at Pearces Lane is again excluded the mean Cl concentration is 87 ± 28 mg L^{-1} (n = 14) with a standard error of 8 mg L^{-1} and a 95 % confidence interval of 16 mg L^{-1}. These Cl concentrations are typical of groundwater in elsewhere in the Avon and neighbouring catchments (Department of Environment and Primary Industries, 2015).

4.4 ^{222}Rn emanation rates

Emanation rates were determined via Eq. (7) from ^{222}Rn activities of extracted pore water that had equilibrated with the sediments. The matrix density was assigned as 2700 kg m^{-3}, which is appropriate for sediments rich in quartz (ρ = 2650 kg m^{-3}), and a porosity of 0.4 was used, which is appropriate for unconsolidated poorly-sorted riverine sediments (Freeze and Cherry, 1979). γ values range from 288 to 4950 Bq m^{-3} with a mean value of 2308 ± 1197 Bq m^{-3} (n = 44) and a standard error of 183 Bq m^{-3}. ^{222}Rn activities of water that is in equilibrium with the sediments are given by γ/λ, and the mean γ/λ values are 12 751 ± 6615 Bq m^{-3} with a standard error of 1009 Bq m^{-3}. These γ/λ values are not significantly different ($p \sim 0.5$) to the measured ^{222}Rn activities in groundwater. The mean emanation rates for sediments from the different sites vary between 1484 and 3461 Bq m^{-3}; however there is no systematic variation with position in the catchment.

4.5 Geochemistry of water from the alluvial gravels

Water was extracted from the alluvial gravels at a number of locations along the Avon River during low flow periods either from open holes or from piezometers driven 1–2 m below the surface of the gravels (in total 52 samples were collected). EC values of water within the gravels further than 1 to 2 m from the edge of river edge are in the range 120 to 550 µS cm^{-1} (Fig. 5b); these EC values are higher than those of the adjacent river water but similar to those of the groundwater. Only water extracted from within 1 to 2 m from the river had EC values similar to the river and in some cases the EC of water from the gravels within a few centimetres of the river edge was higher than the adjacent river. ^{222}Rn activities measured in 21 of these samples were between 7000 and 28 000 Bq m^{-3} (Fig. 5a), which are also significantly higher than the ^{222}Rn activities in the adjacent river.

5 Discussion

The following observations imply that overall the Avon is a gaining river: (1) even during periods of low rainfall the river continues to flow and streamflow commonly increases between The Channel and Chinns Bridge, (2) ^{222}Rn activities are higher than those that could be maintained by hyporheic exchange alone (Cartwright et al., 2011; Cook, 2013), (3) Cl concentrations increase downstream; and (4) there are seeps of water (presumed to be groundwater) at the base of steep slopes at the edge of the floodplain. In the following section the ^{222}Rn activities and Cl concentrations will be used to assess the location and magnitude of groundwater inflows.

5.1 Distribution of groundwater inflows

The region between Smyths Road and Ridleys Lane where ^{222}Rn activities increase and remain high (Fig. 4a), especially at lower streamflows, and where there is a marked increase in Cl concentrations (Fig. 4b) is interpreted as receiving major groundwater

inflows. This section of the Avon River is incised up to 4 m below the floodplain which likely produces steep hydraulic head gradients that will result in groundwater discharge on the floodplain and into the river. There are also groundwater seeps and patches of perennial wetland vegetation at the edge of the floodplain in this area. In February 2009 and April 2010, the highest ^{222}Rn activities were recorded at Pearces Lane, while in March 2014 and February 2015 the highest ^{222}Rn activities were recorded at Bushy Park (Fig. 4a). The major floods between 2011 and 2013 (Fig. 3a) changed the location of pools and sediment banks on the Avon River probably also changed the locations of groundwater inflow. The reaches between Browns and Wombat Flat and Stewarts Lane and Stratford are also characterised by increasing ^{222}Rn activities and are again interpreted as recording groundwater inflows.

The reaches between Wombat Flat and Smyths Road, Ridleys Lane and Stewarts Lane, and Knobs Reserve and Chinns Bridge show gradual decline in ^{222}Rn activities and little change in Cl concentrations (Fig. 4); these are interpreted as either losing or receiving minor groundwater inflows. In these areas, the landscape is flatter and the river less incised which likely results in lower hydraulic gradients and consequently less groundwater discharge to the river.

5.2 Quantifying groundwater inflows

Groundwater inflows were calculated from the ^{222}Rn activities for February 2015 (Table S1) by solving Eq. (1) using a finite difference approach in a spreadsheet with a spatial discretisation of 10 m; comparisons for subsets of the data indicate that finer-scale discretisation does not significantly change the results. The streamflow at The Channel gauge was used as the initial streamflow and Q was increased after each distance step via Eq. (2). The calculations specified all parameters except I and matched the observed ^{222}Rn activity at the sampling sites by varying I in each reach (Fig. 6a).

For the initial set of calculations, the groundwater ^{222}Rn activity was assumed to be 13 000 Bq m^{-3}, which is consistent both with the measured ^{222}Rn activities in the bores and the calculated ^{222}Rn activities of water in equilibrium with the alluvial sediments.

