



MONASH University

**Surface water - groundwater interactions
in an upland catchment**

(Gellibrand River, Otway Ranges, Victoria, Australia)

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Thesis submitted for the degree of Doctor of Philosophy

Monash University

School of Earth, Atmosphere and Environment

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General Declaration

Monash University

Declaration for thesis based or partially based on conjointly published or unpublished work

In accordance with Monash University Doctorate Regulation 17.2 Doctor of Philosophy and Research Master's regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original papers published in peer reviewed journals and two unpublished publications. The core theme of the thesis is surface water – groundwater interactions in an upland catchment. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the School of Earth, Atmosphere and Environment under the supervision of Prof. Ian Cartwright

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research

In the case of Chapter 2, 3 and 4 my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status	Nature and extent of candidates contribution
Ch. 2	A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry	Published	Data collection, analysis and synthesis (85%)
Ch. 3	Using ^{14}C and ^3H to understand groundwater flow and recharge in an aquifer window	Under Review	Data collection, analysis and synthesis (85%)
Ch. 4	Determining the mean residence time and water sources of a first order stream in a temperate rainforest environment; the role of pipeflow	In preparation	Data collection, analysis and synthesis (85%)

I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

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Abstract

The upland area of the Gellibrand River encompasses the upper catchment (where perennial headwater streams drain native eucalypt rainforest underlain by bedrock) and the upland plain (where the river winds through an alluvial floodplain that has been predominantly cleared for agriculture). This thesis focuses on a number of aspects concerning surface water - groundwater interactions in this part of the catchment, namely: (1) the temporal and spatial variation of groundwater influxes into the Gellibrand River (2) the residence times of groundwater in the upland plain (3) the importance of recharge via direct precipitation and river water infiltration on the upland plain and (4) the sources of water and residence times of water draining the upper catchment of the Gellibrand River. These processes are investigated using environmental tracers in combination with water level monitoring and stream discharge data.

The Gellibrand River is gaining throughout the year with groundwater inflows accounting for between 10 and 50% of river flow. Groundwater residence times in the upland plain determined by ^{14}C measurements are between 100 and 10,000 years with groundwater originating from the regional recharge zone, the Barongarook High. Regional discharge of groundwater from the Barongarook High in the upland plain limits the depth to which local recharge infiltrates and additionally, the river does not recharge local groundwater even during high discharge events. The upper catchment contributes significant amounts of water to the Gellibrand River, especially during rainfall events. This is attributed to rapid preferential flow through soil pipes which drain soil water on hillslopes, with little contribution from the Riparian Zone. Mean residence times of a first order stream (Barramunga River) and the upper Gellibrand River are between 6 and 16 years with the application of ^3H providing the first age estimates of water draining headwater catchments in Australia. The process understanding gained and use of environmental tracers throughout the thesis can be applied to catchments worldwide.

Chapter 1

Introduction, background and research aims

1.1 Overview of surface water - groundwater interactions

Water is our greatest resource and represents a vital component of the natural environment. Although the hydrological cycle has been understood for some time, historically, surface water and groundwater have been treated as separate resources (Winter *et al.*, 1999). Over the last two decades, this notion has changed considerably in the scientific community, which now views surface water bodies and surrounding aquifers as part of a continuum (Bencala, 1993; Woessner, 2000; Sophocleous, 2002). Surface water in the form of rivers, streams, lakes and wetlands, and groundwater are intrinsically linked, with the exploitation of one of these resources significantly affecting the quantity and quality of the other (Brodie *et al.*, 2008). These interconnected hydrogeological systems interact in a number of complex ways which are not yet fully understood and are poorly defined. Many rivers depend on groundwater to maintain flow during periods of low rainfall whilst groundwater has also been shown to contribute a significant portion of water during high flow events (Sklash, 1979). Conversely during high flows, rivers have the potential to recharge the surrounding aquifer. From a management perspective, quantifying fluxes between connected groundwater and surface water systems is crucial for the sustainable use of water resources. The aim of this section is to give an overview of how surface water (SW) and groundwater (GW) bodies are understood to interact. This covers the basic concepts and complexities involved. Further relevant literature is reviewed in each of the chapters that follow.

GW and SW interact in a variety of landscapes, heavily influenced by the ‘hydrogeologic environment’. This term coined by Toth (1963) describes the combined effects of topography, geology and climate on the development of groundwater systems. Precipitation patterns form areas of recharge, whilst groundwater movement is controlled by the height of the potentiometric surface (which often mirrors topography) and the hydraulic conductivity of geological units through which groundwater flows (Larkin & Sharp 1992). The resultant groundwater flow paths can be organized into regional, intermediate and local flow systems and where these flowpaths intersect a surface water body, SW-GW interactions take place (Sophocleous, 2002).

The hydrologic exchange between SW and GW is controlled by a number of factors, including; the relative position of the stream stage and adjacent groundwater level, the hydraulic conductivity of channel and alluvial sediments, and the geometry and position of the stream channel within the alluvial plain (Woessner, 2000). In gaining systems rivers receive groundwater inflows through the riverbed and banks, whilst in losing systems outflow of river water to the aquifer occurs. This is determined by the height of the watertable in the river relative to the groundwater (Winter *et al.*, 1998). During low flows or baseflow conditions, the position of the water table is often sufficiently higher in the surrounding aquifer to sustain river flows, whereas when rapid rises in river stage occur during high flows, the hydraulic gradient reverses and the resulting water flux is from the river into the aquifer through the stream banks. The movement of river water into the adjacent aquifer can also be induced by hydrological stress resulting from groundwater abstraction (Theis, 1941).

Rivers may be gaining or losing throughout the year, or have reaches that are variably gaining or losing dependent on flow conditions (Figure 1.1 A, B). Understanding the temporal and spatial interaction of rivers with groundwater and locations of groundwater discharge can aid in conserving river flows, constraining recharge of aquifers by surface water bodies and enhancing water quality, particularly where saline groundwater discharge occurs or where either resource is contaminated. Where groundwater discharge into surface waters occurs, this also transports considerable nutrients upon which freshwater biota may thrive (Fiebig & Lock, 1991; Eamus *et al.*, 2006). Groundwater dependent ecosystems (GDEs) which rely on groundwater discharge or access to groundwater reservoirs include vegetation, springs, wetlands, lakes and aquifer and cave systems (Eamus, 2009). Understanding where groundwater discharge zones occur and the vulnerability of GDEs to groundwater abstraction aids in the management and conservation of these ecosystems (Brunke & Gonser, 1997; Cook, 2012). The protection of river flows may also be important where GDEs are reliant on the transfer of dissolved and particulate organic matter from surface water to groundwater (Maden & Ghiorse, 1993).

In addition to gaining and losing streams, disconnected streams also exist whereby the stream is separated from the underlying aquifer by an unsaturated zone, with leakage rates determined by streambed and aquifer permeability (Figure 1.1 C). These systems may be completely or temporarily

disconnected. Where complete disconnection occurs, changes in the water table have no effect on infiltration rates, whilst in the case of temporary disconnection the flux of water to the aquifer may be affected by changes to the water table (Brunner 2009 a b; Banks, 2011).

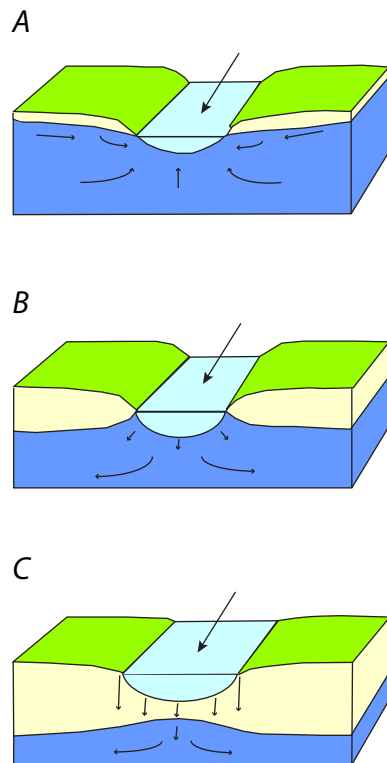


Figure 1.1 – Conceptual models of:

A. *Gaining river system*: Where the water table is higher in the aquifer than in the river.

B. *Losing river system*: Where the water table is higher in the river than the adjacent aquifer.

C. *Disconnected river system*: Where the river is separated from the underlying aquifer by an unsaturated zone.

In river catchments, constraining groundwater residence times may also provide important information for catchment managers. Aquifers dominated by modern precipitation are known to refill quickly, whilst those dominated by ancient groundwater may not recharge on human timescales. An understanding of groundwater residence times can be used to assess the vulnerability of aquifers to over-exploitation, deduce groundwater flow paths and velocities and evaluate the dynamics of groundwater recharge (Bohlke *et al.*, 2002; Foster & Chilton, 2003; Garnder *et al.*, 2011; Cartwright *et al.*, 2012). A knowledge of recharge areas may also be required to determine the potential threat to groundwater by near-surface contamination through direct precipitation and surface water flows.

Estimates of large scale regional groundwater discharge into rivers are often complicated by smaller scale processes. Here river water enters the aquifer for a period of time before later returning to the river. Bed topography and channel sinuosity cause water to undertake flowpaths through the stream bed (hyporheic flow), and flow through rivers bars and the surrounding riparian and floodplain

sediment (parafluvial flow). Additionally, the movement of water from the river into the riverbanks during high flow can result in storage in the adjacent unsaturated zone. This process known as bank storage can reduce the intensity of flood events, and for some time after the flood peak has passed, contribute to river discharge through bank return flow. Hyporheic flow, parafluvial flow and bank storage are important ecologically in that they transport oxygen-rich and solute-laden water into the sub-surface. From the perspective of surface water – groundwater studies, they are important in that they can be misinterpreted as groundwater inflows, with the chemistry of returning river water being significantly altered through contact with sediment and shallow groundwater. Understanding the extent to which hyporheic exchange occurs in river catchments and separating bank return flow from groundwater discharge has been the subject of a number of studies (Chanat & Hornberger 2003; Cook *et al.*, 2006; Jones *et al.*, 2006; McCallum *et al.*, 2010). These processes are yet to be fully understood in SW-GW studies.

Surface water – groundwater studies on river catchments have been largely focused on lowland rivers (rivers flowing through low-gradient alluvial valleys), with little work being carried out in upland catchments (steep headwater areas above the alluvial valleys). Headwater streams often constitute a significant proportion of the total stream length in many drainage basins and transmit large quantities of water downstream into adjacent lowlands (Tetzlaff & Soulsby, 2008). In lowland rivers it is well known that groundwater comprises a significant proportion of river discharge, providing a long term store over periods of drought and also contributing to river discharge during high flows. By contrast, headwater areas streams are often underlain by bedrock which is deemed impermeable. That many headwater streams flow perennially indicates long term stores must be contributing to river flow (Sklash, 1979; Neal and Rosier, 1990; Kirchner, 2003). Though water is likely stored in soils or weathered basement rocks, the location of these stores remains unclear and the residence times of water and transmit times from rainfall to streamflow in upper catchment areas is poorly understood (Bachmair & Weiler, 2012). This is important as water used for domestic, agricultural and industrial use derives from upper catchment areas. Often these areas retain native vegetation and drain under natural flow regimes, however pressure from population growth and economic development has led to changes in land-use (including forestry, agricultural and peri urban development). The consequences of future changes in land-use and the long term threat of climate change on hydrological regimes in upland catchments is unknown (Pilling & Jones, 2002).

To summarise, SW-GW interactions can occur at different scales (from small hyporheic fluxes to river reach scale exchange) with complex spatial and temporal dynamics. In many river catchments, surface water - groundwater interactions (at the regional and local scale), groundwater residence times, the dynamics of groundwater recharge and the sources of water in headwater areas require further elucidation. This is of great scientific importance not only to catchment managers, but in improving our overall picture of the hydrological cycle. A number of different techniques exist to assess the direction and magnitude of fluxes between groundwater and rivers (Kalbus *et al.*, 2006), including numerical modelling (Arnold *et al.*, 1993) and detailed temperature profiles in the river bed (Hatch, 2006). In this research SW-GW interactions are investigated using analysis of stream and groundwater hydrographs (Nathan & McMahon, 1989; Aksoy *et al.*, 2009), Darcy flux calculations (Kroeger *et al.*, 2007) and environmental tracers (Cook, 2012). Environmental tracers have been used to constrain baseflow contributions and water residence times for some time (Sklash and Farvolden, 1979). These include electrical conductivity (Oxtobee & Novakowski, 2003), chloride (Cartwright *et al.*, 2011), dissolved gases such as ^{222}Rn and CFC's (Cook *et al.*, 2003, 2008; Mullinger *et al.*, 2007, 2009; Burnett *et al.*, 2010; Cartwright *et al.*, 2011; Unland *et al.*, 2013) radiogenic isotopes such as ^{14}C and ^3H (Cartwright *et al.*, 2012; Stewart, 2012); and the stable isotopes of water (Tetzlaff *et al.*, 2008; Liu *et al.*, 2008). The use of environmental tracers often lies on different chemical signatures between stores i.e. surface water and groundwater. As most environmental tracers interact with the surrounding environment, where possible a suite of tools, or multi-tracer approach is used throughout the study to develop robust models.

1.2 Study Area – The Gellibrand River Catchment, Victoria.

The Gellibrand River Catchment occupies an area of 1,200 km², located in the Otway Basin of South-West Victoria (Figure 1.2). The catchment falls under the Corangamite Catchment Management Authority (CCMA) which develops policies relating to the health of the catchment. In addition Southern Rural Water acts as the water resource management body and is responsible for allocating licences for groundwater and surface water extraction. This must be performed in a manner which enhances the sustainability of the groundwater resource as required in the Victoria Water Act of 1989 (http://www.austlii.edu.au/au/legis/vic/consol_act/wa198983/).

Annual abstraction allocations from the Gellibrand River are ~1450 ML/year. This is predominantly used as municipal supply for the towns of Warrnambool, Colac and many Western District townships; however it also provides a water resource for agricultural use. In recent years surface water abstraction have been below allocated values (07/08 1367 ML/Day: 08/09 475 ML/Day; 09/10 246 ML/Day) (Southern Rural Water, 2011). To protect surface-water flow, currently there are no allocations for groundwater pumping within the Gellibrand Catchment, however, it represents a significant reservoir that may be developed to secure future long-term water supplies for SW Victoria (Leonard *et al.*, 1982; Barwon Water, 2012).

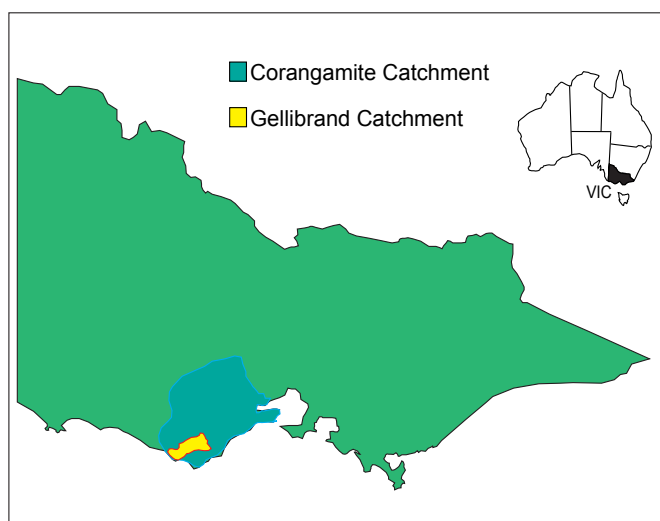


Figure 1.2 – Location of the Gellibrand Catchment in Victoria and within the Corangamite Catchment.

The Department of Environment and Primary Industries (DEPI) is responsible for overseeing monitoring and management of the health of and availability of water resources throughout Victoria. In the Gellibrand Catchment an extensive network of groundwater monitoring bores form part of the Victorian State Observation Bore Network (SOBN). These are monitored by Thiess Services Pty Ltd for DEPI and provide information on head measurement and groundwater chemistry. Additionally a number of stream gauges are present throughout the catchment. Data from groundwater bores and stream gauges is extensively used in this study and is available through the Water Measurement Information System run by DEPI (<http://data.water.vic.gov.au/monitoring.htm>)

1.3 Catchment Characteristics

The Otway Basin is a passive margin rift basin formed during the break up of Gondwana and subsequent rifting between Australia and Antarctica which began 150 million years ago (Wilcox and Stagg,

1990). Basin sediments are late Jurassic to Cenozoic in age and form a number of important aquifers and aquitards. The geology of the Gellibrand catchment is dealt with in detail in later chapters however major groundwater resources are shown in Figure 1.3. The primary aquifer in the Gellibrand region is the Eastern View Formation (equivalent to the Dilwyn Formation) composed of quartz sand, sandy clay and minor gravels (Van den Berg, 2009). This is underlain by the thinner Pebble Point Formation composed of dolomitic, quartz sandstone, clays and mudstone, whilst alluvial sediments in contact with the river represent another likely store (Figure 1.3). The upper catchment of the Gellibrand is underlain by the Eumeralla Formation. This forms the bedrock across much of the Otway Basin and is composed of compacted volcanolithic sandstone, siltstone and mudstone.

Age		Group	Formation		Importance
Cenozoic	Quaternary				Alluvium in contact with river
	Tertiary	Heytesbury	Gellibrand Marl		Confining Layer
			Clifton Formation		
		Nirranda	Demon's Bluff Formation		Minor basaltic dykes
		Wangerrip	Dilwyn/ Eastern View Formation		Major aquifer
			Pember Mudstone		
		Pebble Point Formation		Secondary Aquifer	
Mesozoic	Cretaceous	Otway Group	Eumeralla Formation		Bedrock

Figure 1.3 – Stratigraphy of the Gellibrand River Catchment and major aquifer formations

In the following research we focus on a 250 km² area which includes the upper catchment (dominated by bedrock) and upland plain (dominated by aquifer material). The study region has a Mediterranean climate with rainfall occurring predominantly through winter months, and evapotranspiration dominant during summer months. Terrain in the upper catchment consists of steep slopes covered with wet eucalypt and cool temperate rainforest, whilst the middle and lower reaches wind through cleared agricultural pasture with native vegetation on the valley sides. Average precipitation varies across the catchment from 800 - 900mm/yr in the lower reaches to 1000 – 1200 mm/yr in the upper watershed (Bureau of Meteorology, 2014). Average daily discharges in the Upper Gellibrand River

are ~ 80 ML/Day, with high discharges (> 1000 ML/Day) occurring during winter months and low discharges (< 50 ML/Day) during the summer months.

1.4 Research Objectives

In Australia, the National Water Initiative (NWI) is as an intergovernmental agreement between the Australian, state and territory governments which acts to improve the management of water resources. Although the importance of surface water – groundwater interactions is acknowledged, currently the impact of groundwater abstraction on many surface-water systems has not been appropriately addressed, and conversely the impact of surface-water diversions on groundwater resources is generally not understood.

Research from the scientific community into the interactions between groundwater and surface-water reservoirs will be intrinsic in shaping future development, and offer sustainable solutions to future demand for water, not only for water management in Australia, but around the world. The need for advanced research in these water issues within Australia led to the foundation of the National Centre for Groundwater Research and Training in 2009 (NCGRT). The NCGRT is funded by the Australian Research Council and National Water Commission to establish a national centre of excellence in groundwater research and advance our understanding of Australia's groundwater resources. The research in this thesis was performed as part of the research performed within the NCGRT.