Average evaporation rates in southeast Australia in February to April are 3×10^{-3} to 5×10^{-3} m day^{-1} (Bureau of Meteorology, 2015) and a value of 4×10^{-3} m day^{-1} was adopted. Average river width and depth is 10 and 0.5 m, respectively, upstream of Wombat Flat and 20 and 1 m, respectively, for the rest of the river. The gas transfer coefficient was estimated as 0.3 day^{-1} from the decline in ^{222}Rn activities between Ridleys Lane and Schools Road (Fig. 4a). Assuming that this is a losing stretch of the river, which is consistent with the lack of increase in Cl concentrations (Fig. 4b), the decrease in ^{222}Rn activities will be mainly due to degassing with a small contribution from decay. A value of 0.3 day^{-1} is at the lower end of estimates of Rn gas transfer coefficients (Genereux and Hemond, 1992; Cook et al., 2003, 2006; Cartwright et al., 2011, 2014b; Atkinson et al., 2013; Unland et al., 2013; Yu et al., 2014). However, as the Avon River is dominated by slow-flowing pools, degassing rates are expected to be low.

As there are few processes that increase the EC of water in the hyporheic or parafluvial zones, the water in the river gravels within 1 to 2 m of the river that has high EC values (Fig. 5b) represents groundwater or a mixture of river water and groundwater. Consequently, the width of the hyporheic zone has been assigned as the river width. The thickness of the hyporheic zone is less well known; however, by analogy with rivers elsewhere, it is likely to be a few centimetres thick (Boulton et al., 1998; Hester and Doyle, 2008; Tonina and Buffington, 2011) and a value of 10 cm is initially adopted. The flux of ^{222}Rn from the hyporheic zone was estimated from Eq. (3) using the mean γ value of 2300 Bq m^{-3} day^{-1} (Table 2), a porosity of 0.4 (which is appropriate for coarse-grained unconsolidated sediments), and a value for c_{in} that is the ^{222}Rn activity of the river in that reach. The residence time of water within the parafluvial zone is likely to be short (Boulton et al., 1998; Tonina and Buffington, 2011; Zarnetske et al., 2011; Cartwright et al., 2014b), and t_h = 0.1 days is assumed here; for t_h < 1 day, F_h is relatively insensitive to the actual residence times in the hyporheic zone (Lamontagne and Cook, 2007; Cartwright et al., 2014b)

Using these parameters it is possible to model the observed ^{222}Rn activities in the Avon River in February 2015 (Fig. 6a). Calculated groundwater inflows are up to 2.7 $m^3 m^{-1} day^{-1}$ in the reaches between Smyths Road and Pearces Lane (Fig. 6b), which is the region where Cl concentrations also increase markedly (Fig. 4b). Most reaches of the river between Ridleys Lane and Stewarts Lane and downstream of Knobs Reserve have negligible groundwater inflows or are losing (Fig. 6b). The change in Cl concentrations (Fig. 6d) was calculated from the groundwater inflows assuming that groundwater has a Cl concentration of 85 mg L^{-1}. The calculated Cl concentrations are higher than observed, although the calculations do predict the marked increase in Cl concentrations between Smyths Road and Ridleys Lane. Given the uncertainty in groundwater Cl concentrations, the discrepancy between observed and predicted Cl concentrations is not large. If the Cl concentration of the groundwater is allowed to vary by the 95 % confidence interval (±16 mg L^{-1}) the observed trend can be reproduced (Fig. 6d).

The calculated net groundwater inflow of 28 300 $m^3 day^{-1}$, however, exceeds the measured increase in streamflow between The Channel and Chinns Bridge of 15 500 $m^3 day^{-1}$ by 180 % (Fig. 6c). Much of the mismatch between observed and calculated streamflow results from the high estimates of groundwater inflows upstream of Stratford (Fig. 6b). The net increase in streamflow between The Channel and Stratford in February 2015 is 10 500 $m^3 day^{-1}$, whereas the predicted net groundwater inflow from the ^{222}Rn mass balance was 26 700 $m^3 day^{-1}$. While the February 2015 sampling round represents the end of summer when the small ephemeral tributaries were dry and there was no overland flow, there were still flows from Valencia Creek and Freestone Creek of 1410 and 200 $m^3 day^{-1}$, respectively. If these were included, the mismatch between calculated and observed streamflow increases.

Although constrained by fewer data points, the predicted distribution of groundwater inflows in the other low to moderate flow sampling campaigns calculated using the same parameters as for February 2015 are similar (Fig. 7a). In February 2009, April 2010, and March 2014, groundwater inflows are up to 3.1 $m^3 m^{-1} day^{-1}$ and the

calculated net groundwater inflows are 21 700, 15 900, and 21 300 $m^3 day^{-1}$, respectively (Fig. 7b). These calculated groundwater inflows are up to 490 % of the measured increases in streamflow between The Channel and Chinns Bridge. Groundwater inflows were also calculated for the higher streamflow sampling rounds (September 2010 and July 2014) using widths of 15 m upstream of Wombat Flat and 25 m elsewhere, depths of 1.25 upstream of Wombat Flat and 1.6 m elsewhere, k = 0.3 day^{-1}, and F_h adjusted for the higher river widths. The estimated groundwater inflows are lower (up to 1.3 $m^3 m^{-1} day^{-1}$) than at the periods of low streamflow and the net groundwater discharges of 32 100 $m^3 day^{-1}$ in September 2010 and 44 600 $m^3 day^{-1}$ in July 2014 are lower than the measured increases in streamflow between The Channel and Stratford or Chinns Bridge (Fig. 7b).