The objective of this thesis is to advance understanding of surface water - groundwater interactions in upland catchments through the use of environmental tracers. The following research is directly applicable to future water management decisions in the Gellibrand Catchment whilst the conclusions and techniques used in this research can be applied to upland catchments worldwide. In tackling the main research objective, the thesis is broken down into 3 main chapters each with unique sub-objectives. Collectively these address surface water – groundwater interactions in the upland plain, the residence times and recharge dynamics of groundwater in the upland plain and streamflow generation and residence times in the headwaters of the Gellibrand River Catchment.

Chapter 2: ‘A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry’

- To better understand the importance of groundwater to flow in the Gellibrand River.
- Determine reaches where significant volumes of groundwater discharge to the river occur.
- Examine temporal changes in groundwater discharge.
- Compare results of ^{222}Rn , Cl and ^3H as tracers of groundwater discharge.
- Evaluate the role that variable groundwater chemistry has on studies that use end-member mixing analysis (EMMA) to quantify groundwater discharge.

Chapter 3: ‘Using ^{14}C and ^3H to understand groundwater flow and recharge in an aquifer window’

- Determine the origins of groundwater within the Gellibrand River Valley.
- To investigate the residence time of groundwater in the surrounding Eastern View Formation (Dilwyn Formation) using ^{14}C and ^3H .
- To identify areas of recharge on a regional and local scale.
- To assess the importance of surface water recharge and bank storage processes through the use of continuous electrical conductivity time series data.

Chapter 4: ‘Determining the mean age and water sources of a first order stream in a temperate rain-forest environment; the role of pipeflow’

- Characterise stream response to rainfall using continuous flow and electrical conductivity data.
- Utilise geochemical tracers (^3H , Cl, EC & major ions) to understand sources of streamflow generation in headwater catchments.
- Calculate the mean residence times of water stores and mean age of water draining the Upper Gellibrand catchment.
- Identify the first order controls on hillslope processes in the Upper Gellibrand catchment.

In Chapter 5 the understanding gained from Chapters 2, 3 & 4 is combined to provide an overall picture of hydrological processes in the upland plain of the Gellibrand River and further our understanding of surface water – groundwater processes. The use of environmental tracers in this research and their application in other surface water – groundwater studies is also discussed. Chapter 2 is published in the journal *Hydrological Processes*, Chapter 3 is currently under review at *Hydrology and Earth System Sciences* and Chapter 4 is in preparation for submission.

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Monash University

Declaration for Thesis Chapter 2

Declaration by candidate

In the case of Chapter 2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Collection of data, analysis and interpretation, manuscript production	85%

The following co-authors contributed to the work.

Name	Nature of contribution	Extent of contribution (%)
Ian Cartwright	Supervisory role, review of manuscript.	7%
Benjamin Gilfedder	Data collection assistance, manuscript review	3%
Harald Hofmann	Data collection assistance	1%
Nicolaas Unland	Data collection assistance	1%
Dioni Cendón	Data collection assistance, manuscript review	2%
Robert Chisari	Date collection assistance	1%

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature

Date

Main Supervisor's Signature

Date

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Chapter 2

A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry

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Abstract

Understanding the behaviour and variability of environmental tracers is important for their use in estimating groundwater discharge to rivers. This study utilises a multi-tracer approach to quantify groundwater discharge into a 27 km upland reach of the Gellibrand River in southwest Victoria, Australia. Ten sampling campaigns were conducted between March 2011 and June 2012, and the distribution of ^{222}Rn activities, Cl and ^3H concentrations imply the river receives substantial groundwater inflows. Mass balances based on ^{222}Rn , Cl and ^3H yield estimates of groundwater inflows that agree to within $\pm 12\%$, with cumulative inflows in individual campaigns ranging from 24346 – 88467 m^3/day along the studied river section. Groundwater discharge accounts for between 10 and 50% of river flow dependent on the time of year, with a high proportion ($> 40\%$) of groundwater sustaining summer flows. Groundwater inflow is largely governed by regional groundwater flowpaths; between 50 and 90 % of total groundwater inflows occur along a narrow 5- 10 km section where the river intersects the Eastern View Formation, a major regional aquifer. Groundwater ^{222}Rn activities over the 16 month period were spatially heterogeneous across the catchment, ranging between 2000 Bq/m^3 and 16,175 Bq/m^3 . Although groundwater ^{222}Rn activities display temporal variation, spatial variation in groundwater ^{222}Rn is a key control on ^{222}Rn mass balances in river catchments where groundwater and river ^{222}Rn activities are within an order of magnitude of each other. Calculated groundwater discharges vary from 8.4 to 15 $\text{m}^3/\text{m}/\text{day}$ when groundwater ^{222}Rn activities are varied by $\pm 1 \sigma$.

2.1 Introduction

Groundwater (GW) and surface water (SW) in the form of rivers, lakes and wetlands are intrinsically linked. Instead of being two isolated components of the water cycle, they are coupled reservoirs, with changes in one potentially affecting the other (Winter *et al.*, 1998; Sophocleous, 2002). This inter-connection is of vital importance not only in the hydrological cycle for water balances, but also from an ecological perspective, with consequences for water quality and groundwater dependent ecosystems (Hancock, 2005). In the case of rivers, an understanding of groundwater inflows enables sustainable rates of groundwater extraction to be estimated, protection of river flows, and can provide important information on the pathways of nutrients and pollutants.

Recent advances in our understanding of GW-SW connectivity has shown that exchange between the two water reservoirs occurs along a variety of flowpaths, each with a unique transmission time (McDonnell *et al.*, 2010). Regional flowpaths refer to groundwater that discharges into rivers 100's to 1000's of years after initially entering the aquifer (Larkin & Sharp, 1992). On the regional scale, rivers may be gaining (where they receive groundwater), or losing (where the net flux is from the river to the adjacent aquifer) (Cendón *et al.*, 2010; Banks *et al.*, 2011). Rivers are likely to have both gaining and losing reaches distributed along their course and this distribution may change at different flows, with a transition from gaining behaviour at low flows to losing at high flows.

Imposed on these regional flows are smaller scale hyporheic (Boulton *et al.*, 1998; Mutz & Rohde, 2003) and parafluvial flows (Deforet *et al.*, 2009). Here water travels several metres or less within the streambed sediments, re-emerging within a matter of hours to days. Though knowledge of both processes is important in order to accurately estimate groundwater inflows, at the catchment scale, regional groundwater provides the largest quantities of water, with many river systems dependent on groundwater contributions during periods of drought.

A range of techniques may be used to assess the direction and magnitude of the flux between groundwater and rivers. These include analysis of stream hydrographs (Nathan & McMahon, 1990; Aksoy *et al.*, 2009), numerical modelling (Arnold *et al.*, 1993), Darcy flux calculations (Kroeger *et al.*, 2007) and detailed temperature profiles in the river bed (Hatch, 2006). Groundwater fluxes can also be determined using environmental tracers (Cook, 2012), including electrical conductivity (Oxtobee & Novakowski, 2003), chloride (Cartwright *et al.*, 2011), dissolved gases in the form of ^{222}Rn and Chlorofluorocarbons (CFC's) (Cook *et al.*, 2003, 2006; Mullinger *et al.*, 2007; Burnett *et al.*, 2010), and the stable isotopes of water (Tetzlaff *et al.*, 2008; Liu *et al.*, 2008). The use of geochemical tracers to estimate groundwater fluxes into rivers relies on the groundwater having significantly different concentrations of the tracers to river water and the concentrations of these tracers in groundwater being uniform, or any variations being well known. Tracers may be conservative such as Cl and the stable isotopes, or have well-defined non-conservative behaviour (such as degassing rates or radioactive decay in the case of ^{222}Rn or CFC's).

With the evolution of both discrete (Freyer, 1997) and continuous (Burnett *et al.*, 2010; Hofmann *et al.*, 2011) field measurement techniques, ^{222}Rn has increasingly been used to estimate groundwater influxes into rivers. ^{222}Rn is produced by the decay of ^{226}Ra in the $^{238}\text{U} - ^{206}\text{Pb}$ decay chain. With a half life of 3.8 days, the activity of ^{222}Rn reaches secular equilibrium with ^{226}Ra in the aquifer matrix over a few weeks (Cecil & Green, 2000). Concentrations of ^{226}Ra in minerals in the aquifer matrix are several orders of magnitude higher than the dissolved ^{226}Ra concentrations in surface water (Ellins *et al.*, 1990; Cecil & Green 2000; Stellato *et al.*, 2008; Mullinger *et al.*, 2009) or the suspended ^{226}Ra in river sediments (Santos & Eyre, 2011); hence groundwater ^{222}Rn activities are commonly two or three orders of magnitude higher than those of surface water. Consequently, high ^{222}Rn activities in rivers indicate groundwater inflows. Due to its relatively short half-life and degassing to the atmosphere, ^{222}Rn activities decline downstream from these zones of groundwater inflow (Ellins *et al.*, 1990; Genereux & Hemond 1990; Cook *et al.*, 2003; Mullinger *et al.*, 2007).

Tritium (^3H) is another powerful tracer for determining the movement and residence time of water in the hydrosphere. ^3H has a half life of 12.43 years and is generally used as a technique for dating recently (< 100 years) recharged groundwater (Han *et al.*, 2012; Manning *et al.*, 2012). Although not commonly used in this way, the inflow of old groundwater with low ^3H into surface water that has high ^3H concentrations can also be used to detect groundwater inflows.

This study uses ^{222}Rn , ^3H , electrical conductivity, chloride and stable isotopes ($\delta^{18}\text{O}$ & $\delta^2\text{H}$) over a 16 month period to estimate groundwater fluxes into the upland catchment of the Gellibrand River, Victoria, Australia. In particular, the spatial and temporal variability in groundwater ^{222}Rn activities are assessed to understand the impact that variations in groundwater chemistry have on groundwater fluxes calculated using ^{222}Rn .

2.1.1 Hydrogeological Setting

The Gellibrand River is located in southwest Victoria and has a catchment area of $\sim 950 \text{ km}^2$. It rises in the Otway Ranges and flows west and southwest for 75 km, before entering the ocean via Bass Strait. This study focuses on a 27 km section of river within the upland plain of the catchment (Figure

2.1a), which covers an area of $\sim 250 \text{ km}^2$. This part of the catchment consists of a mixture of cool temperate rainforest and wet sclerophyll on the valley sides and in the headwaters, whilst the river plains have been cleared for dairy farming. With an average annual rainfall of between 800 - 1200 mm per year, the area is one of the wettest in Victoria with the majority of rainfall falling in the Australian winter between June and September (Figure 2.2).

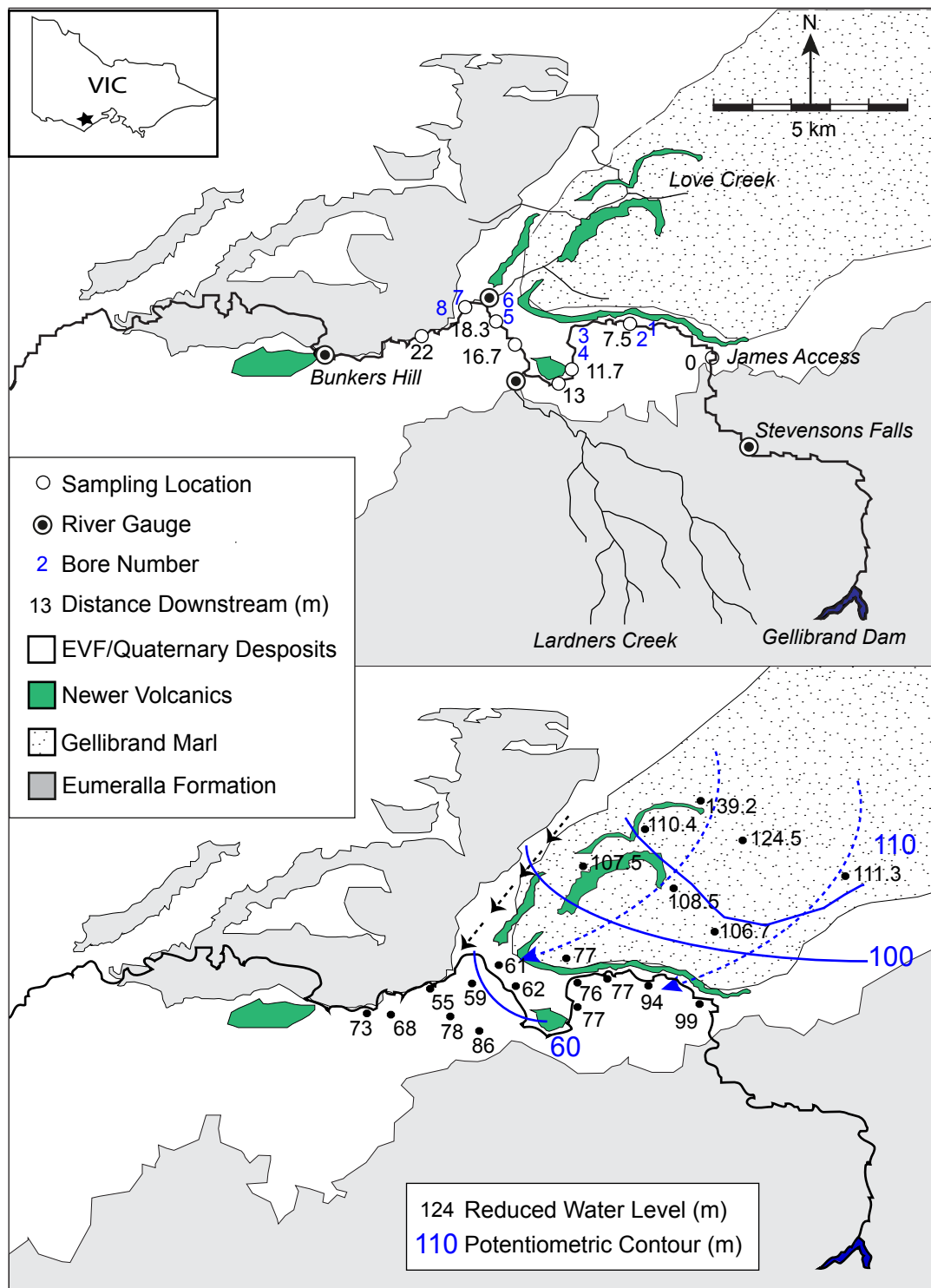


Figure 2.1- (a) – Location map of the Gellibrand catchment, showing the generalised geology and sampling locations (b) Potentiometric flow map constructed from local bore network; regional groundwater flow is predominantly in a SW direction toward the river.

Situated in the Otway Basin which was formed by late Jurassic to early Cretaceous rifting, Cretaceous volcanolithic sandstone, siltstone and mudstone of the Otway Group forms the basement of the catchment. This unit crops out in the southern and eastern margins of the upper catchment (Tickell *et al.*, 1991). The primary aquifer in the upland area is the Eastern View Formation; this is composed of non-marine sands with lenses of silt and clay, and has an average thickness across the catchment of 150 m (Leonard *et al.*, 1981). Together, the Eastern View Formation and near-stream Quaternary alluvial deposits constitute the likely sources of groundwater discharging into the Gellibrand River. To the northeast of the river, the Eastern View Formation is overlain by a regional clay aquitard – the Gellibrand Marl; this and a number of intrusions of the basaltic Quaternary Newer Volcanics confine the aquifer in this area.

The Gellibrand River has a shallow gradient (0.9 m/km) with relatively low turbulence along the study reach and no significant rapids or pool and riffle sequences. Its width is between 5 and 10 metres along most of its length, and depth varies dependent on flow conditions between 1 and 6 metres. Outflow from the Gellibrand Dam is gauged, with a further two gauges located in the upper catchment (Stevensons Falls) and at the end of the study reach (Bunkers Hill) (Figure 2.1a). Annual flow at Stevensons Falls ranges between 10 and 100 ML/day and Bunkers Hill between 50 and 500 ML/day (Victorian Water Resources Data Warehouse, 2012), with high flows occurring during the wet season (June – September) and low flows during the summer months (Figure 2.2). A number of small gauged tributaries enter the Gellibrand River in the study region; the largest of these joining from the south, Lardners Creek, has flows of 20 - 100 ML/day, and Love Creek joining from the North, has flows of 1 - 50 ML/day (Victorian Water Research Data Warehouse, 2012).

Groundwater flow in the Eastern View Formation is towards the river (Victoria Water Research Data Warehouse, 2012), indicating a potentially gaining system (Figure 2.1b). Over the 16 month study period the stream was sampled 10 times between March 2011 and June 2012 in order to encompass a range of different flow conditions and to assess temporal variations in groundwater discharge. The majority of these sampling campaigns were conducted during baseflow conditions, however June 2011 and June 2012 sampling was conducted on the recession curves of major flood peaks (Figure 2.2).

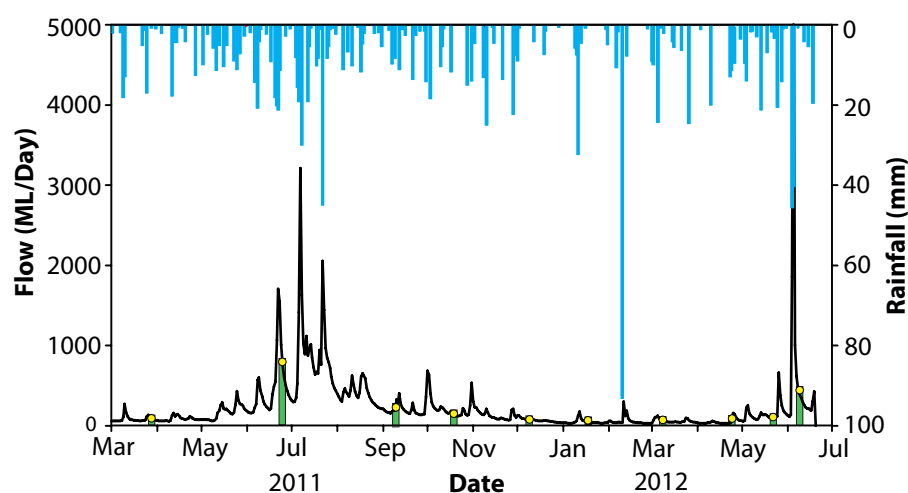


Figure 2.2 - Bunkers Hill discharge record (2011-2012). Sampling times are indicated by yellow circles.

2.2 Methodology & Analytical Techniques

River water was sampled longitudinally downstream over a 27 km stretch at 8 sites, these are designated as distance downstream from James Access (0 km), where the river first encounters the region of the catchment underlain by the Eastern View Formation aquifer (Figure 2.1a). Samples were taken ~1 metre below the river surface to ensure a representative sample of well mixed river water. Groundwater from the Eastern View Formation was sampled from 8 bores that are part of the Victorian State Observation Bore Network. The bores have screen depths of 11 - 16 m, are < 25 m from the river and are located in a 14 km² area of the catchment. Bores were pumped using an impeller pump set in the screen, purging two to three bore volumes before sampling. Electrical conductivity (EC) and pH of groundwater were measured in the field using a calibrated TPS WP-81 conductivity/pH meter and probes. Rainfall samples were also collected in the catchment throughout the study period.