5.3 Uncertainties and variability

The impacts of uncertainties need in the parameters in Eq. (1) on the calculated groundwater inflows need to be considered. This will be done in reference to the February 2015 sampling round but the same considerations apply to the other sampling rounds. The evaporation term in Eq. (1) is one to two orders of magnitude lower than most of the other terms and errors in the assumed evaporation rate have little influence on the calculations (Cook, 2013). The main factor impacting calculated groundwater inflows in reaches where groundwater inflows are high is the assumed ^{222}Rn activity of groundwater (Cartwright et al., 2011; Cook, 2013). Allowing c_{gw} to vary by ±2600 Bq m^{-3}, which represents the 95 % confidence interval of the groundwater ^{222}Rn activities, makes little difference to the discrepancy between the calculated and observed increase in streamflow (Fig. 6c). Increasing c_{gw} to ~ 27 000 Bq m^{-3} would reproduces the observed increase in streamflow along the Avon (Fig. 8). However, there is no known groundwater in the Avon catchment with such high ^{222}Rn activities, and an activity of 27 000 Bq m^{-3} is far higher than would be in equilibrium with the alluvial

sediments, which is where the water that infiltrates the river is derived from. Hence it is considered unlikely that groundwater ^{222}Rn activities could be this high.

In common with most studies, the calculations assumed that the groundwater inflows are uniform along a particular reach. However, because ^{222}Rn is lost from rivers by degassing and decay, lower groundwater inflows are required to replicate the observed ^{222}Rn activities if the groundwater inflows are predominantly just upstream of each sampling point (Cook, 2013). However, even assigning all groundwater inflows in an individual reach to the 10 m section upstream of the measurement point still results in the calculated groundwater inflows that slightly overestimate the measured streamflow in the Avon River (Fig. 6c). The trends in ^{222}Rn activities in the river in this case are also not realistic (Fig. 6a).

There is uncertainty in the gas transfer coefficient. The value of k was estimated assuming that the Avon River contains losing reaches; if those reaches were actually gaining then this methodology underestimates k. However, increasing k from 0.3 day^{-1} produces higher groundwater inflows, which increases the mismatch between the observed and calculated increases in streamflow. k may also be estimated from river velocities and depths. The O'Connor and Dobbins (1958) and Negulescu and Rojanski (1969) gas transfer equations as modified for ^{222}Rn are:

$$k = 9.301 \times 10^{-3} \left(\frac{v^{0.5}}{d^{1.5}} \right) \quad (8)$$

$$k = 4.87 \times 10^{-4} \left(\frac{v}{d} \right)^{0.85} \quad (9)$$

(Mullinger et al., 2007), where v is velocity (m day^{-1}). k estimated from Eqs. (8) and (9) ranges between 0.1 and 0.3 day^{-1}. Using a value of k of 0.1 day^{-1} produces net groundwater inflows that more closely match the observed increase in streamflow between The Channel and Chinns Bridge (Fig. 8). However, adopting k = 0.1 day^{-1} results in the calculated ^{222}Rn activities in a number of reaches being overestimated (Fig. 9). This is because even assuming no groundwater inflows into these reaches,

the loss of ^{222}Rn due to degassing is insufficient to explain the observed decrease in ^{222}Rn. Such a poor correspondence between predicted and observed ^{222}Rn activities implies problems with the adopted variables.

Increasing F_h will also reduce calculated groundwater inflows. Using the same emanation rates, residence times, and porosities but assigning a thickness of the hyporheic zone of 50 cm, increases F_h and produces groundwater inflows that broadly match the increase in streamflow between The Channel and Chinns Bridge (Fig. 8). However, the higher values of F_h again result in the calculated ^{222}Rn activities in many of the reaches being higher than observed (Fig. 9). As with the lower k values, the poor fit between predicted and observed ^{222}Rn activities implies problems with the choice of variables.

Because the error in λ is insignificant and the evaporation term is much smaller than the other terms, it is generally possible to produce observed trends in ^{222}Rn activities with different combinations of k and F_h (Cartwright et al., 2014b). If F_h is calculated assuming a 50 cm thick hyporheic zone, adopting a k value of 0.6 day^{-1} reproduces the observed ^{222}Rn activities. Similarly, if a k value of 0.1 day^{-1} was used, a match between the observed and the predicted ^{222}Rn activities is achieved by ignoring hyporheic exchange. However, these combinations of parameters again result in estimated net groundwater inflows that exceeding the measured increase in streamflow (Fig. 8).

There is likely to be some error in river gauging, but it is unlikely to be sufficient to explain the gross overestimation of groundwater inflows. Uncertainties in the assumed river widths and depths will also impact the calculations. Specifically, reducing the width or depth decreases the magnitude of the last two terms on the right-hand-side of Eq. (1), which in turn reduces I. If widths were reduced by 50 % (an unrealistic error), net groundwater inflows broadly match the increase in streamflow (Fig. 8). However, this again results in ^{222}Rn activities being overestimated in many reaches (Fig. 9). Increasing k to 0.65 day^{-1} would allow the ^{222}Rn activities to be predicted using these lower widths but again results in the estimated net groundwater inflow exceeding the measured increase in streamflow (Fig. 8).

5.4 Incorporating larger-scale parafluvial flow

It is clear that it is difficult to find combinations of parameters that allow the observed variation in ^{222}Rn activities to be replicated without the calculated net groundwater inflows exceeding the measured increase in streamflow. The proposed resolution is that there is large-scale (100's of m to km) parafluvial flow through the alluvial sediments on the Avon River floodplain that contributes to the river in the gaining reaches. This flow represents water that exfiltrates from and then reinfiltrates into the river which is likely hosted mainly within the coarse-grained alluvial sediments (although conceivably it could also include water that flows through the upper levels of the aquifers underlying the alluvial sediments). By contrast with hyporheic flow which contributes ^{222}Rn to the river along all reaches (whether gaining or losing), the inflows from the parafluvial zone will only contribute ^{222}Rn where the river is gaining.