Cations were analysed on a Thermo Finnigan X Series II Quadrupole ICP-MS on samples that had been filtered through 0.45µm cellulose nitrate filters and acidified to pH < 2. Anions were measured on filtered unacidified samples using a Metrohm ion chromatograph. The precision of major ion concentrations based on replicate analyses is $\pm 2\%$. Charge balances are within $\pm 5\%$. Stable isotope ratios were measured using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}\text{O}$ values were measured via equilibration with He-CO₂ at 32°C for 24-48h in a Finnigan

MAT Gas Bench whilst $\delta^2\text{H}$ values were measured by the reaction of water samples with Cr at 850°C using a Finnigan MAT H/Device. Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were measured against an internal standard that has been calibrated using the IAEA, SMOW, GISP and SLAP standards. Data was normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW where $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of SLAP are -55.5‰ and -428‰ respectively. Precision is ± 1 ‰ for $\delta^2\text{H}$ and ± 0.2 ‰ for $\delta^{18}\text{O}$.

^{222}Rn activities in groundwater and surface water were determined using a portable radon-in-air, RAD-7 monitor (DurrIDGE) following methods described by Burnett and Dulaiova (2006) and are expressed in Becquerels per m³ of water (Bq/m³). 500 cm³ of water sample was collected by bottom filling a glass flask and ^{222}Rn was degassed into a closed air loop of known volume. Counting times are 2 hours for river water and 15 minutes for groundwater and typical relative precisions are < 3% at 10,000 Bq/m³ increasing to ~ 10 % at 100 Bq/m³.

^3H concentrations were measured in a number of near-river shallow groundwater bores in April 2012 and at 4 river sites in March 2012 and April 2012. Tritium (^3H) concentrations were measured at the Australian Nuclear Science and Technology Organisation's (ANSTO) Low Level Laboratory. Samples for ^3H were distilled and electrolytically enriched prior to being analysed by liquid scintillation counting (Neklapilova *et al.* 2008a,b). ^3H concentrations are expressed in Tritium Units (TU) with a relative uncertainty of $\pm 5\%$ and a quantification limit of 0.13 - 0.14 TU.

2.3 Results

2.3.1 SW & GW geochemistry, Major Ion Concentrations and Stable Isotopes

Both GW and SW are sodium chloride-bicarbonate type waters. River water has an average pH of 6 - 8 and an EC that varies between 80 and 250 $\mu\text{S}/\text{cm}$ dependent on flow conditions. Cl concentrations in the Gellibrand River increase downstream in all sampling campaigns from 22 to 28 mg/L at James Access, to 35 – 49 mg/L at Bunkers Hill (Figure 2.3a). A similar increase occurs for major ions such as Na (Figure 2.3b) which increases downstream from 15 – 22 mg/L (James Access) to 18 – 32 mg/L (Bunkers Hill), Mg from 4.7 to 6.3 mg/L and Li from 0.7 $\mu\text{g}/\text{L}$ to 1.7 $\mu\text{g}/\text{L}$. The increase in solute

concentrations corresponds to an increase in EC values downstream from 125 - 175 to 179 - 251 $\mu\text{S}/\text{cm}$ over the sampling campaigns (Figure 2.3c).

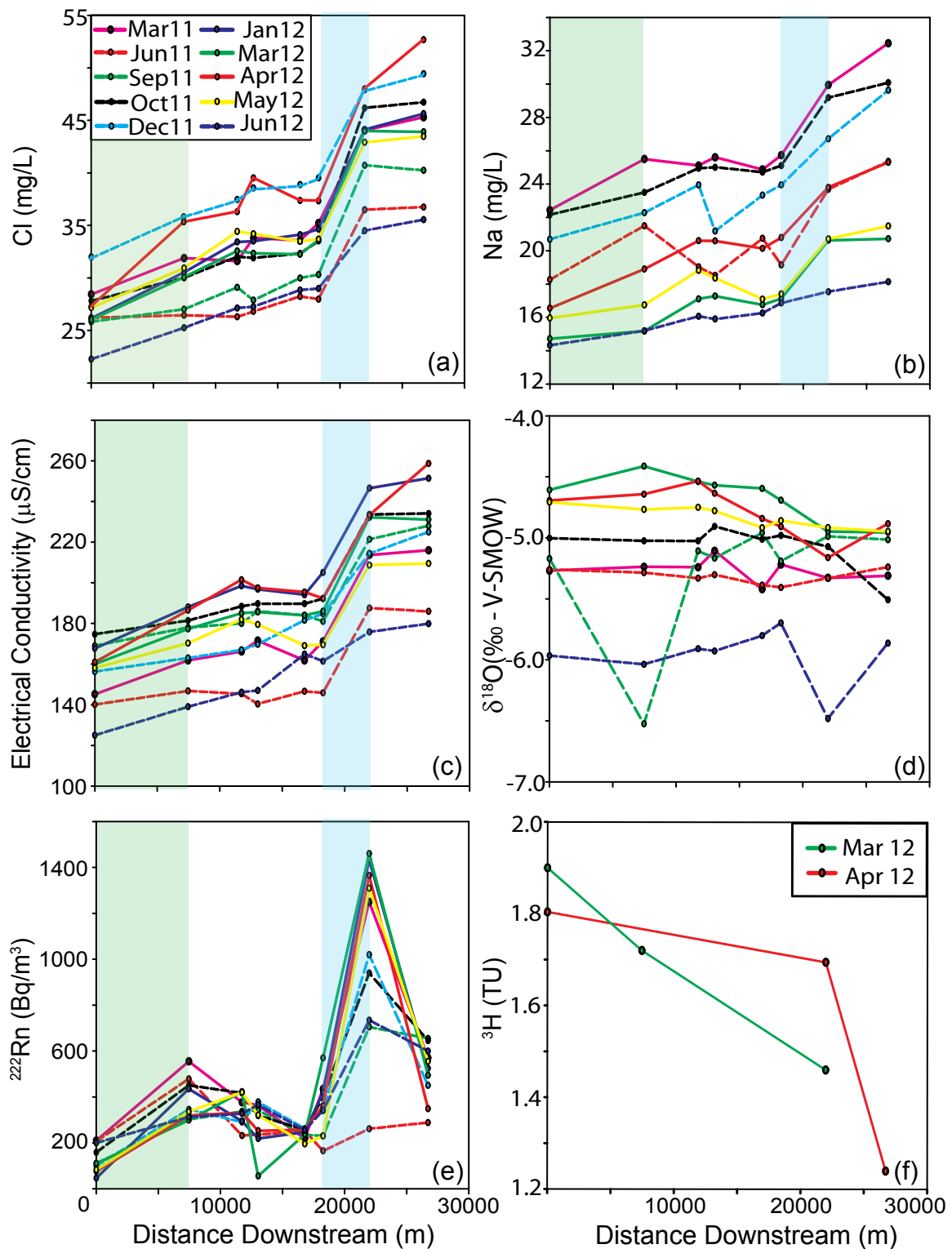


Figure 2.3 - Chloride (2.3a), Sodium (2.3b), EC (2.3c), ^{18}O (2.3d), ^{222}Rn activities (2.3e) and ^3H (2.3f) concentrations over 10 sampling campaigns. Major increases in Cl, Na, EC and ^{222}Rn are seen between two reaches at 0 - 7.5 (green) and 16.8 - 22km (blue).

Major increases in EC values and Cl and Na concentrations occur between sampling points at 0 – 7.5 km and 16.8 – 22 km downstream. This spatial pattern is observed in all sampling campaigns (Figure 2.3 a,b,c). A notable decrease in EC and Cl occurs between 13 and 16.8 km; this is due to low EC water from the upper catchment entering the Gellibrand River via Lardners Creek.

The EC of regional groundwater is substantially higher than river water, ranging between 200 and 500 $\mu\text{S}/\text{cm}$. Major ions concentrations are also higher: Na (32 – 94 mg/L), Mg (2.5 – 13.4 mg/L), K (2 – 8.5 mg/L) and Li (1 – 10 $\mu\text{g}/\text{L}$). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater and river water from all campaigns lie close to the local meteoric water line which is defined by rainfall samples in the catchment and the meteoric water line for Melbourne some 150 km to the East (Figure 2.4). There are no substantial changes in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values downstream in any of the sampling rounds (Figure 2.3d).

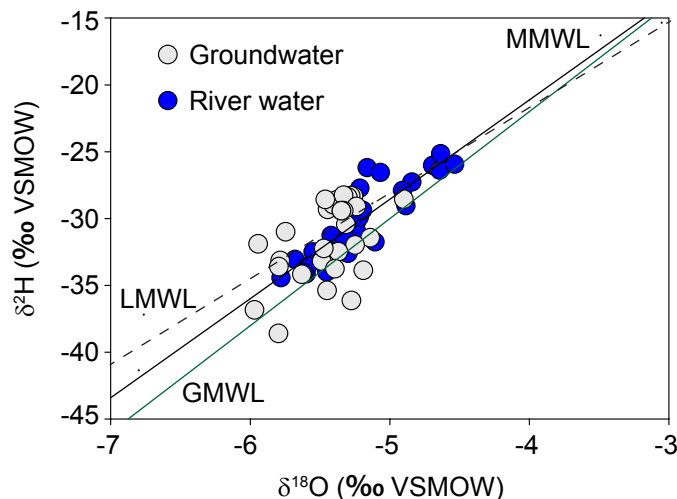


Figure 2.4 - $\delta^{18}\text{O}$ v $\delta^2\text{H}$ values for SW and GW in the Gellibrand Catchment. The Global Meteoric Water Line (GMWL) Melbourne Meteoric Water Line (MMWL) and Local Meteoric Water Line (LMWL) are shown.

2.3.2 ^{222}Rn activities in the Gellibrand River

^{222}Rn activities in the Gellibrand River range between 100 and 1500 Bq/m^3 across all sampling campaigns. Highest activities were recorded during summer months (March 2011) and lowest during the winter (June 2011). ^{222}Rn activities vary systematically downstream for all sampling rounds (Figure 2.3e). ^{222}Rn activities are lowest (46 – 210 Bq/m^3) at 0 km (James Access) and increase downstream between 0 and 7.5 km (302 – 555 Bq/m^3). This is followed by a more substantial increase in ^{222}Rn activities between 16.8 and 22 km (705 – 1460 Bq/m^3). The reaches characterized by increases in ^{222}Rn activities are separated by a large reach between 7.5 and 16.8 km that has lower ^{222}Rn activities

(200 – 400 Bq/m³). These spatial trends in ²²²Rn well correlate with changes in major ions, with high ²²²Rn activities associated with increases in EC values and chloride concentrations.

2.3.3 ²²²Rn activities and chloride concentrations in groundwater samples

Groundwater ²²²Rn activities for the eight near-river bores range from 1700 to 16,000 Bq/m³, with an average ²²²Rn for all groundwater samples of 5636 Bq/m³ and standard deviation ($\pm 1\sigma$) of 2781 Bq/m³. There is no systematic spatial variability of groundwater ²²²Rn activity within the catchment, and little relationship between groundwater ²²²Rn activity and screen depth. As well as spatial variations in groundwater ²²²Rn activities, temporal variations in groundwater ²²²Rn activities are observed between sampling campaigns, as shown by the lower and upper quartiles for each sampled bore (Figure 2.5).

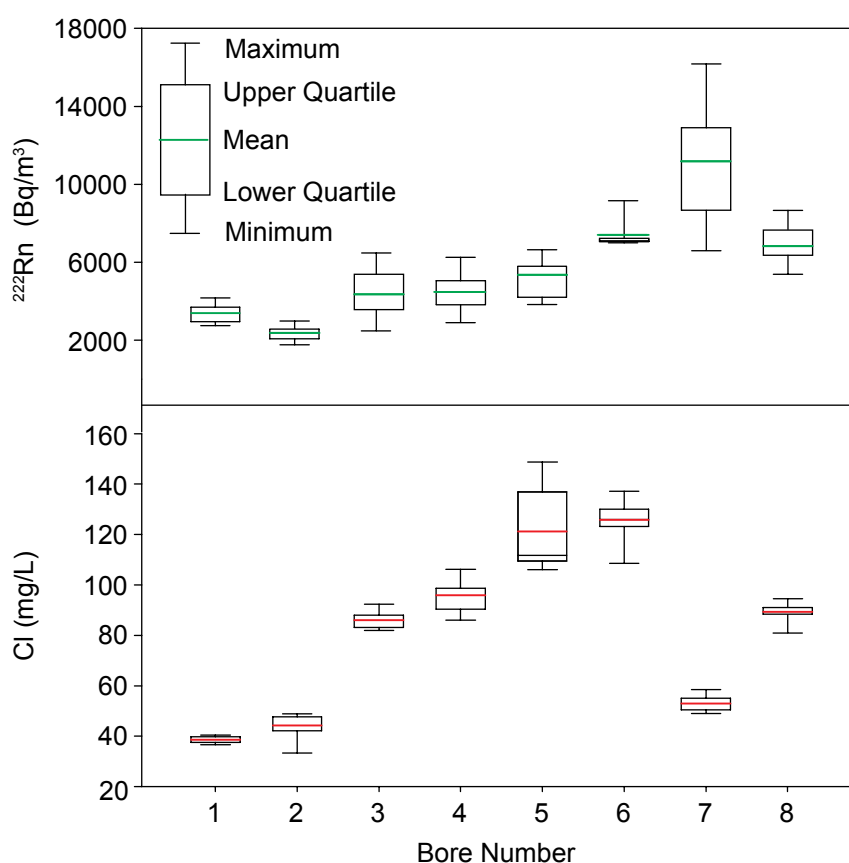


Figure 2.5 - Variation in groundwater ²²²Rn activities and Cl concentrations; the mean and interquartile range values for each bore are calculated over all sampling campaigns

The degree of temporal variation differs between bores. Large variations in the interquartile range are observed in a few bores (Bore 7: 8704 – 12,963 Bq/m³, Bore 3: 3608 – 5405 Bq/m³), however the majority remain relatively stable (Bore 1: 3166 – 3542 Bq/m³, Bore 2: 2181 – 2521 Bq/m³, Bore 6: 7138 – 7269 Bq/m³). No systematic pattern to this temporal variation in terms of screen depths or position in the catchment was observed. Average groundwater chloride concentrations exhibit a large range (38.6 – 125.5 mg/L), with a ~325 % difference between highest and lowest values, albeit lower than the magnitude of variation observed in average groundwater ²²²Rn activities (~470 % difference between highest and lowest values). Temporal variations of chloride are significantly lower, with interquartile ranges generally no higher than 6 mg/L with the exception of Bore 5 (109.8 – 131.6 mg/L).

2.3.4 ³H concentrations in surface-water and groundwater samples

The ³H concentration in near-river groundwater from bores 1-8 was below the quantification limit (0.14TU). ³H concentrations of river water in both March and April 2012 (Figure 2.3f) decline downstream, from 1.9 to 1.46 TU in March 2012 and 1.8 to 1.24 TU in April 2012. Though the largest decreases in ³H occur in different reaches, between 7.5 and 22 km in March 2012, and 22 and 27 km in April 2012, the lowest ³H concentrations in both campaigns occur after 20 km.

2.4. Discussion

With the combination of major ions, ²²²Rn activities and ³H concentrations, patterns of groundwater-surface water interaction in the Gellibrand can be distinguished. Over the 27 km of river studied, there are downstream increases in the concentrations of all major ions, a decrease in ³H concentrations, and ²²²Rn activities show a pronounced increase between 0 and 7.5 km and 18.3 and 22 km. In the following sections the changes in geochemistry are used to quantify groundwater influxes and compare calculated groundwater fluxes from different tracers.

2.4.1 Constraining groundwater inputs using ^{222}Rn

Groundwater inflows (I in $\text{m}^3/\text{m}/\text{day}$) may be estimated via:

$$I = \frac{\left(Q \frac{dC_r}{dx} - wEC_r + kdWC_r + \lambda dWC_r \right)}{(C_i - C_r)} \quad (1)$$

(Mullinger *et al.*, 2007; Cartwright *et al.*, 2011; Cook, 2012) where C_i is the ^{222}Rn activity in groundwater and C_r is the ^{222}Rn activity in the river (Bq/m^3). Q is river discharge (m^3/day), w is river width (m) and d is river depth (m). E is the evaporation rate (m/day), λ is the radioactive decay rate (0.181 day^{-1}) and k is the reaeration coefficient (day^{-1}). Evaporation rates (E) are taken from the nearest meteorological station at Mt Gellibrand, Colac, and range between 10^{-2} to $10^{-3} \text{ m}/\text{day}$ through the year (Bureau of Meteorology, 2012). In agreement with these low evaporation rates the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of river water lie on the meteoric water line rather than defining evaporation trends (Figure 2.4) and do not increase downstream (Figure 2.3d). Evaporation is, therefore, unlikely to significantly increase the concentration of solutes in the river. Groundwater ^{222}Rn activities are taken as the mean value from bores sampled during each campaign.

The reaeration coefficient (k) is related to river turbulence and defines the rate of exchange or degassing of ^{222}Rn across the air-water interface. River velocity and depth are the two most important factors in driving degassing. k is estimated using Equations (2) & (3), which are modifications of the gas transfer models of O'Connor & Dobbins (1958) and Negulescu & Rojanski (1969), where (v) is river velocity in m/s and (d) depth in metres.

$$K_1 = 9.301 \times 10^{-3} \left(\frac{v^{0.5}}{d^{1.5}} \right) \quad (2)$$

$$K_2 = 4.87 \times 10^{-4} \left(\frac{v}{d} \right)^{0.85} \quad (3)$$

Although a number of other empirical relationships between velocity, depth and k exist (St John

et al., 1984); these two formulations yield values of k that bracket those of most of the other models and thus provide upper and lower estimates of groundwater inflow (Mullinger 2007; Unland *et al.*, 2013). k values for the Gellibrand range between 0.5 and 5 across a range of flows. These are similar to values estimated in other studies of rivers with low gradients and without significant rapids or pool and riffle sequences which can enhance degassing (Mullinger *et al.* 2007). Values of k_2 are higher than k_1 ; therefore, larger groundwater inflows are calculated where k_2 is used in the mass balance. Groundwater inflows calculated using Equation 1 fluctuate along the river from 0 to 11.1 $\text{m}^3/\text{m}/\text{day}$ (Figure 2.6). Two gaining reaches provide most of the groundwater discharge, separated by a variably losing and gaining section of river. The first gaining reach is between 0 and 7.5 km, with inflows of 0.5 to 1.5 $\text{m}^3/\text{m}/\text{day}$ during non-flood campaigns. During the June 2011 flood event, inflows here rise considerably to 5.4 (k_1) – 7.7 (k_2) $\text{m}^3/\text{m}/\text{day}$. A second highly-gaining reach at 18 – 22 km then follows, with groundwater inflows that range between 4.3 and 11.1 $\text{m}^3/\text{m}/\text{day}$. Dramatic increases in groundwater inflows are not observed here during flood events.

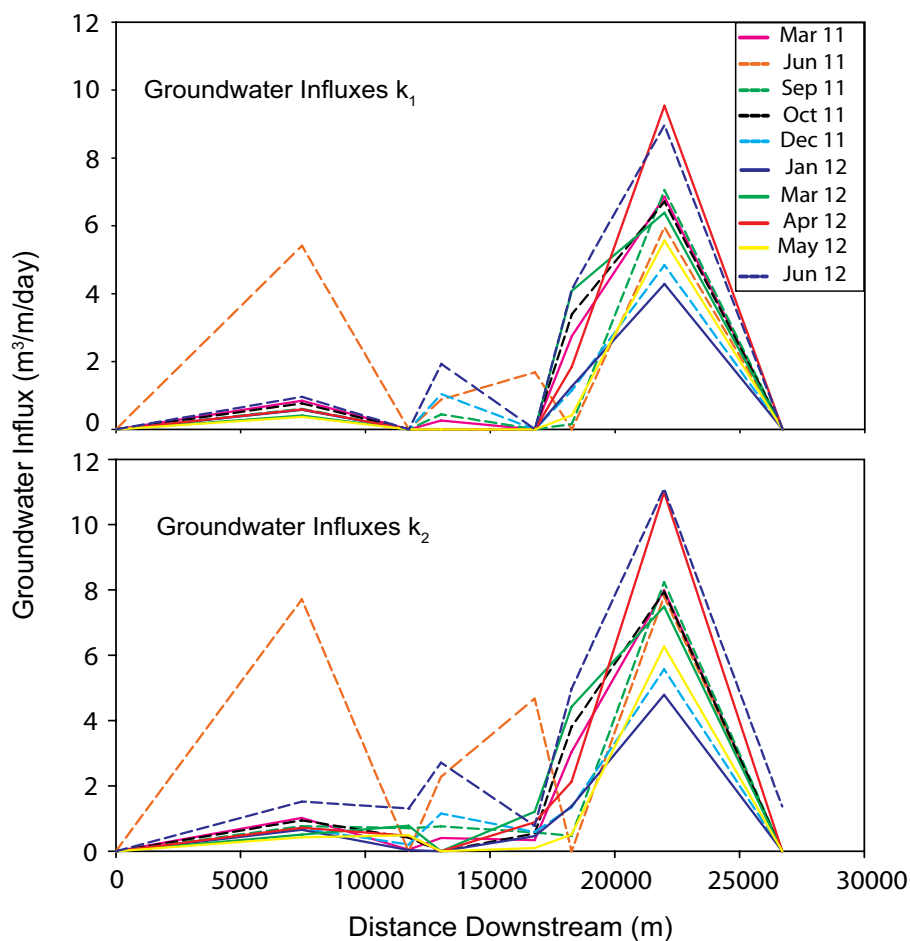


Figure 2.6 - Calculated groundwater inflows downstream using two degassing models (k_1 and k_2).

Between 7.5 and 16.8 km groundwater discharge into the river varies throughout the year. For non-flood events groundwater fluxes are low (0 - 1.1 m³/m/day), and depending on the k value chosen, this reach can be interpreted as either gaining or losing. During the June 2011 flood event, the maximum groundwater discharge along this reach increased to 4.7 m³/m/day, with a similar increase (2.7 m³/m/day) seen during the recession of the June 2012 flood. Cumulative groundwater inflow rates along the river range between 22,079 - 42,526 m³ (k₁) and 29,677 - 54,681 m³ (k₂) in non-flood campaigns; these increase to 69,937 – 106,997 m³/day during the June 2011 flood event. As a proportion of the total river flow at Bunkers Hill (27 km downstream), cumulative groundwater inputs account for 25 - 46% of river water during non-flood periods, dropping to 8 - 21% in the June 2011 event.

2.4.2 Constraining groundwater inputs using chloride

As groundwater sampled from near river bores generally has higher chloride concentrations (70 – 80 mg/L) than river water (22 - 49 mg/L), changes in river chloride concentrations (Cl_r) downstream (Figure 2.3a) can be used to calculate groundwater inflow rates via:

$$I = \frac{\left(Q \frac{dCl_r}{dx} - wEC_r \right)}{(Cl_i - Cl_r)} \quad (4)$$

Cartwright *et al.*, 2011), where Cl_i is the average groundwater chloride concentration in the near-river bores (78 mg/L) and E was again assumed to be 10⁻² to 10⁻³ m/day (Bureau of Meteorology, 2012). Groundwater fluxes calculated by the chloride mass balance (Figure 2.7) are consistent with those calculated by the ²²²Rn mass balance (Figure 2.6). Groundwater inflows to the river in non-flood events range between 0 and 11.7 m³/m/day, and areas of high groundwater discharge are consistent with the two dominant gaining reaches at 0 - 7.5 km and 18 - 22 km. Between 7.5 and 16.8 km the stream consists of a number of small reaches which transition between losing and gaining conditions, with groundwater inputs varying between sampling campaigns from 0 to 2.3 m³/m/day. Again a significant increase in groundwater discharge is seen here during the June 2011 flood event (5.6 m³/m/day).

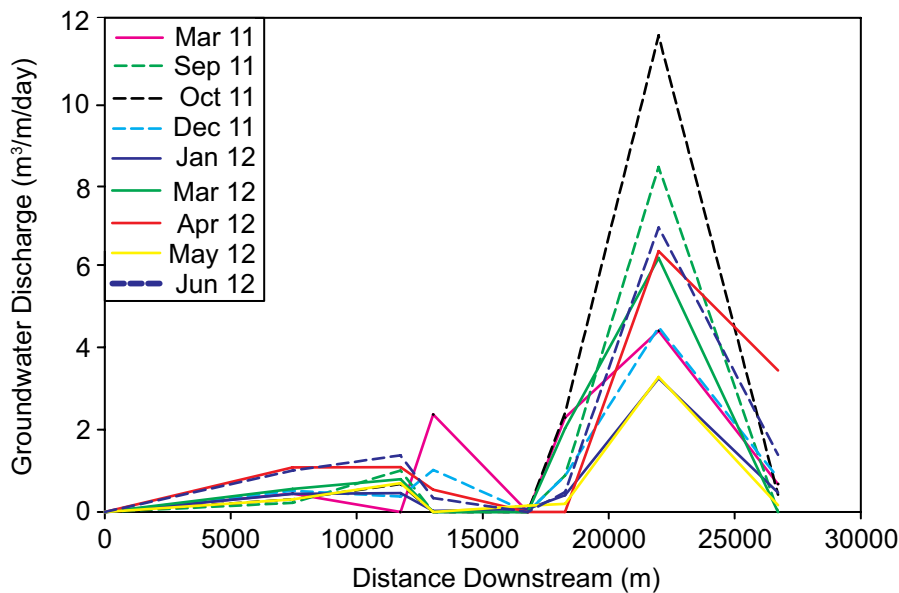


Figure 2.7 - Groundwater discharge calculated via chloride mass balance (June 2011 flood omitted).

Cumulative groundwater inflows of 29,300 - 51,700 m³/day occur during non-flood sampling campaigns, with groundwater accounting for 18 – 60% of total river flow at Bunkers Hill (27 km downstream). As with the ²²²Rn mass balance, the chloride mass balance predicts increased groundwater inflows (134,000 m³/day) during the June 2011 flood event. However, the Cl data implies that significant groundwater inflows occur between 18 and 22 km (31.8 m³/m/day), whereas the ²²²Rn mass balance indicates significant groundwater discharges between 0 and 7.5 km.

2.4.3 Constraining groundwater inputs using ³H

Decreases in ³H downstream coincide with the region between 16.8 – 22 km where ²²²Rn activities and Cl concentrations are highest. The decreases in river ³H concentrations downstream can be attributed to the influx of ³H-free regional groundwater. Total groundwater discharges during March and April 2012 were estimated via Equation (4), using river water ³H concentrations and a ³H concentration of 0 TU in the groundwater. Evaporation rates are low and the lack of fractionation of ²H within the river (Figure 2.4) implies that there will be negligible in-river ³H fractionation due to evaporation. Calculated groundwater discharges using ³H concentrations are 28,391 m³/day for March 2012, and 55,242 m³/day for April 2012. These results correspond well for both months with discharges calculated by ²²²Rn and Cl (Table 2.1).

Date	Cumulative Groundwater Discharge (m ³ /day)		
	²²² Rn	Cl	³ H
03/11	39,900	29,350	-
06/11	88,450	134,000	-
09/11	37,350	38,400	-
10/11	37,175	51,700	-
12/11	28,900	28,650	-
01/12	24,350	18,300	-
03/12	39,500	33,500	28,500
04/12	48,600	53,300	55,250
05/12	26,840	19,140	-
06/12	63,700	47,000	-

Table 2.1 – Cumulative groundwater discharges for Cl, ²²²Rn & ³H calculated for all campaigns.

2.4.4 Uncertainties in calculated groundwater fluxes

It is important to understand the potential uncertainties in calculated groundwater inflows that arise from hyporheic exchange and uncertainties in the degassing coefficient and groundwater end-member. The flux of water through the hyporheic zone can potentially introduce ²²²Rn to rivers, where water flowing beneath the streambed accumulates ²²²Rn from ²²⁶Ra in the sediments and returns to the river with increased ²²²Rn activities. Hyporheic flow may contribute a significant amount of ²²²Rn in rivers that are losing or have low groundwater inflows, and failure to account for hyporheic flow in rivers with low ²²²Rn activities may lead to overestimates in groundwater inflows. For example, Cook *et al.* (2006) calculated that ²²²Rn introduced into the Cockburn River, NSW by hyporheic flow resulted in an overestimation of groundwater inflows by 60%.

With high ²²²Rn activities and groundwater inflow rates (up to 11.7 m³/m/day) in the Gellibrand River, the ²²²Rn mass balance becomes less sensitive to the small relative contribution of ²²²Rn introduced by hyporheic flow. The river is largely gaining throughout the year and with a consolidated, low hydraulic conductivity clay rich river bed along most of its length, hyporheic flux is likely to be of little significance. Chloride concentrations are unaffected by hyporheic processes and with groundwater inflows calculated using chloride in the majority of campaigns within $\pm 12\%$ of those calculated using ²²²Rn and ³H (Figure 2.8) it appears unlikely that hyporheic exchange has a substantial impact on groundwater discharges estimated via the ²²²Rn mass balance.

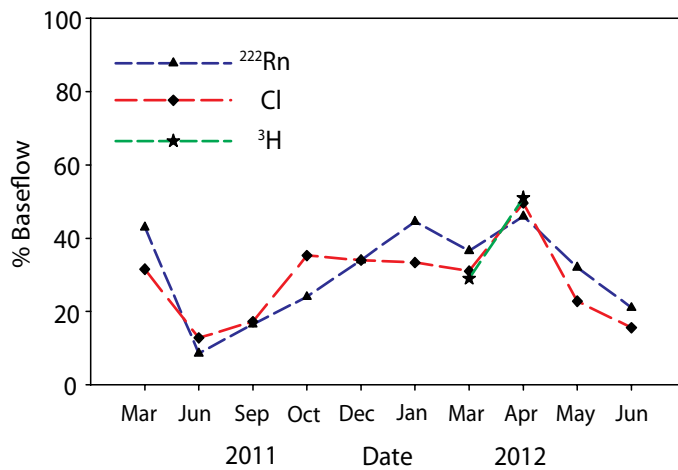


Figure 2.8 - Baseflow as a % of total river discharge calculated for ^{222}Rn , Cl and ^3H over all sampling periods.

Another potential error in the calculations is the uncertainty in ^{222}Rn reaeration rates (k). The two empirically derived values of k bracket the range of likely values and the resulting range of estimated groundwater inflows takes into account the uncertainty in k . In the variably gaining/losing section of the river between 7.5 and 16.8 km where groundwater inputs are low ($< 1 \text{ m}^3/\text{m}/\text{day}$), the river may be interpreted as gaining (k_2) or losing (k_1) depending on the value of k applied. However, the groundwater contribution from this area relative to cumulative groundwater inputs along the entire study reach is insignificant due to the dominance of the 16.8 – 22 km discharge zone. Further to this, it is unlikely losing conditions exist as Cl values increase through the 7.5 – 16.8 km reach and the potentiometric maps (Figure 2.1b) also indicate that the river is gaining.

Variations in groundwater ^{222}Rn activities are another uncertainty in studies using tracer mass balances. Systematic spatial variations in groundwater ^{222}Rn activities have been reported in river catchments (Mullinger *et al.*, 2007, 2009), however few studies have considered the importance of both spatial and temporal variations in the groundwater end-member. Spatial variation in groundwater ^{222}Rn activities exists in the Gellibrand catchment, likely related to the heterogeneous mineralogy of the sediments. There is however, no systematic variation with location in the catchment, or with water table fluctuations, such as has been observed in other river catchments (Mullinger *et al.*, 2007).

In the Gellibrand catchment the ^{222}Rn mass balance is highly sensitive to the chosen value of C_i as groundwater ^{222}Rn activities are only an order of magnitude higher than surface water activities. The

relationship between groundwater inflows (I) and the groundwater end-member is asymptotic (Figure 9b); with variation in C_i input into the ^{222}Rn mass balance causing large errors in calculated GW discharge. Mean, groundwater ^{222}Rn activities for March 2011 of 5296 Bq/m^3 yield discharge estimates between 0 and $8 \text{ m}^3/\text{m/day}$ along the river. Allowing C_i in the ^{222}Rn mass balance to vary by 1σ ($1,956 \text{ Bq/m}^3$) produces a range in groundwater inflows from 0 - $5.4 \text{ m}^3/\text{m/day}$ to 0 - $15.4 \text{ m}^3/\text{m/day}$ (Figure 2.9a). This results in cumulative groundwater discharge varying from 25,000 to 67,000 m^3 (Figure 2.9b), and river baseflow percentage from 30% ($C_i - 1\sigma$) to 80% ($C_i + 1\sigma$).

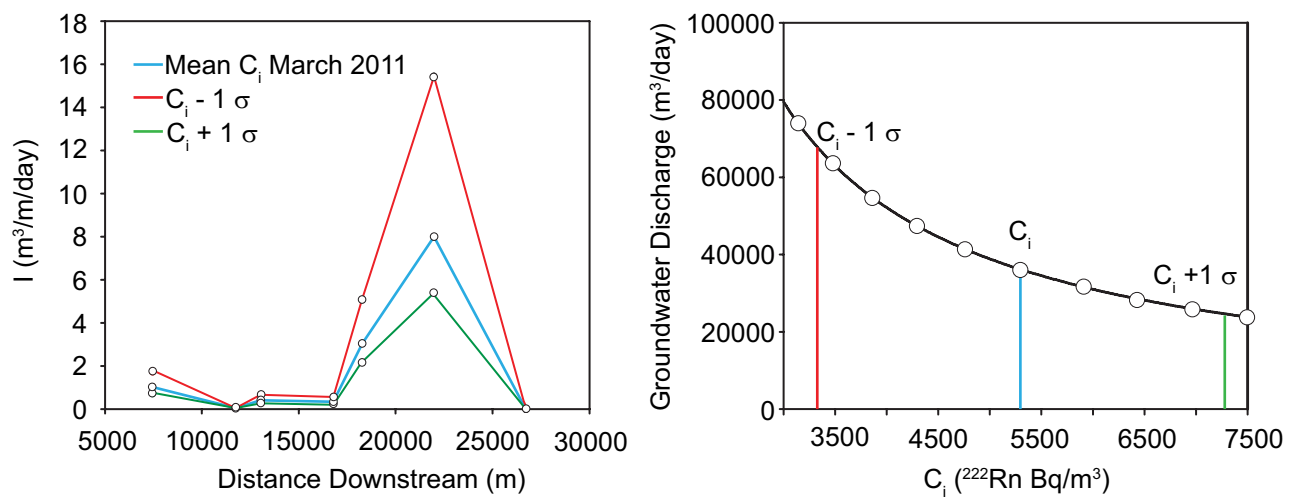


Figure 2.9 - (a). (left) – Importance of variations in the GW ^{222}Rn end-member (C_i) on groundwater discharge (I). 9(b). (right) – The effect of varying C_i on cumulative groundwater influx.

Though groundwater bores display significant variations in ^{222}Rn activity throughout the year, temporal variations have a minor impact when constraining the groundwater end-member for the catchment (C_i). When C_i for each sampling campaign is calculated as the average ^{222}Rn activity across all bores, individual bore variations are smoothed with C_i fluctuating over the study period by a maximum of $\pm 1,270 \text{ Bq/m}^3$ (Table 2.2). This indicates that in the Gellibrand catchment, constraining temporal variations in groundwater ^{222}Rn is less important than constraining spatial variations in ^{222}Rn across the catchment.

Date	C_i ^{222}Rn (Bq/m ³)	C_i Cl (mg/L)
30/03/2011	5297	77.3
23/06/2011	5472	76.5
17/01/2012	5871	78.5
06/03/2012	6273	87.7
25/04/2012	5003	78.6
23/05/2012	6220	79.3

Table 2.2 - Temporal variations in average groundwater ^{222}Rn activities and Cl concentrations

Variations in C_i are also an important factor in the chloride mass balance. Again there is a large spatial variation in groundwater chloride values across the catchment (38.6 - 123.5 mg/L). A $\pm 10\%$ variation in C_i results in a 5 - 10% difference in the calculated baseflow component. (The mass balance is more sensitive to under-estimations in C_i as the relationship to groundwater discharge as with ^{222}Rn is asymptotic; Figure 2.9b). Temporal variations in chloride concentrations are also relatively minor in comparison to spatial variability (Table 2.2), remaining stable throughout the sampling campaigns. In catchments where groundwater ^{222}Rn activities and chloride concentrations are heterogeneous, it is important to ensure a representative groundwater end-member is chosen for both mass balances, this can only be achieved through sampling of a number of bores throughout the catchment, in particular where no spatial trend can be defined.

2.4.5 Controls on groundwater-surface water interaction in the Gellibrand River

The upland plain of the Gellibrand River is a largely gaining system that receives considerable groundwater inputs. Groundwater contribution to the river system varies with discharge, amounting to 10 – 20% of total river discharge at Bunkers Hill in higher winter flows (June to September), increasing up to 40 - 50% in summer months (January to April). This is likely to be related to rainfall patterns where the river becomes increasingly dependent on groundwater contributions in the dry season. The river is deeply incised into the floodplain, with steep banks present on either or both sides of the river. Where shallow water tables intersect the land surface at the base of these banks, this results in the seepage of groundwater into the river.

The majority of groundwater influx occurs in two distinct reaches of the river, in particular a groundwater discharge zone 16.8 – 22 km downstream. Groundwater inflows calculated using ^{222}Rn and Cl suggest that except during flood conditions, between 50 and 90% of the total groundwater discharge in the studied area occurs in this zone. This area corresponds to the region where the Eastern View Formation intersects the river. Total groundwater contributions to the river calculated by mass balances for the tracers ^3H , Cl and ^{222}Rn are within $\pm 12\%$, suggesting that processes such as degassing and hyporheic exchange are not significant. In the Gellibrand catchment obtaining a representative groundwater end-member for ^{222}Rn and Cl is shown to be of vital importance for calculating groundwater fluxes using tracer mass balances.

2.5. Conclusion

A number of studies have used environmental tracers to determine groundwater inflows into rivers, often with considerable variations between fluxes estimated from different tracers (Cartwright *et al.*, 2011). Understanding the factors which limit the use of environmental tracers in constraining groundwater inflow in different environments is integral for their use in groundwater-surface water studies. In this study, groundwater fluxes have been calculated at a high temporal frequency with considerable agreements between estimates made using three different chemical tracers (^3H , ^{222}Rn and Cl). In the Gellibrand River catchment it is shown that the most important factor in constraining groundwater fluxes using environmental tracers is accurate quantification of ^{222}Rn and Cl groundwater end-members. This can only be achieved by capturing the spatial heterogeneity in groundwater chemistry across river catchments, with failure to do so leading to large errors in calculated groundwater discharge. Temporal variations in groundwater chemistry are shown to be of minor importance. In the Gellibrand catchment hyporheic exchange and uncertainties in river degassing rates are considered to be of minor importance when calculating groundwater discharge using ^{222}Rn .

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Declaration for Thesis Chapter 3

Declaration by candidate

In the case of Chapter 3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Collection of data, analysis and interpretation, manuscript production	85

The following co-authors contributed to the work.