If residence times of water in the parafluvial zone are sufficiently long, then the inflowing parafluvial water will have high ^{222}Rn activities and increase the ^{222}Rn activities in the river. However, because it represents exfiltrated river water, the inflows from the parafluvial zone do not add to the overall streamflow. Figure 10 shows the results of assuming that 50 % of the water inflowing in each reach in February 2015 represents parafluvial zone waters that has a residence time in the parafluvial zone sufficiently long for secular equilibrium to be attained. The maximum value of I_p is 1.26 $m^3 m^{-1} day^{-1}$ (Fig. 10b) in the Valencia to Bushy Park reaches where c_r is 2500 to 2900 $Bq m^{-3}$. If the parafluvial zone water is in secular equilibrium with the sediments, $c_p \sim 12\,700$ $Bq m^{-3}$ (Table 2), $c_p - c_r \sim 10\,000$ $Bq m^{-3}$, and $F_p \sim 12\,600$ $Bq m^{-1} day^{-1}$ (Eq. 5). For t_p in excess of ~ 30 days the system is close to secular equilibrium and c_p and I_p are near constant and independent of t_p (Fig. 1). If residence times in the parafluvial zone are shorter than those required to attain secular equilibrium, c_p will be lower and the inflows from the parafluvial zone (I_p) required to produce a given flux of ^{222}Rn (F_p) increases (Fig. 1). For example, if $\gamma = 2300$ $Bq m^{-3} day^{-1}$, $c_r = 2700$ $Bq m^{-3}$, and $t_p = 0.1$ days,

$c_p = 2718$ $Bq m^{-3}$ and if $F_p = 12\,600$ $Bq m^{-1} day^{-1}$, $I_p \sim 70$ $m^3 m^{-1} day^{-1}$. The cross-sectional area of the parafluvial zone A_p required to accommodate these parafluvial flows with $\phi = 0.4$ and t_p between 0.1 and 100 days is between 17 and 350 m^2 (Eq. 6). The floodplain of the Avon River is tens of metres wide with sediment thicknesses of several metres and even the higher estimates of the cross-sectional area are not unreasonable. For the lower estimates of A_p, the flow could be accommodated in a zone < 1 m thick beneath the river.

The proposal that inflows of parafluvial zone waters augment groundwater inflows is justifiable hydrologically as the conditions required for high groundwater inflows (gaining river with steep hydraulic gradients and high-hydraulic conductivity sediments) will likely drive the return of parafluvial waters to the river. By contrast losing reaches are likely to be where the water enters the parafluvial sediments. The riffle sections of the Avon River commonly have steep longitudinal gradients and may transition from losing at their upstream end to gaining at the downstream end. Additionally, there may be parafluvial flow through the numerous sediment banks and point bars.

By allowing the parafluvial input to vary between reaches, both the variations in ^{222}Rn activities (Fig. 10a) and calculated increases in streamflow are predicted (Fig. 10c). There is no process in the parafluvial zone that increases the Cl concentrations of the through-flowing water. Thus the Cl concentrations in the river reflect only the groundwater inflows. The calculated Cl concentrations are again higher than observed (Fig. 10d) but not substantially when the uncertainty in groundwater Cl concentrations is taken into account.

While the model of parafluvial zone flow explains the geochemical observations and is consistent with the hydrogeology of the Avon River, it is difficult to test. The inflows from the parafluvial zone have been assumed to vary proportionally to the groundwater inflows, which may not necessarily be the case. Nevertheless, this conceptualisation utilises a process that is known to occur in river valleys to explain observations that are otherwise difficult to resolve. An alternative explanation for the discrepancy between the calculated inflows and the increase in streamflow is that significant pumping of water

from the river occurred. While the surface water is licenced for use, streamflow during February 2009 and March 2014 was below the minimum levels where that is permitted and the streamflows in April 2010 and February 2015 were such that use would be restricted; hence, large-scale pumping of river water at those times is unlikely.

Similar parafluvial flow is likely to occur under higher flow conditions. Thus, while the calculated groundwater inflows during the higher streamflow periods are plausible in as much as they are less than the observed increase in streamflow, if significant parafluvial flow occurs at those times they too will overestimate the actual groundwater inflows.

6 Conclusions

While this study has illustrated some of the difficulties in using geochemical tracers to understand groundwater inflows to rivers, it also shows that additional information may be gleaned from such tracers. The patterns of variation of ^{222}Rn activities and Cl concentrations clearly define the reaches of the Avon River that are gaining. Differences in the location of the zones of high groundwater inflows between the 2009 to 2010 and 2014 to 2015 sampling rounds reflect changes to the river and its floodplain following major floods and demonstrate the utility of ^{222}Rn in determining changes to the location of groundwater inflows in dynamic environments. The difficulty in calculating groundwater inflows using ^{222}Rn activities indicates that there were processes that were not initially correctly accounted for; in this case it was concluded that significant large-scale parafluvial flow occurs. Parafluvial flow is likely to be important in rivers with coarse-grained alluvial sediments on their floodplains, especially where there are alternating gaining and losing reaches, and must be taken into account in ^{222}Rn mass balance calculations. Unlike hyporheic exchange, which occurs in all stretches, parafluvial inflows are likely to dominantly occur in gaining reaches augmenting the groundwater inflows.

Theoretically, a conservative tracer such as Cl that is unaffected by parafluvial flow could be used to determine the groundwater inflows. However, the relatively high variability of groundwater Cl concentrations and the relative small difference between groundwater and river Cl concentrations reduce its utility in quantifying groundwater inflows in this instance. Nevertheless using multiple tracers is potentially valuable and may indicate the importance of other water stores that can feed rivers such as bank return flows or parafluvial flow (c.f. Cook et al., 2003; Mullinger et al., 2007; Cartwright et al., 2011, 2014b; Unland et al., 2013).

The Avon study also illustrates the importance of carrying out geochemical studies at baseflow conditions where the majority of inflows into the river are likely to be from groundwater. While this might appear redundant in terms of determining the water balance, it does provide for a test of assumptions and parameterisation. In the Avon River, the calculated groundwater inflows for the higher flow sampling rounds (Fig. 7) are plausible in as much as they are lower than the net increases in streamflow; however, the results from the low flow sampling rounds make it likely that the ^{222}Rn activities reflect both groundwater inflows and parafluvial exchange. Without the data from the baseflow sampling rounds this would not have been evident and possible erroneous estimated of groundwater inflows may have been made.

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Table 1. Summary of parameters used in calculations.

Symbol	Parameter	Units	Comments
Q	Streamflow	$m^3\ day^{-1}$	
E	Evaporation	$m\ day^{-1}$	
x	Distance downstream	m	
w	Stream width	m	
d	Stream depth	m	
v	Strem velocity		
c_{gw}, c_r, c_h, c_p	^{222}Rn activities in groundwater, river, hyporheic zone, parafluvial zone	$Bq\ m^{-3}$	
k	Degassing constant	day^{-1}	
λ	Decay constant	$0.181\ day^{-1}$	
I	Groundwater inflows	$m^3\ m^{-1}\ day^{-1}$	Eq. (1)
F_h	^{222}Rn flux from hyporheic zone	$Bq\ m^{-1}\ day^{-1}$	Eq. (4)
F_p	^{222}Rn flux from parafluvial zone	$Bq\ m^{-1}\ day^{-1}$	Eq. (5)
γ	^{222}Rn emanation rate	$Bq\ m^{-3}\ day^{-1}$	Eq. (7)
E_m	^{222}Rn produced from sediments	$Bq\ kg^{-1}$	
ρ_s	Sediment density	$kg\ m^{-3}$	
I_p	Inflows from parafluvial zone	$m^3\ m^{-1}\ day^{-1}$	
t_h, t_p	Residence time in hyporheic or parafluvial zone	day	
ϕ	porosity		
V_p	Volume of sediments that parafluvial inflows interact with	$m^3\ m^{-1}$	
A_h, A_p	Cross-sectional area of the hyporheic or parafluvial zone	m^2	$A_p = V_p$

Table 2. ^{222}Rn emanation rates from floodplain sediments.

Site[a]/Sample	E_m $Bq\ kg^{-1}$	γ $Bq\ m^{-3}\ day^{-1}$	γ/λ $Bq\ m^{-3}$
Chinns Bridge 1	2.01	1473	8138
Chinns Bridge 2	4.02	2949	16293
Wombat Flat 1	4.04	2964	16376
Wombat Flat 2	4.52	3311	18295
Wombat Flat 3	4.19	3075	16988
Wombat Flat 4	6.13	4492	24819
Valencia 1	3.95	2899	16016
Valencia 2	1.86	1362	7525
Pearces Lane 1	0.62	454	2506
Pearces Lane 2	3.25	2383	13167
Pearces Lane 3	1.41	1034	5722
Pearces Lane 4	2.63	1925	10636
Pearces Lane 5	6.76	4952	27360
Pearces Lane 6	5.60	4107	22689
Pearces Lane 7	4.12	3018	16674
Pearces Lane 8	1.54	1127	6225
Stewarts Lane 1	3.41	2497	13797
Stewarts Lane 2	5.78	4239	23418
Stewarts Lane 3	3.08	2258	12475
Stewarts Lane 4	2.88	2110	11656
Stewarts Lane 5	4.63	3391	18732
Stewarts Lane 6	3.64	2669	14745
Stewarts Lane 7	4.52	3311	18294
Stewarts Lane 8	4.58	3354	18530
Stewarts Lane 9	1.96	1434	7925
Stewarts Lane 10	5.09	3733	20622
Stewarts Lane 11	4.25	3119	17230
Stewarts Lane 12	3.68	2699	14910
Stewarts Lane 13	1.77	1294	7150
Stewarts Lane 14	2.89	2122	11723
Stratford 1	2.13	1563	8634
Stratford 2	0.66	482	2663
Stratford 3	3.01	2206	12190
Stratford 4	3.77	2762	15259
Stratford 5	0.39	288	1591
Stratford 6	1.24	911	5032
Stratford 7	2.00	1469	8117
Stratford 8	2.71	1985	10965
Stratford 9	0.91	668	3692
Stratford 10	1.01	738	4077
Stratford 11	4.55	3334	18419
Stratford 12	3.13	2293	12667
Stratford 13	0.81	491	3282
Mean		2308	12751
σ		1197	6615

[a] Sites on Fig. 2.