Name	Nature of contribution	Extent of contribution (%)
Ian Cartwright	Supervisory role, review of manuscript.	7.5%
Benjamin Gilfedder	Data collection assistance and manuscript review.	3%
Dioni Cendón	Data collection assistance and manuscript review.	2%
Nicolaas Unland	Data collection assistance	1.25%
Harald Hofmann	Data collection assistance	1.25%

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature

Date

Main Supervisor's Signature

Date

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Chapter 3

Using ^{14}C and ^3H to understand groundwater flow and recharge in an aquifer window

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Abstract

Knowledge of groundwater residence times and recharge locations are vital to the sustainable management of groundwater resources. Here we investigate groundwater residence times and patterns of recharge in the Gellibrand Valley, southeast Australia, where outcropping aquifer sediments of the Eastern View Formation form an ‘aquifer window’ that may receive diffuse recharge and recharge from the Gellibrand River. To determine recharge patterns and groundwater flowpaths, environmental isotopes (^3H , ^{14}C , $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$) are used in conjunction with groundwater geochemistry and continuous monitoring of groundwater elevation and electrical conductivity. Despite the water table fluctuating by 0.9 to 3.7 m annually producing estimated recharge rates of 90 and 372 mm yr⁻¹, residence times of shallow (11 to 29 m) groundwater determined by ^{14}C ages are between 100 and 10,000 years. ^3H activities are negligible in most of the groundwater and groundwater electrical conductivity in individual areas remains constant over the period of study. Although diffuse local recharge is evident, the depth to which it penetrates is limited to the upper 10 m of the aquifer. Rather, groundwater in the Gellibrand Valley predominantly originates from the regional recharge zone, the Barongarook High, and acts as a regional discharge zone where upward head gradients are maintained annually, limiting local recharge. Additionally, the Gellibrand River does not recharge the surrounding groundwater and has limited bank storage. ^{14}C ages and Cl concentrations are well correlated and Cl concentrations may be used to provide a first-order estimate of groundwater residence times. Progressively lower chloride concentrations from 10,000 years BP to the present day are interpreted to indicate an increase in recharge rates on the Barongarook High.

3.1 Introduction

Groundwater residence time can be defined as the period of time elapsed since the infiltration of a given volume of water (Campana & Simpson, 1984), or perhaps more accurately, the mean time that a mixture of waters of different ages have resided in an aquifer (Bethke & Johnson, 2008). The residence time of water within an aquifer is a key parameter in describing catchment storage and may be used to estimate historical recharge rates (Le Gal La Salle *et al.*, 2001; Cook *et al.*, 2002; Cartwright & Morgenstern, 2012; Zhai *et al.*, 2013), elucidate groundwater flowpaths (Gardner *et al.*, 2011; Smerdon *et al.*, 2012), calibrate hydraulic models (Mazor & Nativ, 1992; Reilly *et al.*, 1994; Post *et al.*, 2013) and characterize the rate of contaminant spreading (Böhlke and Denver 1995; Tesoriero *et*

al., 2005). From a water resource perspective, information on groundwater residence times is required for sustainable aquifer management by identifying the risk posed to groundwater reserves against over-exploitation (Foster & Chilton, 2003), climate change (Manning *et al.*, 2012) and contamination (Böhlke, 2002).

Unconfined aquifers may be recharged over broad regions leading to young groundwater at shallow depths (Cendón *et al.*, 2014). On the other hand, the residence time of groundwater in confined aquifers generally increases away from discrete recharge areas. The geology of catchments is often complex and heterogeneous and, where aquifer material is exposed in more than one location, this offers a potential ‘window’ for groundwater recharge (Meredith *et al.*, 2012). It is important to document groundwater flow in such aquifer windows. If they act as recharge areas, changes in land-use such as agricultural development may introduce contaminants to the deeper regional groundwater systems. By contrast, if they are local discharge areas, use of regional groundwater may impact rivers, lake or wetlands that are receiving groundwater.

High river flows may also recharge shallow groundwater if the hydraulic gradient between the river and the groundwater is reversed during high flows (Doble *et al.*, 2012). Episodic recharge of aquifers by large over-bank floods is also locally important (Moench & Barlow, 2000; Cendón *et al.*, 2010; Doble *et al.*, 2012), particularly in arid areas (Shentsis & Rosenthal, 2003); however, the potential for over-bank events to recharge aquifers in temperate areas is still poorly understood. Additionally, during high flow, water from rivers is likely stored temporally in the banks (McCallum *et al.*, 2010, Unland *et al.*, 2014); however, the depth and lateral extent to which bank exchange water infiltrates the aquifer is not well documented. Understanding the capacity of rivers to recharge regional groundwater is important in understanding exchange within the hydrological cycle (Stichler *et al.*, 1986; Chen & Chen, 2003). Furthermore, where surface-waters transport contaminants and have the potential to recharge the surrounding aquifer, this may lead to contamination and degradation of groundwater quality (Newsom & Wilson, 1988; Stuyfzand, 1989). Lastly, knowledge of residence times of groundwater in close proximity to the river can provide important information on groundwater-river interactions (Gardner *et al.*, 2011). Local groundwater flowpaths in connection with rivers are often underlain by deeper regional flowpaths (Tóth, 1963) however the role these flowpaths play in con-

tributing to river baseflow remains unclear (Sklash & Farvolden, 1979; McDonnell, 2010; Frisbee & Wilson, 2013; Goderniaux *et al.*, 2013). This may be elucidated from understanding residence times of near-river groundwater (Smerdon *et al.*, 2012).

3.1.1 Radiogenic Tracers

Radioactive environmental isotopes, in particular ^{14}C and ^3H have proven useful tools for determining groundwater residence times (Vogel, 1974; Wigley, 1975). Produced in the atmosphere via the interaction of N_2 with cosmic rays, ^{14}C has a half life of 5730 years and can be used to trace groundwater with residence times up to 30 ka. The use of ^{14}C in dating groundwater was first discussed by Muennich (1957), and has subsequently been widely used due to the ubiquitous presence of dissolved inorganic carbon (DIC) in groundwater (Cartwright *et al.*, 2012; Samborska *et al.*, 2012; Stewart, 2012). The calculation of ^{14}C ages may be complicated if groundwater DIC is derived from a mixture of sources (Clark and Fritz, 1997). Where a large proportion of DIC is derived from the dissolution of ^{14}C -free carbonate minerals in the aquifer matrix, the ^{14}C originating from the atmosphere or soil zone will be significantly diluted. Additionally, geogenic CO_2 and CO_2 generated by the breakdown of organic matter during methanogenesis may provide additional sources of ^{14}C -free DIC. Groundwaters recharged post 1950 may have anomalously high ^{14}C activities ($a^{14}\text{C}$) due to the ^{14}C produced during atmospheric nuclear tests. Objective ^{14}C dating requires recognition and quantification of these processes. A number of models based on both major ion and stable C isotope geochemistry have been proposed to correct apparent ^{14}C ages (Han & Plummer, 2013)

With a significantly shorter half-life (12.33 years), ^3H can be used to date groundwater with residence times of up to 100 years (Vogel *et al.*, 1974). With the decay of the 1960s ^3H bomb-pulse peak in the southern hemisphere to near background levels unique ages may now be determined from single ^3H measurements (Morgenstern *et al.*, 2010). As ^3H is part of the water molecule, there is negligible change to ^3H activities other than decay, providing an excellent tracer for the movement of water through hydrological systems (Michel, 2004). Used in conjunction with ^{14}C data, ^3H may also be used to study mixing in shallow aquifers (Le Gal La Salle, 2001; Cartwright & Morgenstern, 2012).

3.1.2 Study Site

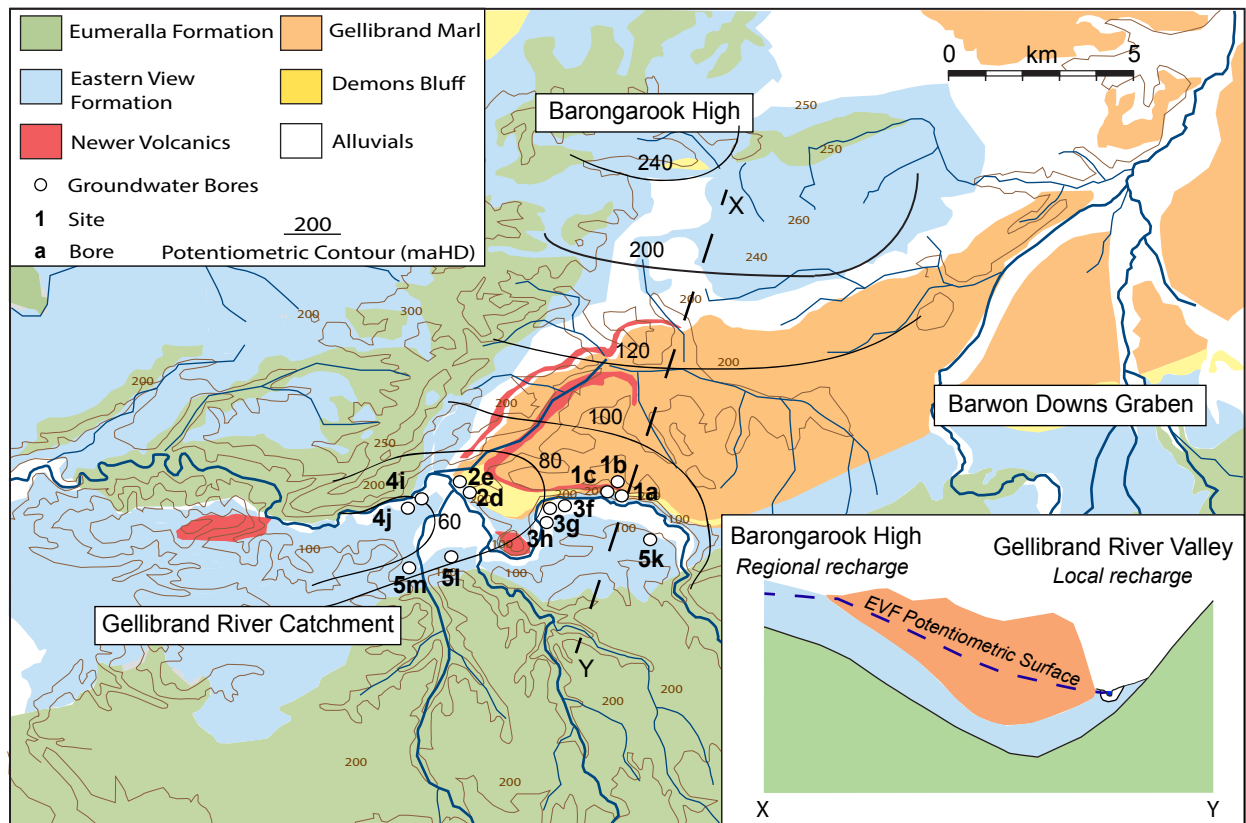


Figure 3.1 – Geology, groundwater flow, and cross sectional view of the Gellibrand River Catchment. Potentiometric contours for the Eastern View Formation are created from groundwater data (Water Resources Data Warehouse, 2013) and are expressed in metres above Australian Height Datum (mAHD). Sampled groundwater bores are also shown. Letters refer to bores listed in Table 3.1.

The Otway Basin is located in southwest Victoria, covering an area of 150,000 km². The basin was formed during the Cretaceous rifting of Australia and Antarctica (Briguglio *et al.*, 2013) and is infilled with Upper Cretaceous and Cenozoic siliciclastic and calcareous sediments that form several aquifers and aquitards. The basin is divided into a number of sub-basins with regional groundwater flow paths originating at topographic highs. The Gellibrand catchment is one of these sub-basins. This study focuses on a 250 km² upland area of the catchment, the Gellibrand River Valley, which lies at the foothills of the Otway Ranges, directly south of the Barongarook High, a regional recharge zone, from which groundwater flows southwest along the Gellibrand River Catchment as well as eastward into the Barwon Downs Graben (Figure 3.1).

Cretaceous Otway Group sediments of the Eumeralla Formation form the basement of the catch-

ment and crop out in areas of higher relief. The Eumeralla Formation consists of thickly bedded siltstone, mudstone and volcanolithic sandstone. It has a low primary porosity and hydraulic conductivity and acts as a poor aquifer (Lakey & Leonard, 1982). Cenozoic sediments of the Wangerrip group overlie the bedrock and form major aquifers in the region to which groundwater flow is constrained (Van den Berg, 2009). The primary aquifer in the study area is the Eastern View Formation or equivalent Dilwyn Formation (Van den Berg 2009; Petrides & Cartwright 2006; Atkinson *et al.*, 2013), composed of gravel, fine to coarse grained sand and major clays. The Eastern View Formation comprises predominantly quartz, feldspars and carbonates ($< 2\%$) and has hydraulic conductivities of 10^{-2} to 10^2 m d⁻¹ (Hortle *et al.*, 2011). The Eastern View Formation is underlain by another productive aquifer, the Pebble Point Formation, however this is much thinner and is separated from the above layers by the Pember Mudstone. To the north the Eastern View Formation is confined by the Gellibrand Marl, a regional aquitard, which comprises 100 to 200 m of clay, and fine-grained silts of the Demons Bluff formation. Basaltic intrusions of the Quaternary Newer Volcanics are also present. The floodplain is covered with recent alluvial deposits of sand and clay.

The Gellibrand Valley contains a mixture of cool temperate rainforest on the valley sides and cleared agricultural pasture through which the Gellibrand River flows. Rainfall across the catchment averages ~ 1000 mm yr⁻¹, with the majority of rainfall falling in the Australian winter between June and September (Bureau of Meteorology, 2013). The Gellibrand River is gaining and groundwater contributes between 10 and 50% to total river flow dependent on flow conditions (Atkinson *et al.*, 2013). River flows are between 5×10^4 m³ day⁻¹ to 2×10^6 m³ day⁻¹ (Figure 3.2c), with low flows during summer months (December to March) and high flows and flooding during winter (June to August) (Victorian Water Resources Data Warehouse, 2013), during which, there is the potential for aquifer recharge from overbank flow and bank storage. Regional recharge occurs on the Barongarook High where the Eastern View Formation crops out, however there is also potential for localised recharge within the Gellibrand River Valley, as the Eastern View Formation crops out there.

Though groundwater residence times in the Otway Basin have been explored in the Gambier Embayment (Love *et al.*, 1994) and nearby Barwon River catchment (Petrides & Cartwright, 2006), little is known of the residence times of groundwater in the Gellibrand River catchment. Here we evaluate

groundwater residence times in the upper Gellibrand River Catchment, where the Eastern View Formation is exposed and regular episodic river floods occur, to identify whether groundwater recharge occurs in this part of the groundwater system. This is important in understanding the potential impacts of landuse change and pollution in the catchment as well as understanding the dynamics of recharge in catchments where aquifer material is exposed in more than one location. Radioactive tracers ^{14}C and ^3H are used to determine residence times and define groundwater flow paths whilst major ion chemistry is employed to determine dominant geochemical processes. Water table fluctuations and groundwater electrical conductivities are also continuously monitored. These easily measurable, robust parameters can be used to observe changes in storage and infer sources of aquifer recharge (Vogt *et al.*, 2010) and allow for comparison with radioisotopes in understanding the dynamics of groundwater systems.

3.2 Methods

A number of groundwater monitoring bores which form part of the Victorian State Observation Bore networks are present in the Gellibrand Valley (Victorian Water Resources Data Warehouse, 2013). These are screened in the Eastern View Formation, with depths of between 0 and 42 m. Bores located within 25 m from the Gellibrand River generally have screen depths between 11 and 15 m, whilst bores located on the flood plain have depths between 21 and 42 m. Groundwater from the Eastern View Formation was sampled from 13 bores. 10 of these are located within 25 m from the river in a 14 km² area of the catchment, with 3 further samples taken from bores situated on the flood plain between 1 and 2 km from the river. Groundwater was sampled using an impeller pump set in the screen with 2 to 3 bore volumes purged before sampling. Electrical conductivity (EC) and pH of groundwater were measured in the field using a calibrated TPS WP-81 conductivity/pH meter and probes. To assess transient changes in groundwater levels and EC, Aqua Troll 200 (In-Situ) data loggers were deployed in June 2011. A significant drop in EC in near-river groundwater is shown in some bores following flooding in June 2012 when bores were overtopped. However immediately upon pumping in October 2012 (B108934, B108940) and April 2013 (B108916), the EC of the groundwater returned to pre-flood EC values. We interpret this as floodwater that infiltrated down the bore which was not displaced by groundwater prior to pumping, and these data have been omitted. Rainfall samples were also collected in the catchment throughout the study period for chemical analysis.

Cations were analysed on a Thermo Finnigan X Series II Quadrupole ICP-MS on samples that had been filtered through 0.45µm cellulose nitrate filters and acidified to pH < 2. Anions were measured on filtered unacidified samples using a Metrohm ion chromatograph. The precision of major ion concentrations based on replicate analyses is $\pm 2\%$. Charge balances are within $\pm 5\%$. Stable isotope ratios were measured using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}\text{O}$ values were measured via equilibration with He-CO₂ at 32°C for 24 to 48hr in a Finnigan MAT Gas Bench whilst $\delta^2\text{H}$ values were measured by the reaction of water samples with Cr at 850°C using a Finnigan MAT H/Device. Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were measured against an internal standard that has been calibrated using the IAEA, SMOW, GISP and SLAP standards. Data was normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW where $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of SLAP are -55.5‰ and -428‰ respectively. Precision is $\pm 1\%$ for $\delta^2\text{H}$ and $\pm 0.2\%$ for $\delta^{18}\text{O}$.

^{14}C and ^3H samples of groundwater were measured at the Australian Nuclear Science and Technology Organisation (ANSTO) and the Tritium and Water Dating Laboratory, Institute of Geological and Nuclear Sciences (GNS), (New Zealand). For ^{14}C analysis performed at ANSTO, CO₂ was extracted from water samples in a vacuum line using orthophosphoric acid and converted to graphite through reduction with excess H₂ gas in the presence of an iron catalyst at 600°C. ^{14}C concentrations were measured using a 10kV tandem accelerator mass spectrometer. $\delta^{13}\text{C}$ values for these samples are derived from the graphite fraction used for radiocarbon via EA-IRMS. For ^{14}C samples measured at GNS, CO₂ was extracted from groundwater samples through addition of orthophosphoric acid. CO₂ was made into a graphite target and analysed by AMS. An aliquot of the extracted CO₂ was used for $\delta^{13}\text{C}$ analysis. ^{14}C activities are expressed as pMC (percent modern carbon) where pMC = 100% corresponds to 95% of the ^{14}C concentration of NBS oxalic acid standard (Stuiver and Polach, 1977), with a precision of $^{14}\text{C}/^{12}\text{C}$ ratios of ± 0.5 (Fink et al 2004). At both ANSTO and GNS, samples for ^3H were distilled and electrolytically enriched prior to being analysed by liquid scintillation counting as described by Neklapilova *et al.* (2008a,b) and Morgenstern and Taylor (2009). ^3H activities are expressed in Tritium Units (TU) with a relative uncertainty of $\pm 5\%$ and a quantification limit of 0.13 to 0.14 TU at ANSTO and 0.02 TU and a relative uncertainty of 2 % at GNS.

3.3 Results

3.3.1 Groundwater elevations

Groundwater elevations decrease from 230 m relative to the Australian Height Datum (AHD) on the Barongarook High to < 60 mAHD within the Gellibrand Valley (Figure 3.1), with groundwater flowing from the Barongarook High towards the Gellibrand Valley and then westward. Groundwater elevations from all depths and positions within the Gellibrand Valley are in phase and fluctuate between 1 and 3 m annually (Figure 3.2a). Rising water tables follow winter rainfall between June and August (Figure 3.2c) and head gradients at nested sites are upwards (Figure 3.2b). The Gellibrand River has high water levels that result in flooding during winter months (June to August) and low flows in summer (December to March) (Figure 3.2c).

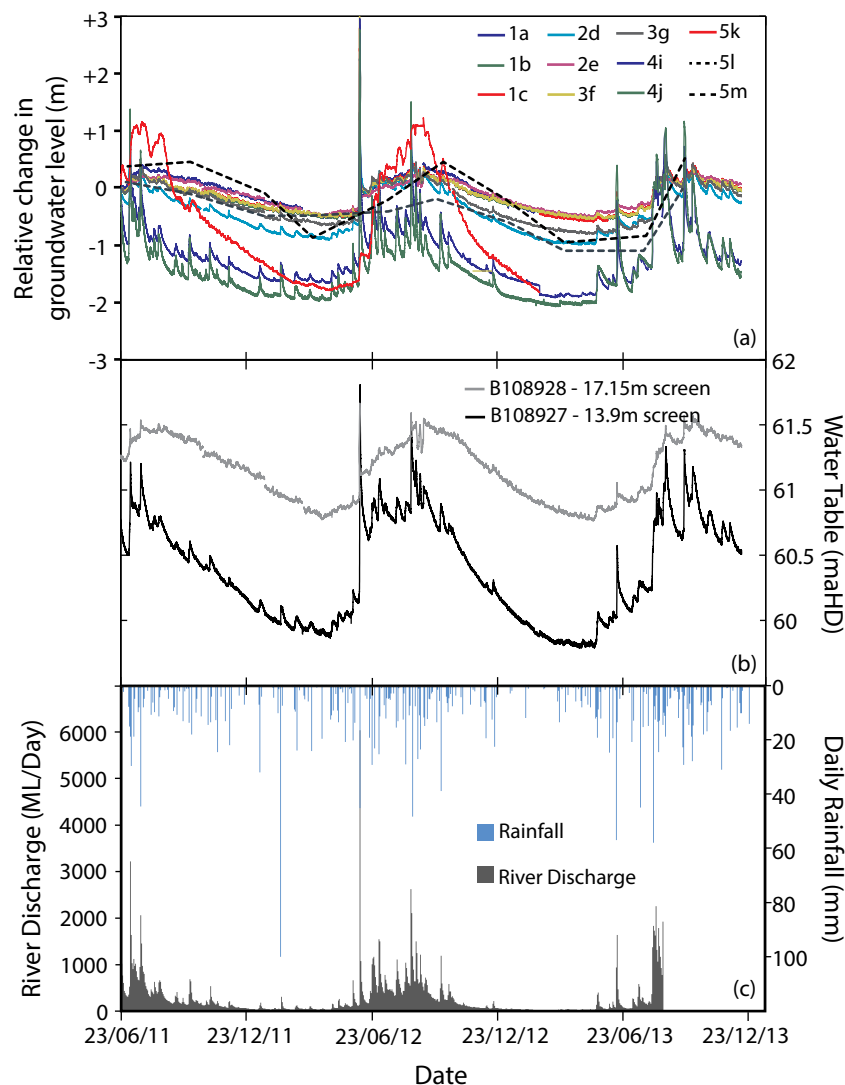


Figure 3.2 - (a) Water table in groundwater bores display clear annual cycles (b) Groundwater head-gradients in the Gellibrand River Valley are upwards implying a discharge zone (Victorian Water Resources Data Warehouse, 2013) (c) Flow in the Gellibrand River. Baseflow conditions during summer months transition into high flows in winter following winter rainfall. (Bureau of Meteorology, 2013)

Table 3.1 – Screen depth, Cl, ¹⁸O, ²H, ¹³C, ^a¹⁴C and ³H activities of groundwater samples.^aRefers to letter numbers on Figure 3.1^bMeasured as depth to the middle of the well screen.^c³H activities that are below detection.

Sample No.	Screen Depth (m)	EC (μS cm ⁻¹)	Cl (mg L ⁻¹)	Br (mg L ⁻¹)	Na (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	K (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	δ ¹⁸ O (‰ VSMOW)	δ ² H (‰ VSMOW)	δ ¹³ C (‰ PDB)	a ¹⁴ C		3H	
														pMC	1σ	TU	1σ
108899 (a) ^a	29 ^b	282	60	0.18	35.1	4.8	2.9	2.2	0.23	0.14	-5.6	-32.7	-21.4	81	0.34	bd ^c	-
108916 (b)	14.5	197	38.6	0.12	29.3	3.4	4.1	1.9	0.24	0.09	-5.3	-30.4	-22.1	83.3	0.28	bd	-
108917 (c)	14.5	238	44	0.08	20.3	1.0	2.6	0.7	0.44	0.08	-5.3	-31.1	-21.5	77.8	0.29	bd	-
108927 (d)	14	430	86	0.07	69.1	16.3	9.9	7.4	0.5	0.36	-5.6	-32	-20	39.5	0.2	bd	-
108928 (e)	17	446	96	0.08	76.3	19.9	11	8.6	0.58	0.27	-5.5	-33.6	-19.8	40.9	0.21	bd	-
108933 (f)	11.2	491	121	0.1	84	8.6	5.3	9.1	0.52	0.16	-5.6	-34.1	-20.1	33.8	0.20	bd	-
108934 (g)	11.5	545	125	0.06	103.8	13.5	8.5	10.5	0.78	0.2	-5.8	-32.4	-20.4	29	0.16	bd	-
108940 (h)	11.5	243	53	9.02	35.4	3.6	3.21	2.2	0.56	0.11	-5.8	-34	-22.3	64	0.24	bd	-
108941 (i)	11.5	414	89	0.03	80.3	7.1	3.9	11.5	0.64	0.03	-5.7	-34.3	-21.5	49	0.21	bd	-
110737 (j)	42	149	31	0.02	16.9	0.9	2.3	0.7	0.08	0.03	-5.11	-29.4	-22.4	100	0.3	1.24	0.06
80732 (k)	21	200	48	0.1	30	0.33	4.2	0.5	0	0.1	-4.5	-29.7	-24.2	101.5	0.17	1.02	0.03
80735 (l)	21	217	30	0.03	16.5	0.32	10.5	3.6	0	0.11	-4.2	-29.1	-25.3	100.7	0.17	1.47	0.04
108935 (m)	11.5	144	27	0.04	19.9	1.7	2.7	0.7	0.12	0.07	-4.8	-31.2	-21.3	88.6	0.17	bd	-

3.3.2 Groundwater Geochemistry

The chemistry of groundwater in the Gellibrand Valley is summarised in Table 3.1. Groundwater has electrical conductivities between 140 and 600 $\mu\text{S cm}^{-1}$ and pH ranging from 4.8 to 6.0. Groundwater from close proximity to the river generally has higher EC values (144 to 545 $\mu\text{S cm}^{-1}$) than groundwater further back on the floodplain (149 to 220 $\mu\text{S cm}^{-1}$). The major ion chemistry of groundwater is similar across the catchment, and the groundwater is Na-Cl type. Cl constitutes between 68 and 92% of total anions on a molar basis, with HCO_3^- accounting for 0 to 25%. Increases in Cl concentrations are associated with a decrease in HCO_3^- . Na comprises between 60 and 85% of total cations with Ca constituting 1 to 10%, Mg constituting 0 to 10% and K constituting 0 to 10%. Increased Na concentrations are associated with decreases in both Ca and Mg concentrations. Molar Cl/Br ratios are between 400 and 600 and do not increase with increasing Cl (Figure 3.3b), molar Na/Cl ratios are 0.7 to 1.3 and also remain stable with increasing Cl concentrations (Figure 3.3a). Both Cl/Br and Na/Cl ratios of groundwater samples are similar to those measured in rainfall in southeast Australia (Blackburn and Mcleod, 1983). There is a weak correlation between Ca and HCO_3^- (Figure 3.3c) and between Ca and SO_4 (Figure 3.3d).

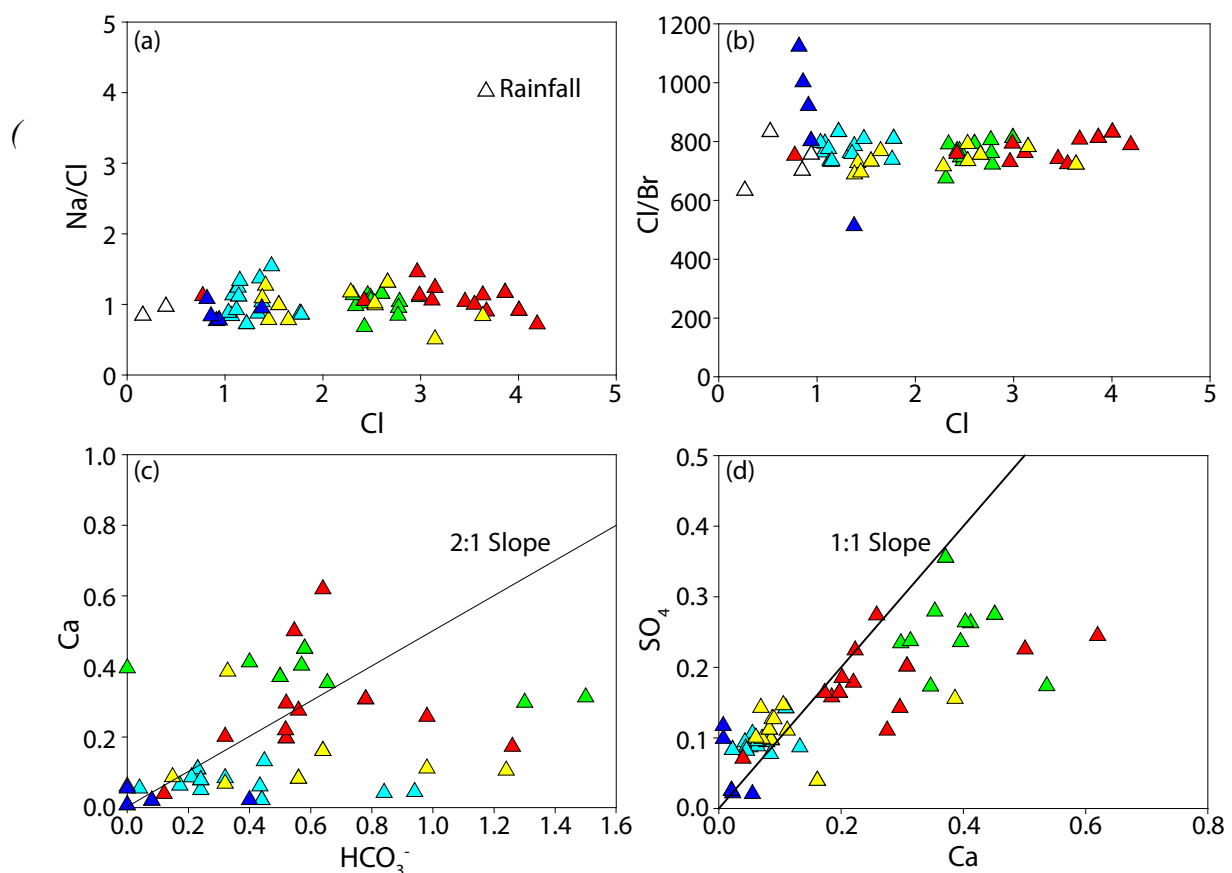


Figure 3.3 – Geochemical characteristics of groundwater in the Eastern View Formation; (a) mNa/Cl v mCl (b) mCl/Br v mCl (c) mCa v m HCO_3^- (d) m SO_4 v mCa. Rainfall samples are also plotted where measured. Data is from Table 1 with repeat measurements over the sampling period included.

3.3.3 Stable Isotopes (δ^2H , $\delta^{18}O$, $\delta^{13}C$)

$\delta^{18}O$ and δ^2H values of groundwater define a narrow field ($\delta^{18}O = -4$ to -6 ‰ and $\delta^2H = -30$ to -40 ‰) that is close to both the global and local meteoric water lines (Figure 3.4). The Gellibrand Valley is located between Melbourne and Adelaide, with groundwater generally plotting between the average isotopic compositions of meteoric waters located in these areas. $\delta^{13}C$ values of DIC from groundwater range from -19.8 to -25 ‰, with an average of 21.7 ‰ (Table 3.1)

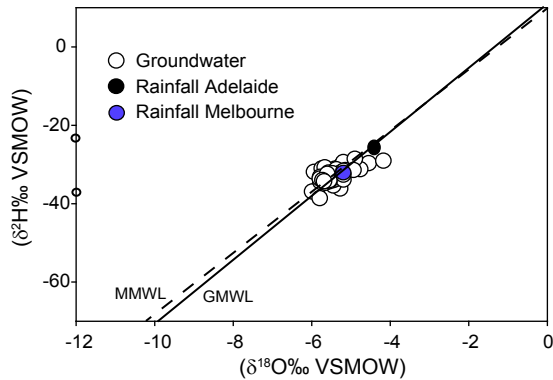


Figure 3.4 – δ^2H v $\delta^{18}O$ values for the Gellibrand River and surrounding groundwater sampled over March 2011 – August 2013 and the weighted average for rainfall from Adelaide and Melbourne.

MMWL = Melbourne Meteoric Water Line (Hughes and Crawford, 2012).

GMWL = Global Meteoric Water Line. Data is from Table 1 with repeat measurements over the sampling period included.

3.3.4 ^{13}C , $\alpha^{14}C$ and 3H concentrations

The $\alpha^{14}C$ of groundwater ranges from 29 to 101.5 pMC. 3H activities are below detection for the majority of groundwater samples (Table 3.1), with the exception of bores 80732, 80735 and 110737 which have activities of 1.02, 1.47 and 1.24 TU, respectively. Groundwater from these bores has $\alpha^{14}C > 90$ pMC. The distribution of $\alpha^{14}C$ and 3H values across the catchment is heterogeneous with no relationship to depth or along lateral groundwater flowpaths. A strong inverse correlation ($R^2 = 0.87$) is observed with Cl values. High $\alpha^{14}C$ groundwater is associated with low Cl concentrations, with the decrease in $\alpha^{14}C$ through radioactive decay matched by an enrichment of chloride ions. A similar correlation is also observed for Na ($R^2 = 0.855$), K ($R^2 = 0.82$), Ca ($R^2 = 0.6$) and Mg ($R^2 = 0.54$).

3.4.5 Continuous Electrical Conductivity

Continuous groundwater EC records for a number of near-river bores (excluding B110737, situated on the flood-plain) are shown in conjunction with changes in river height for the study period (Figure 3.5). Groundwater EC in all bores for the majority of the dataset show little or no response to changes in river height. Minor changes in EC correlate to sampling events in which groundwater bores were

pumped

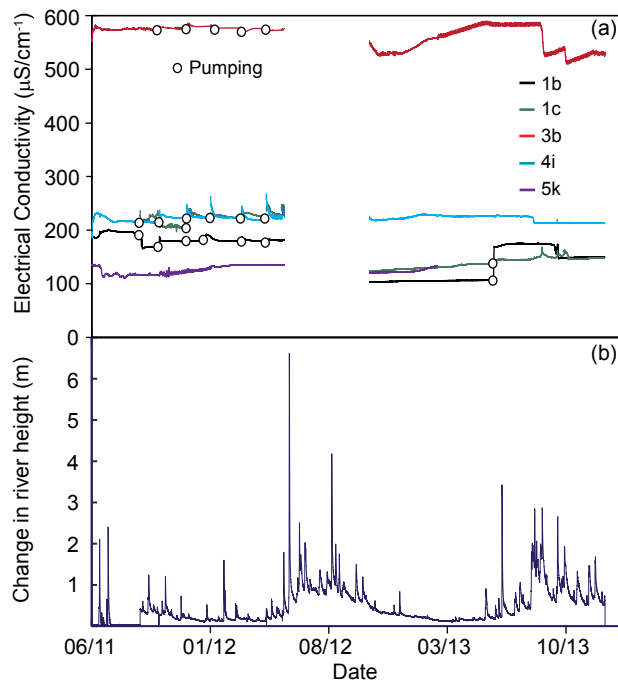


Figure 3.5

(a) Continuous electrical conductivity monitoring of near-river groundwater and its relationship to

(b) Changes in river height over the study period. Groundwater EC and river level data from deployed Aqua troll 200 (In-Situ) Data Loggers.

3.4 Discussion

3.4.1 Groundwater Chemistry

Understanding geochemical processes in groundwater is required for correction of ^{14}C ages and in documenting groundwater flow and recharge. Processes which govern the evolution of groundwater geochemistry and sources of solutes in the Eastern View Formation can be determined from the major ion geochemistry. The observation that Cl/Br ratios are between 500 and 1000, which is similar to those expected in rainfall, and do not increase with increased TDS implies that evapotranspiration rather than halite dissolution is the major process controlling groundwater salinity (Herczeg *et al.*, 2001; Cartwright *et al.*, 2006). This conclusion is also consistent with an absence of halite in the aquifer lithologies. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater do not define evaporation trends, implying that transpiration in the soil zone or upper parts of the aquifer is likely to be more dominant over evaporation. Na/Cl ratios in groundwater are also similar to those in local rainfall (~ 1.00) implying that silicate weathering is limited (Edmunds *et al.*, 2002), whilst the increase in Na concentrations at the expense of Ca may indicate ion exchange reactions on the surface of clay minerals. That Ca and mHCO_3 are poorly correlated suggests that only negligible dissolution of calcite has occurred.

A handful of groundwater samples have a 1:1 Ca:SO₄ ratio indicating some minor gypsum dissolution may take place. Together, the major ion geochemistry suggests that water-rock interaction is limited with minimal silicate weathering, negligible dissolution of halite and carbonate minerals and some minor dissolution of gypsum. As is the case elsewhere in southeast Australia, including within the Otway basin, the primary geochemical process is evapotranspiration promoted by the moderate rainfall and water-efficient native vegetation, and the groundwater salinity is largely controlled by the degree of evapotranspiration during recharge (Herczeg *et al.*, 2001; Bennetts *et al.*, 2006; Petrides & Cartwright, 2006).

3.4.2 Water Table Fluctuations

Annual cycles of groundwater elevations are present in all groundwater bores, which were screened 11 to 40 m below the ground surface. Fluctuations in groundwater levels across the Gellibrand River Valley are likely to reflect changes to the water table in response to recharge. The magnitude of annual water table fluctuations recorded in data loggers is similar to those over the previous 30 years (Figure 3.6). Recharge was estimated for years 2012 and 2013 using the water-table fluctuation method Equation (1):

$$R = S_y * \Delta h \quad (1)$$

(Scanlon *et al.*, 2002), where S_y is specific yield, Δh is the change in water table height between the hydrograph recession and hydrograph peak and Δt is time. The water table rise is estimated as the difference between peak groundwater levels and the extrapolated antecedent recession. The estimate of recharge from this method is sensitive to the estimate of the specific yield. S_y is assumed to be 0.1 which is close to the measured effective porosity of the Eastern View Formation (Love *et al.*, 1993), and takes into account the presence of finer sized sediments such as silt and clay in the aquifer. Annual water table fluctuations are between 0.9 and 3.7 m across all bores, which for S_y values of 0.1, imply that $R = 130$ to 372 mm yr⁻¹ in 2012 (mean of 200 mm yr⁻¹) and 90 to 300 mm yr⁻¹ in 2013 (mean of 164 mm yr⁻¹). This equates to between 11 and 32 % of rainfall in 2012 and 12 and 28 % of rainfall in 2013. The bores are screened 11.2 to 42 m below the ground surface and thus these recharge estimates will be minima due to the attenuation of pressure variations with depth (Scanlon *et al.*, 2002).