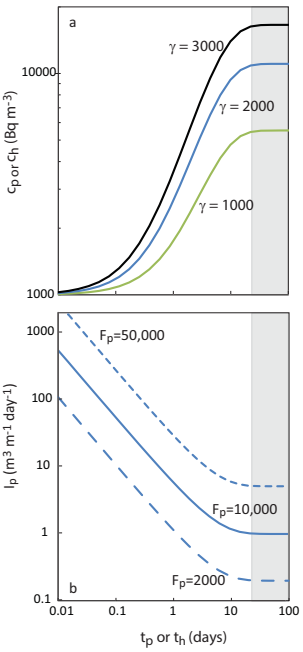

Figure 1. (a) Variation in the ^{222}Rn activity in the parafluvial or hyporheic zone (c_p or c_h) with residence time (t_p or t_h) and ^{222}Rn emanation rate (γ) (Eq. 3). **(b)** Variation in the water flux from the parafluvial zone (I_p) with the flux of ^{222}Rn from the parafluvial zone (F_p) and t_p (Eq. 5). In both cases $c_{in} = 1000\,\mathrm{Bq\,m^{-3}}$.

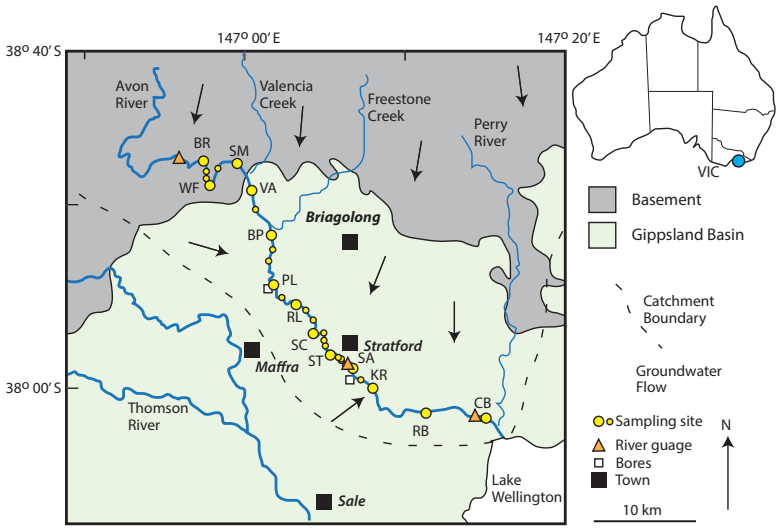

Figure 2. Summary geological and hydrogeological map of the Avon River catchment (Hofmann and Cartwright, 2015; Department of Environment and Primary Industries, 2015). Main sampling sites are BP = Bushy Park, BR = Browns, CB = Chinns Bridge, PL = Pearces Lane, RL = Ridleys Lane, RB = Redbank, SA = Stratford, SC = Schools Lane, ST = Stewarts Lane, SM = Smyths Road, VA = Valencia, WF = Wombat Flat. Unnamed sampling sites are the additional sites from February 2015 (Table S1).

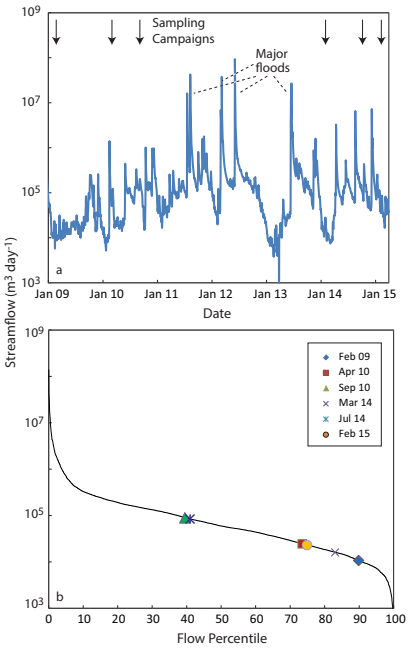

Figure 3. (a) Variation in streamflow at Stratford (Fig. 1) between January 2009 and March 2015. The major floods (highlighted) caused significant changes to the geometry of the floodplain. **(b)** Flow frequency curve for Stratford for streamflows between January 2000 and March 2015 and the percentiles of discharge in the sampling campaigns. Data from Department of Environment and Primary Industries (2015).

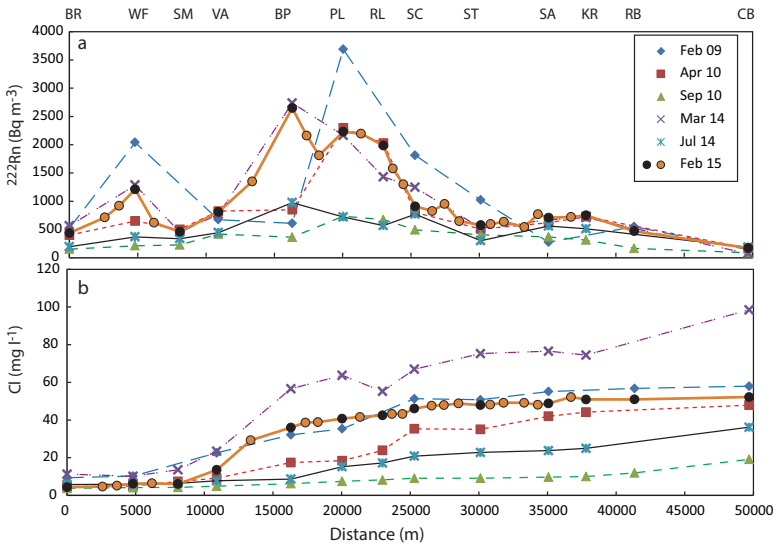

Figure 4. Downstream variations in ^{222}Rn activities **(a)** and Cl concentrations **(b)** for the six sampling campaigns (Data from Table S1, abbreviations as for Fig. 2). Closed symbols for February 2015 are from the main sites, open symbols are from the additional sites specific to that sampling campaign (Table S1). Site abbreviations as for Fig. 2.

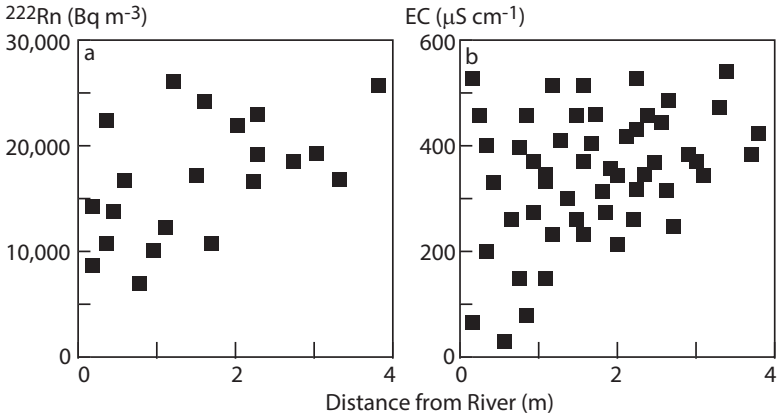

Figure 5. (a) Variations in ^{222}Rn activities **(a)** and EC values **(b)** of water extracted from river bank gravels.

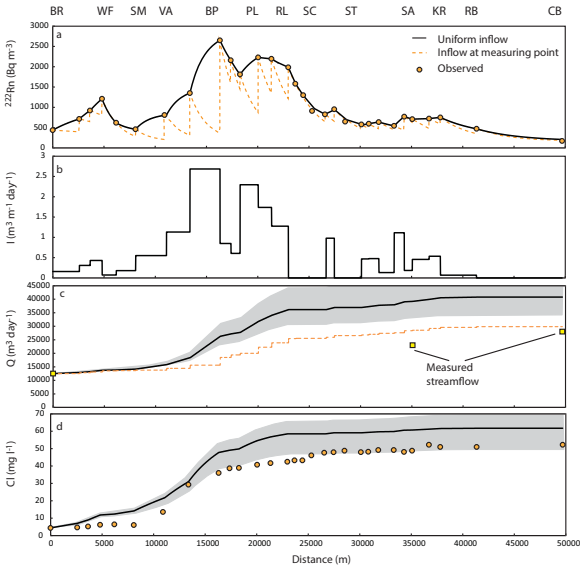

Figure 6. (a) Calculated vs. observed ^{222}Rn activities in the Avon River for February 2015 assuming both uniform groundwater inflow within each reach and the situation where groundwater inflow occurs immediately upstream of the measurement point. Site abbreviations as for Fig. 2. **(b)** Calculated groundwater inflows (I) assuming uniform inflows within each reach. **(c)** Calculated increase in streamflow from groundwater inflows (Eq. 2). Both uniform groundwater inflow within each reach and the situation where groundwater enters the river immediately upstream of the measurement point overestimate the measured streamflow. Shaded area is the range of streamflow resulting from varying c_{gw} within the 95 % confidence interval. **(d)** Predicted vs. observed Cl concentrations. Shaded field is the range resulting from varying groundwater Cl concentrations within the 95 % confidence interval.

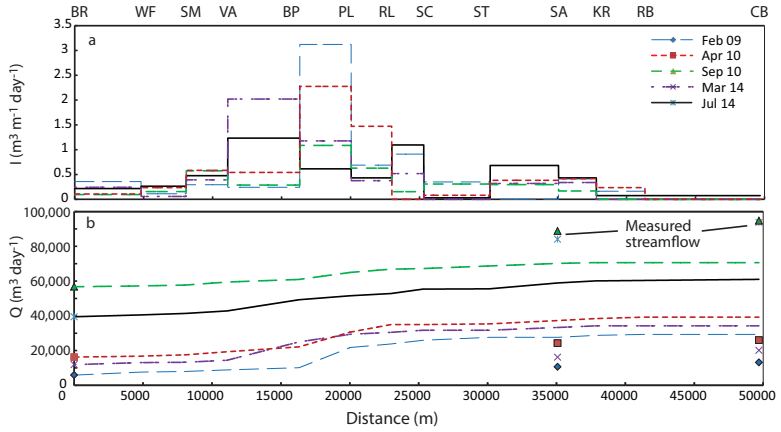

Figure 7. Calculated groundwater inflows **(a)** and increases in streamflow due to groundwater inflows **(b)** for the sampling rounds excluding February 2015. Aside from the high flow periods (September 2010 and July 2014) the calculated increase in streamflow exceeds the observed streamflow at Stratford and Chinns Bridge. Site abbreviations as for Fig. 2.