Recharge estimates are also susceptible to the value of specific yield, particularly where the aquifer is composed of finer sized sediments such as silt and clay. Regardless, estimates using bore hydrographs indicate that significant groundwater recharge to the unconfined Eastern View aquifer in the valley occurs via diffuse recharge.

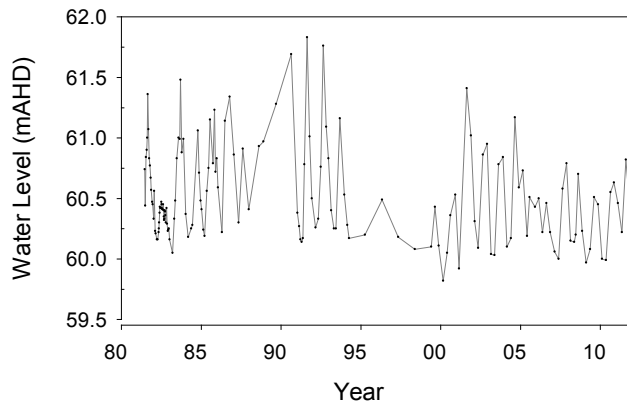


Figure 3.6 – Historical water table fluctuations 1988-2011 for bore 108927 (Victorian Water Resources Data Warehouse, 2013). The magnitude of annual recharge cycles are coherent with those recorded in data loggers over the study period (2011 to 2013)

3.4.3 ^{14}C ages

The groundwater in the Eastern View Formation is not anoxic (Victorian Water Resources Data Warehouse, 2013), nor are there coal seams hence methanogenesis is unlikely to be a source of DIC. Likewise there are no obvious sources of geogenic CO_2 in this area. Based on the major ion geochemistry, only minor calcite dissolution occurs in the Eastern View Formation, which is to be expected as the Cenozoic aquifers are siliceous and contain only minor carbonate minerals. While only minor carbonate dissolution is likely, determination of groundwater residence times requires this to be taken into account. If it is assumed that closed system dissolution of calcite in the aquifers is the major process, the fraction of C derived from the soil zone (q) may be derived from the $\delta^{13}\text{C}$ values of DIC ($\delta^{13}\text{C}_{\text{DIC}}$), carbonate ($\delta^{13}\text{C}_{\text{cc}}$) and recharging water ($\delta^{13}\text{C}_r$) via Equation (2):

$$q = \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{cc}}}{\delta^{13}\text{C}_r - \delta^{13}\text{C}_{\text{cc}}} \quad (2)$$

(Clark & Fritz 1997). The calcite is assumed to have a $\delta^{13}\text{C}$ of $\sim 0\text{‰}$ (Love *et al.*, 1994; Petrides and Cartwright, 2006) as is appropriate for marine sediments. $\delta^{13}\text{C}_r$ is calculated from the $\delta^{13}\text{C}$ of the soil carbon in the recharge zone. Pre-land clearing vegetation in southeast Australia was dominated by eucalypts that have $\delta^{13}\text{C}$ values of -30 to -27‰ (Quade *et al.*, 1995). Assuming a $\sim 4\text{‰}$ ^{13}C fractionation

during outgassing (Cerling *et al.*, 1991), $\delta^{13}\text{C}$ values of soil CO_2 would be -26‰ to -23‰ (average of -24.5‰). At 20 °C and pH 6.5, $\delta^{13}\text{C}_r$ calculated from the fractionation data of Vogel *et al.* (1970) and Mook *et al.* (1974) is $\sim$ -20‰. Although the calculated $\delta^{13}\text{C}_r$ values require the pH and temperature of recharge and the $\delta^{13}\text{C}$ of the soil zone CO_2 to be estimated, they are similar to those from other studies in southeast Australia and consistent with the predicted $\delta^{13}\text{C}$ values of DIC in equilibrium with calcite in the regolith (Quade *et al.*, 1995; Cartwright, 2010). Calculated q values are between 0.85 and 0.97 (Table 3.2), implying that only 10% to 15% of DIC in groundwater from the Eastern View formation is derived from calcite in the aquifer, this is similar to the expected contribution of calcite dissolution in siliceous aquifers (Vogel *et al.*, 1970) and similar to other estimates from the Otway Basin (Love *et al.*, 1994; Petrides and Cartwright, 2006).

Sample	q	Radiocarbon Age (years)	Uncertainty (years)
108899	0.93	1150	+ 630 / - 980
108916	0.96	1190	+ 360 / - 940
108917	0.93	1520	+ 590 / - 970
108927	0.86	6530	+ 940 / - 1050
108928	0.86	6170	+ 950 / - 1060
108933	0.87	7870	+ 950 / - 1050
108934	0.89	9260	+ 930 / - 1040
108940	0.97	3440	+ 290 / - 930
108941	0.93	5310	+ 630 / - 980
108935	0.93	380	+ 630 / - 380

Table 3.2 – Radiocarbon ages of groundwater in the Gellibrand Catchment corrected for calcite dissolution. Uncertainties are calculated varying q by ± 0.1 plus the analytical uncertainty of $a^{14}\text{C}$ from Table 3.1

Using the q values from Table 3.2, ^{14}C ages (t) corrected for closed-system calcite dissolution are calculated from Equation (3); where $a^{14}\text{C}$ is the activity of ^{14}C in groundwater DIC, and $a_0^{14}\text{C}$ is the activity during recharge (assumed to be 100 pMC).

$$t = -8376 \ln \left(\frac{a^{14}\text{C}}{q * a_0^{14}\text{C}} \right) \quad (3)$$

Radiocarbon ages for groundwater in the Eastern View Formation range from 380 to 9260 years (Table 3.2) with the exception of bores B110737, B80732, B80735 which have a ^{14}C > 100 pMC and represent groundwater that has a large component of water recharged during or after the atmospheric nuclear tests in the 1950s to 1960s. The majority of ^{14}C ages however, suggest that groundwater in the valley has long residence times (Figure 3.7).

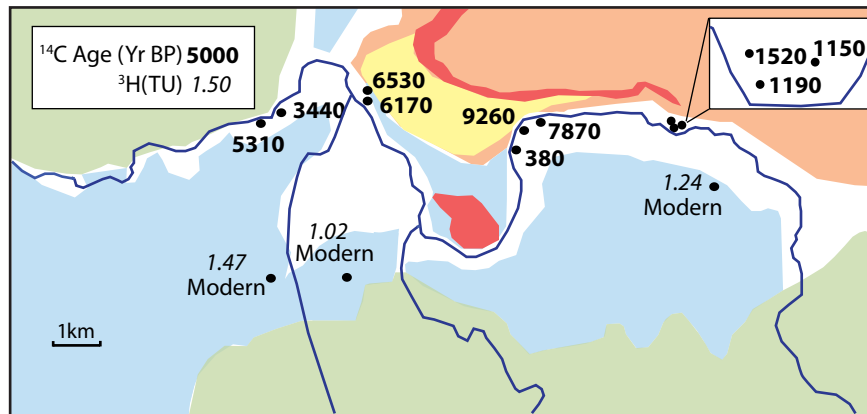


Figure 3.7 – Groundwater residence times within the Gellibrand Valley. Residence times up to 9260 years are found in close proximity to the river. Modern local groundwaters with a ^{14}C > 100 pMC are situated back on the floodplain. Data from Tables 3.1 and 3.2.

3.4.4 ^3H Activities and Recharge Rates

With a shorter half-life, ^3H activities can infer the presence of modern groundwater. The water table fluctuations imply that the Gellibrand Valley receives considerable recharge year (90 to 370 mm yr^{-1}). Although head gradients at nested sites are upwards implying that the valley is a groundwater discharge zone (Figure 3.2b), these may be reversed during periods of high rainfall. If local recharge is significant in recharging the groundwater system across the valley, it would be expected that the groundwater would have relatively high ^3H activities. Recently-recharged groundwater in other Victorian catchments has ^3H activities up to 3.6 TU (Cartwright & Morgenstern, 2012).

^3H activities in most of the groundwater from the Gellibrand Valley are negligible. Much of this groundwater is from within 5 to 10 m of the water table, suggesting that any recharge penetrates only to a limited depth, and does not mix with the bulk of the water in the Eastern View Formation. The exception to this is groundwater from the southern edge of the valley where the Eastern View Forma-

tion overlies the basement rock (Eumeralla Formation). Here both ^3H activities and ^{14}C activities are higher implying that recharge to the deeper parts of the aquifer occurs locally.

The Gellibrand River has the potential to recharge regional groundwater during high river stages and episodic floods. Aquifer recharge from surface water can be assessed by combining data from groundwater EC values and ^3H activities. The EC of river water varies between 120 and 200 $\mu\text{S cm}^{-1}$ and is lower than that of groundwater in the catchment throughout the year. ^3H activities of river water are between 1.24 and 2.0 TU during baseflow conditions (Atkinson *et al.*, 2013), and may be higher during high flow events as local modern rainfall, which is likely to comprise a significant component of river flow at those times, has activities of 2.4 to 3.2 TU (Tadros *et al.*, 2014). Significant amounts of aquifer recharge through overbank events or bank exchange should result in groundwater with low EC values, and high ^3H activities near the river.

Except for in June 2012 when the bores were overtopped, groundwater EC was constant throughout the study period and there is no inverse relationship to river height (Figure 3.6). This indicates there is little exchange of river water to the depth of the aquifer sampled by the bores. Additionally the activities of ^3H in near-river bores are negligible, again suggesting that recharge from the river does not penetrate more than a few metres into the adjacent aquifer. Thus, flow through the river bank or river flooding does not appear to be a significant mechanism of recharge in the Gellibrand Valley.

3.4.5 Groundwater Flowpaths and Conceptual Model

Radiocarbon ages are up to 10 ka implying that the groundwater in the Gellibrand Valley has a long residence time; in turn this implies that the area is a regional discharge zone. Most of the groundwater originates on the Barongarook High, and this region potentially provides a substantial proportion of baseflow to the Gellibrand River. The large range of ^{14}C ages in the valley is a likely result of heterogeneous geology, where the presence of low hydraulic conductivity sediments such as silt and clays in the Eastern View formation lead to variable velocities along groundwater flowpaths. Groundwater travel times may also be determined using the present day hydraulic gradients. From Darcy's law

and assuming a porosity of 0.1 (Love *et al.*, 1994) and a hydraulic conductivity of 0.2 to 2 m day⁻¹ (Love *et al.*, 1993) calculated travel times are between 1000 and 10,000 years, which are similar to those implied by the ¹⁴C ages. This supports the idea that groundwater in the valley is predominantly regional groundwater derived by recharge on the Barongarook High. The high ³H activities in groundwater bores situated away from the river imply local recharge in that area to depths of 21 to 42 m. However for the most-part, shallow groundwater in the Gellibrand valley, including in the near-river environment is predominantly regional groundwater. Though groundwater elevations display clear annual cycles and winter months are punctuated by high river flow, localised recharge from both of these processes combined is stored in the upper < 10 m of the aquifer. The presence of silts and clays on the floodplain and riverbanks combined with strong upwards hydraulic gradients in the Eastern View Formation, driven by groundwater flow from the Barongarook High, ensure that recharge in the near-river environment does not penetrate deep within the aquifer (Figure 3.8).

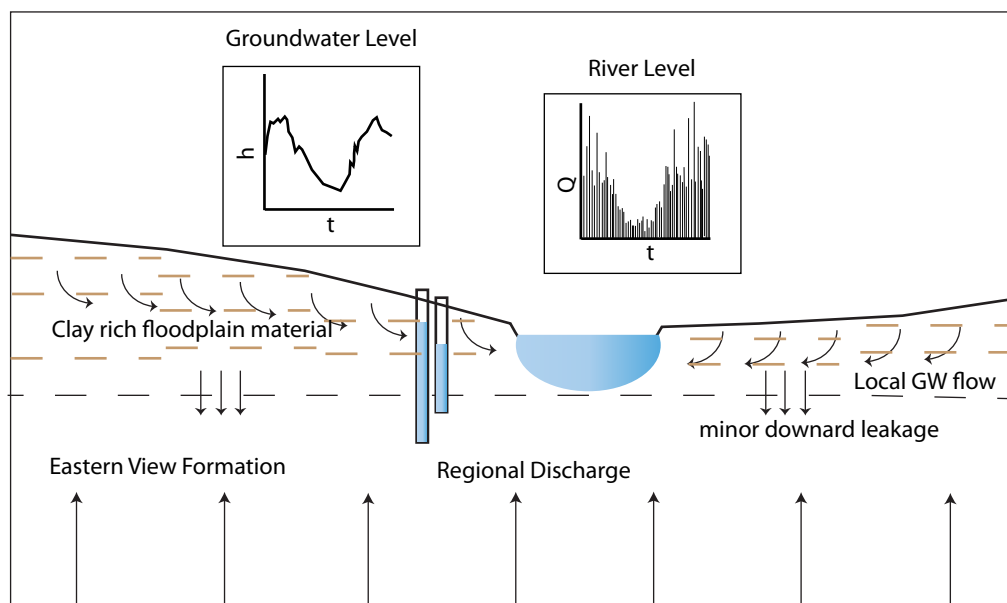


Figure 3.8 – Groundwater flow conceptualisation in the Gellibrand River Valley. Though appreciable amounts of recharge are estimated from bore hydrographs and high river flows, the depth to which recharging waters infiltrate into the Eastern View Formation (downward leakage) is limited by strong upward head gradients, and a floodplain which consists of appreciable amounts of silt and clay.

3.4.6 ¹⁴C ages & Cl

The good correlation of a ¹⁴C with chloride implies that chloride concentrations correspond to groundwater age (Figure 3.9). Correlations between ¹⁴C and Cl have also been documented in groundwater from the Eastern View Formation in other regions of the Otway Basin (Love *et al.*, 1994). In assessing

this relationship, chloride sources must be considered. That the Cl/Br ratios in the groundwater are similar to those of rainfall preclude significant halite dissolution by the groundwater from the Eastern View Formation, and there are no extensive occurrences of halite in the aquifer matrix.

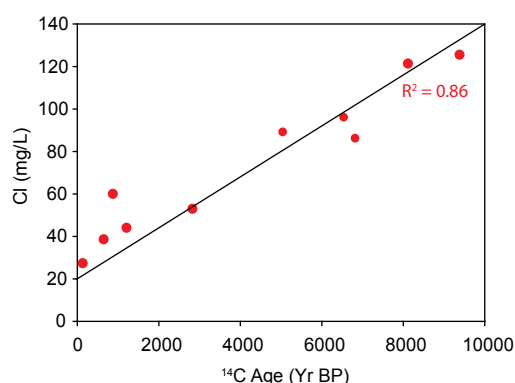


Figure 3.9 – ¹⁴C age v Cl. ¹⁴C ages are taken from the calcite corrected ages in Table 3.1

We propose two explanations of this trend. Firstly, the relationship between a ¹⁴C and Cl may be explained by mixing of low salinity groundwater that is locally recharged within the valley and high salinity regional groundwater from the Barongarook High. However, the groundwater with high a ¹⁴C and low Cl also has high ³H activities (0.99 to 1.47 TU) and if mixing has occurred it must do so at a very slow rate otherwise the resultant groundwater would be expected to contain measurable ³H. This implies that mixing between the shallow groundwater system and the deeper groundwater is limited.

Alternatively the recharge on the Barongarook High may be spatially variable due to the heterogeneous nature of the Eastern View Formation or may have undergone changes over time due to climate fluctuations. If evapotranspiration is a dominant process Cl concentrations are likely to be inversely correlated with recharge rates. In the Otway Basin Love *et al.* (1994) report a decrease in Cl concentrations in groundwater recharged between 18 and 10 ka, followed by an increase in Cl concentrations in groundwater recharged from 10 ka to the present day, which they attribute to increased evapotranspiration rates during a warm Holocene climate. However, in this study decreasing Cl concentrations with increasing a ¹⁴C would imply that recharge rates on the Barongarook high increased from 10,000 years BP to the present, which is not likely given the warming trend. There is also the possibility that recharge is spatially variable on the Barongarook High, resulting in groundwater flowpaths with a large distribution of groundwater ages and that the high Cl low a ¹⁴C groundwater is derived from regions with locally low recharge rates (as is the case in the Murray Basin of southeast Australia: Cartwright *et al.*, 2006). Regardless of which model is correct, the chloride measurements provide a

useful first order estimate of groundwater residence times.

3.5 Conclusion

Though widely available water-table measurements offer an insight into recharge, the dynamics of groundwater flow systems and recharge patterns can only be fully understood when combined with geochemical data, in particular radiogenic tracers such as ^3H and ^{14}C . These can be used to assess the importance of recharge and discharge in aquifer windows, which in turn defines groundwater pathways and allows the potential fate of pollutants to be assessed. Here shallow (11 to 42 m) groundwater bores indicate a significant amount of recharge occurs in the Gellibrand River Valley (90 to 370 mm yr^{-1}). However, the groundwater at 5 to 10 m below the water table has ^{14}C ages between 350 and 10,000 years, and below detection ^3H activities. Furthermore, there is no indication of water from the river penetrating more than ~ 10 m following flood events. In the Gellibrand River Valley, outcropping aquifer sediments act as a regional discharge zone. Upwards head gradients are maintained for long periods of time and aided by the presence of silts and clays on the floodplain, this limits the depth to which diffuse and localised recharge (via over-bank events and bank exchange) penetrate the aquifer.

There is most likely a shallow local flow system within the Gellibrand River Valley that has limited connectivity with the deeper groundwater. This potentially limits the spread of pollutants such as nitrate and pesticides that may derive from the agricultural activities into the regional groundwater. Future land-use, climate change or groundwater exploitation that occurs on the Barongarook High is likely to affect both the chemistry of groundwater within the valley, and groundwater fluxes to the Gellibrand River, highlighting the importance of regional recharge zones.

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Declaration for Thesis Chapter 4

Declaration by candidate

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Collection of data, analysis and interpretation, manuscript production	85%

The following co-authors contributed to the work.

Name	Nature of contribution	Extent of contribution (%)
Ian Cartwright	Supervisory role, review of manuscript.	8%
Benjamin Gilfedder	Data collection assistance, manuscript review	4%
Nicolaas Unland	Data collection assistance	1%
Harald Hofmann	Data collection assistance	1%
Matthew Yu	Data collection assistance	1%

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature

Date

Main Supervisor's Signature

Date

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Chapter 4

Determining the mean residence time and water sources of a first order stream in a temperate rainforest environment; the role of pipeflow

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Abstract

The mean residence times of water stores that contribute to streamflow are investigated in the upper catchment of the Gellibrand River (Victoria, Australia) through analysis of hydrometric data and the application of environmental tracers (electrical conductivity, major ions, stable isotopes and tritium). River flow in the upper catchment demonstrates a rapid response to rainfall events and recession during drought. This rapid response to rainfall is attributed to preferential flow through perennial and ephemeral soil pipes, thought to develop on top of a largely impermeable, clay-rich B-Horizon. The major ion geochemistry (Cl, Na, Ca, Mg, K, HCO_3^-) of water draining in soil pipes is closely similar to that of the river during both baseflow and stormflow conditions, whilst continuous records of electrical conductivity demonstrate the rapid input of event water into both the pipes and stream during rain events. Flow gauging performed on a single pipe indicates it provides 0.5 to 5% of river discharge. A network of pipes likely connects zones of saturation on the hillslope with the stream. Despite representing a large water store, the geochemistry of water within the riparian zone is distinct from the stream, and only likely to contribute locally to stream discharge. This study also provides some of the first estimates on the mean residence times (MRT) of water draining headwater catchments in Australia using tritium (^3H). ^3H activities suggest old water stores contribute to streamflow over a range of flow conditions, with the MRT of water draining the upper Gellibrand River between 5 and 17 years.