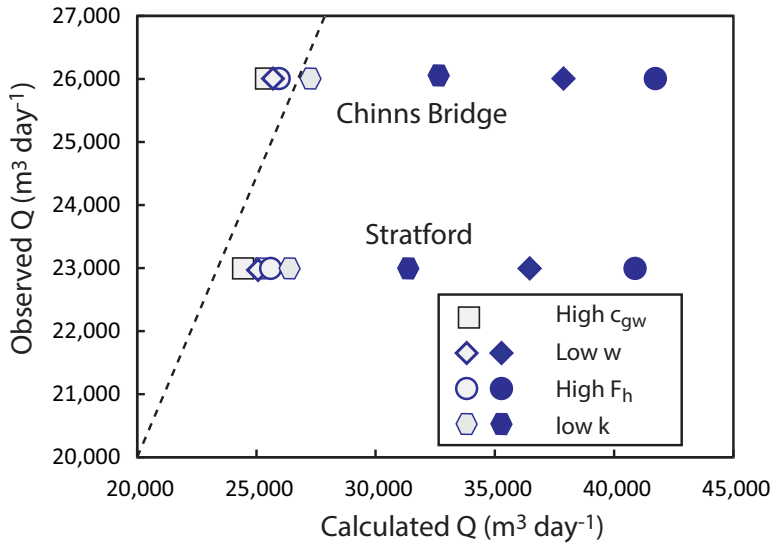

Figure 8. Calculated vs. observed streamflow at Stratford and Chinns Bridge for February 2015 resulting from varying parameters in Eq. (1). High c_{gw} is for a groundwater ^{222}Rn activity of 27 000 Bq m^{-3}; low k is where k is reduced to 0.1 day^{-1}, high F_h increase the thickness of the parafluvial zone to 0.5 m, and low w reduces the width of the Avon River by 50 %. Open symbols represent the result of these changes in isolation (see also Fig. 9); closed symbols represent the results of varying other parameters so that the predicted and observed ^{222}Rn activities match.

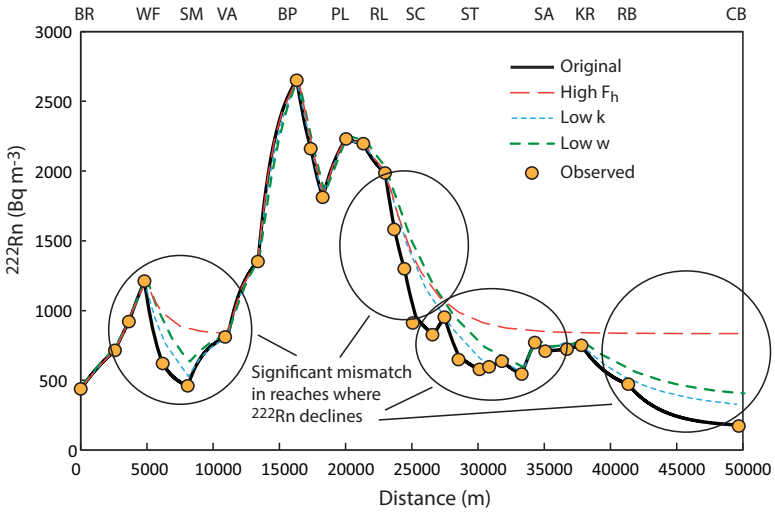

Figure 9. Calculated and observed ^{222}Rn activities for February 2015 resulting from varying individual parameters in Eq. (1) in isolation. Original is the predicted variation in ^{222}Rn activities from Fig. 5, low k is where k is reduced to 0.1 day^{-1}, high F_h increase the thickness of the parafluvial zone to 0.5 m, and low w reduces the width of the Avon River by 50 %. In all cases the new parameters result in significant overestimation of ^{222}Rn activities in many reaches and are unlikely to be realistic. Site abbreviations as for Fig. 2.

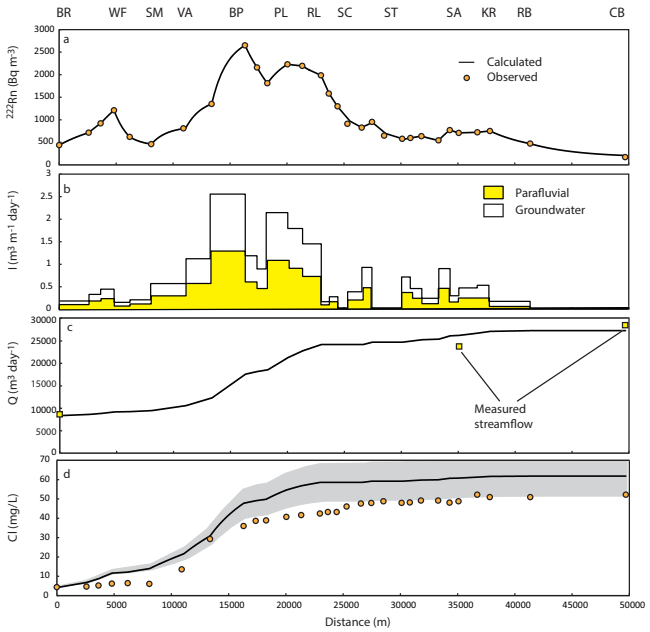

Figure 10. (a) Calculated and observed ^{222}Rn activities for February 2015 resulting from assigning 50 % of the calculated inflows as parafluvial flow. **(b)** Variation in groundwater and parafluvial inflows. **(c)** Calculated streamflow resulting from the groundwater inflows (Eq. 2) vs. measured streamflow at Stratford and Chinns Bridge. **(d)** Predicted vs. observed Cl concentrations. Shaded field is the range resulting from varying groundwater Cl concentrations within the 95 % confidence interval.