4.1 Introduction

The headwaters of river systems often constitute a significant proportion of total stream length and catchment area, and have the potential to provide large volumes of fresh water to the middle and lower reaches of rivers (Tetzlaff & Soulsby, 2008). Whether perennial, ephemeral or intermittent, headwater streams are critical to the health of river systems, influencing the quality and quantity of water flowing downstream (Nadeau & Rains, 2007). Understanding headwater functioning is important in flood forecasting, the transport of nutrients and sediments, and in predicting the response of headwater areas to future land-use or climate change (Pilling & Jones, 2002).

In lowland rivers that occupy alluvial valleys, groundwater represents a significant long-term water store that contributes to river discharge. The water stores in headwater areas and timescales over which they operate are far less well known. Upper catchment or headwater areas are commonly underlain by consolidated basement rocks; however, rainfall-runoff models which assume the basement rocks to be impermeable commonly fail to replicate headwater streamflow generation. This is illustrated by discrepancies in predicted and observed stream chemistry, and the presence of pre-event or ‘old’ water in storm discharge in catchments worldwide (Sklash, 1979; Neal and Rosier, 1990; Kirchner, 2003). Where headwater streams are perennial, long-term water stores must be present, and the rapid input of old water following rainfall requires a long-term water reservoir which can be easily mobilised.

The mechanisms responsible for streamflow generation in headwater areas remain a major question within hillslope hydrology (Bachmair & Weiler, 2012). Understanding hydrological pathways provides crucial information for water management. Where water is used for domestic, industrial and agricultural use this information may be used to predict contaminant transport (Donald & Gee, 1992; Haria & Shand, 2006; Dodds & Oakes, 2008). Rapid subsurface flows through macropores and preferential flowpaths have been shown to exert a substantial control on headwater stream chemistry, especially during storm conditions (Kosugi *et al.*, 2008). These include unsaturated flow in the soil zone (McDonnell, 1990; Torres *et al.*, 1998), perched zones of saturation at the soil-bedrock interface (Feer *et al.*, 2002), and deeper groundwater flowpaths in fractured and weathered bedrock (Haria and

Shand, 2006). The largest form of macropore flow that has been observed is that of preferential flow through vertical and horizontal soil pipes (Jones, 2010). These are thought to occur at the soil-bedrock interface or where lower conductivity soils impede flow within soil profiles. Following the definition of Jones (2010), they are characterized by their ‘water sculpted form’ and the occurrence of soil pipes has been reported in a number of settings, particularly in headwaters with steep, wet hillslopes. Soil pipes are well documented in the Plynlimon catchment, Wales (Jones; 1988,1990,1997,2004) and the Tama Hills, Tokyo, Japan (Noguchi *et al.*, 1999; Terajima *et al.*, 2000; Uchida *et al.*, 1999, 2005). Pipeflow has also been reported in the Pennines, Northern England (Holden, 2009), British Columbia and Northern Canada (Carey & Woo, 2000; Anderson *et al.*, 2009), the Indian tropics (Putty & Prasad, 2000) the humid tropics of Sabah, Malaysia (Sayer *et al.*, 2006) and in Victoria and New South Wales, Australia (Crouch *et al.*, 1986; Boucher and Powell; 1994).

The presence of macropore flow and preferential flowpaths in the soil complicates physically based numerical models that use the Darcy-Richards equation. These assume a constant velocity for the movement of water in a given soil horizon and is unlikely to hold true in hillslopes which drain via preferential flowpaths (Beven & Germann, 2013). Understanding whether rapid sub-surface flow occurs in headwater areas may prove key to understanding how headwater catchments operate and bridge the gap between modelling and field based studies. It has been stressed that due to the complexity and heterogeneity of hillslope hydrology, which encompasses a broad range of spatial scales and a myriad of environments, there is a need to identify the first-order controls on hydrological processes in headwater areas, rather than focussing on the behaviour of individual catchments. This may allow for findings to be extrapolated to ungauged hillslopes and catchments (Hopp & McDonnell 2009; Troch *et al.*, 2009; Uchida *et al.*, 2006). First order ‘static’ controls based on hillslope configuration include topography (McGuire *et al.*, 2005), soil distribution, geology, and depth to the underlying bedrock, whilst ‘dynamic’ controls include the nature of precipitation, vegetation and soil moisture.

The transport of water along different hillslope pathways results in river water being composed of water parcels of various ages or residence times (McDonnell *et al.*, 2010) with the distribution of residence times reflecting how catchments store and release water. Elucidating the mean residence

times of river water and water stores in headwater catchments may be used to identify contributing water sources to streamflow, compare the behaviour of different catchments, and predict watershed responses to climate change. Additionally, the mean residence time controls the retention of soluble contaminants and downstream consequences of pollution in upper catchments (Wenninger *et al.*, 2008; Birkel *et al.*, 2011, Farlin *et al.*, 2013). Although estimates of mean residence times of at least a few years have been made (Malsoszewski *et al.*, 1992; McGlynn *et al.*, 2003), the timescale over which rainfall is transmitted into headwater streams is generally not well understood (Beven, 2010).

Estimations of mean residence times have been made by comparing the temporal variations $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and chloride concentrations in rainfall with those in the river (McGuire *et al.*, 2005, Kirchner *et al.*, 2010; Hrachowitz *et al.*, 2013). This approach however requires high frequency groundwater and rainfall chemical datasets such as those in the Plynlimon catchment (Neal *et al.*, 2012), and where mean residence times are > 5 years, these tracers may be ineffective (Stewart *et al.*, 2010). In the Southern Hemisphere, ^3H has been used to determine catchment residence times (Morgenstern *et al.*, 2010; Morgenstern and Daughney, 2012, Stewart and Fahey, 2010). As ^3H forms part of the water molecule and is only lost through radioactive decay it provides an excellent tracer of water movement through hydrological systems. With a half life of 12.32 years, ^3H can be used to trace waters that are up to 100 years old, rendering it more powerful than stable isotopes (Stewart *et al.*, 2012). The ^3H input function in rainfall is well known. The increased ^3H activities observed during the 1950s and 1960s due to atmospheric nuclear bomb testing were significantly lower in the Southern Hemisphere than in the Northern Hemisphere (Morgenstern *et al.*, 2010; Tadros *et al.*, 2014), allowing unique ages to be obtained from single ^3H measurements.

Here we present results from a first order stream in a temperate rainforest climate in the Otway Ranges of southwest Victoria. The application of ^3H in determining the mean residence time of headwater streams the first in Australia and one of only a few globally. Combining ^3H results with hydro-metric data and geochemistry, sources of river water during high and low flow conditions and the first order controls on catchment functioning are investigated.

4.2 Study Site

The Gellibrand River Catchment located in the Otway Basin of southwest Victoria (Figure 4.1 a) has a total area of 1150 km². The headwaters of the Gellibrand River occupy an area of 100 km² and are located on the Northern slopes of the Otway Ranges at elevations > 400 m (Figure 4.1 b). The terrain in the upper catchment is dominated by steep slopes covered with wet eucalypt and cool temperate rainforest, whilst the middle and lower reaches of the river flow through cleared agricultural pasture with native vegetation on the valley sides. Average precipitation varies across the catchment from 800 to 900 mm/yr in the lower reaches to 1000 to 1200 mm/yr in the upper catchment (Bureau of Meteorology, 2013). Average daily discharges in the Upper Gellibrand River measured at gauge 235227 are ~ 80 ML/Day, with higher discharges (> 1000 ML/Day) occurring during winter months and low discharges (< 50 ML/Day) during the summer months.

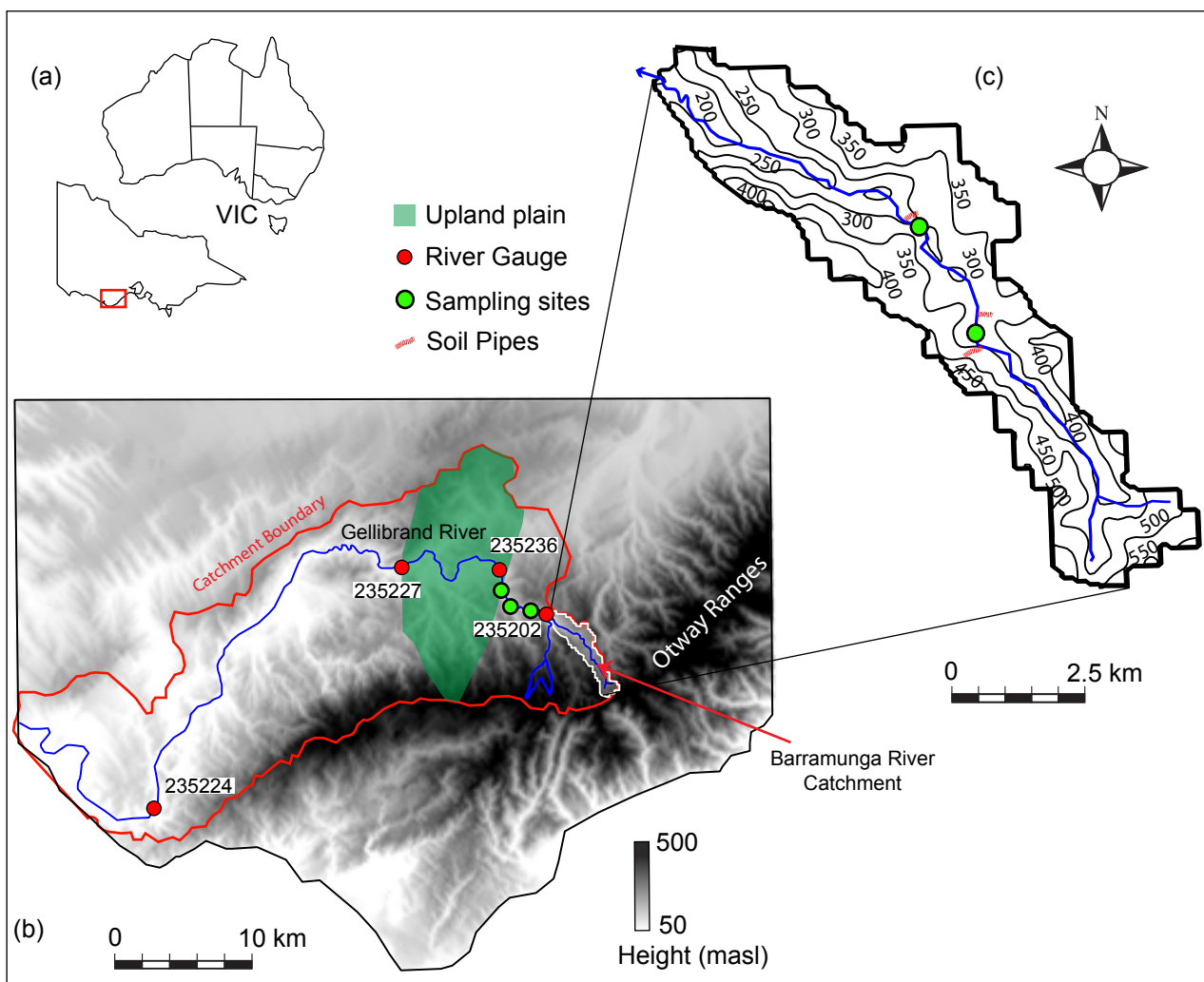


Figure 4.1- (a) Location of the Otway Ranges within Victoria, Australia (b) Digital elevation model of the Gellibrand and Barramunga Catchments and surrounding Otway Ranges (c) Contour map of the Barramunga headwater catchment showing location of sampling sites and observed soil pipes.

Previous work in this area has largely been focused on the upland plain which comprises 250 km² of the catchment (Figure 4.1 b). Here the Gellibrand River receives considerable groundwater inputs from the Eastern View Formation and surrounding alluvial sediments (Atkinson *et al.*, 2013, 2014). This research was conducted in the upper catchment of the Gellibrand River which includes the Barramunga sub-catchment. The upper catchment of the Gellibrand River drains uplifted deposits of the Cretaceous Eumeralla Formation which forms the basement to the Otway Basin and is composed of Cretaceous sediments of highly compacted siltstone, mudstone and volcanolithic sandstone. The Barramunga River is an ungauged perennial first-order tributary of the Gellibrand River that drains under predominantly natural conditions and which is representative of catchments dominated by dense eucalypt forest. The Barramunga catchment covers an area of 16.5 km² with slope angles of ~10° and elevations between 250 to 550 metres. Soils types are classified as Dermosols (Australian Soil Resource Information System, 2014). These consist of a shallow organic layer (0.2 – 0.3 m thick) and a sandy loam A1 horizon (0.2 – 0.3 m thick), which are underlain by a B-Horizon with medium to high clay content (> 45 %). Soil depth is unknown, however field observations indicate a minimum depth of > 1 - 2 m. Soil piping was found at both sampling sites in the Barramunga Catchment (Figure 4.1 c). The pipes were located at the top of the B horizon, forming either gullies (Figure 4.2a) or sub-surface pipes (Figure 4.2b) which became exposed at the stream bank.



Figure 4.2 (a) *Left* Surface gully draining into the Barramunga River (SP3) (b) *Right* Sub-surface pipe observed at the top of the B Horizon emerging at the river bank (later referred to as SP1)

The mean diameter of soil pipes were 0.3 m with the largest having a diameter of 0.5 m. Due to difficult terrain or pipes being submerged they could only be traced for up to ~50 m parallel to the hillslope. Of the 3 observed soil pipes, one flowed throughout the study period (and is referred to as

perennial soil pipe or SP_p) whereas the other 2 pipes were ephemeral (referred to as Ephemeral Soil Pipes or SP_e), with flow ceasing between January to March 2013.

4.3 Methods

Four instrumented sites were established along the Barramunga River and upper Gellibrand River (Figure 4.1). River and soil water was sampled monthly between September 2011 and June 2012 and further samples taken from soil pipes and unsaturated soil zones between June 2012 and August 2013. To sample riparian zone water eleven 80 mm diameter PVC piezometers with screen depths 0.5 to 1 m below the water table were installed < 5 m from the river in the riparian zone. Water from the unsaturated zone was sampled using SK20 (Decagon) ceramic suction cups employed at depths of 0.2, 0.5 and 0.9 m at two sites. Electrical conductivity (EC) and pH of river water, riparian water and soil pipe water were measured in the field using a calibrated TPS WP-81 conductivity/pH meter and probes. Piezometers in the riparian zone and soil pipes were continuously monitoring using HOBOWare U24-00x electrical conductivity data loggers, whilst the Barramunga River and Soil Pipe 1 (SP1_e) were continuously monitored for changes in electrical conductivity and water level using Aqua Troll 200 (In-Situ) Data Loggers. HOBOWare soil moisture smart sensors were used in conjunction with a HOBOWare micro station data logger to record hillslope soil moisture. Four soil moisture probes were installed in soil pits at depths of 0.10, 0.20, 0.40 and 0.80m. Readings are given as volumetric water content in m³ water /m³ soil and are accurate to $\pm 0.041\text{m}^3/\text{m}^3$ (S-SMB-M005, Decagon Devices, USA).

Soil pipe 1 was selected to monitor flow as it could be easily measured at the pipe outlet. Flow was measured by inserting steel guttering into the river bank below the pipe outlet which drained directly into a V-Notch weir. The V-Notch weir was constructed from a 45 x 30 cm plastic tank with a notch angle of 12.5°. In order to calculate the change in water height above the notch with an Aqua Troll 200 (In-Situ) Data Logger was secured inside to measure water depth, and an In-Situ Rugged Baro-TROLL data logger used to compensate for changes in water level due to barometric fluctuations. The V-Notch weir was calibrated by measuring the height above the notch under flow conditions of 0 – 65 litres/minute. The calibration achieved an R² value of 0.96 and is used to converted height above the

V-Notch into discharge (m^3/day). Salt gauging was performed during 5 sampling campaigns in order to estimate river flow in the Barramunga. Flow from the Upper Catchment is derived from the Victorian Water Data Research Warehouse (Gauge 235202), and rainfall over the study period from the nearest rain gauging station at Forrest (090040, Bureau of Meteorology).

HCO_3^- concentrations were measured in the field by titration with a Hach digital titrator. Cations were analysed on a Thermo Finnigan X Series II Quadrupole ICP-MS on samples that had been filtered through $0.45\mu\text{m}$ cellulose nitrate filters and acidified to $\text{pH} < 2$. Anions were measured on filtered unacidified samples using a Metrohm ion chromatograph. The precision of major ion concentrations based on replicate analyses is $\pm 2\%$. Charge balances are within $\pm 5\%$. Stable isotope ratios were measured using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}\text{O}$ values were measured via equilibration with He-CO_2 at 32°C for 24 to 48hr in a Finnigan MAT Gas Bench whilst $\delta^2\text{H}$ values were measured by the reaction of water samples with Cr at 850°C using a Finnigan MAT H/Device. Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were measured against an internal standard that has been calibrated using the IAEA, SMOW, GISP and SLAP standards. Data was normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW where $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of SLAP are -55.5‰ and -428‰ respectively. Precision is $\pm 1\text{‰}$ for $\delta^2\text{H}$ and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$.

^3H samples of river water, soil water, and water from soil pipes were taken during low flow (March 2012 & April 2012) and high flow conditions (October 2012 & August 2013). Whilst rainfall was collected at Monash University (Melbourne) between May 2012 and December 2012. Analysis was performed at the Australian Nuclear Science and Technology Organisation (ANSTO) and the Tritium and Water Dating Laboratory, Institute of Geological and Nuclear Sciences (GNS), (New Zealand). At both ANSTO and GNS, samples for ^3H were distilled and electrolytically enriched prior to being analysed by liquid scintillation counting as described by Neklapilova *et al.* (2008a,b) and Morgenstern and Taylor (2009). ^3H activities are expressed in Tritium Units (TU) with a relative uncertainty of $\pm 5\%$ and a quantification limit of 0.13 to 0.14 TU at ANSTO and 0.02 TU and a relative uncertainty of 2% at GNS.

4.4 Results

4.4.1 Upper Catchment Hydrology

Flow duration curves for the upper Gellibrand (Gauge 235236) and the entire catchment (Gauge 235224) are similar and display steep high-flow regimes with flat curves over moderate to low flows (Figure 4.3). During periods of low-flow a steep drop-off in discharge occurs in the Upper Gellibrand (< 5 ML/Day), whilst flows are maintained above 50 ML/Day in the lower catchment. Specific high flows (Q10) and low flows (Q95) in the lower catchment are 1609 and 236 ML/Day. In the upper catchment high (Q10) and low flows (Q95) are 46 and 4 ML/Day, equivalent to 15% and 8% of total river flow during these periods.

Figure 4.3 – Flow duration curves for: The Upper Catchment (235236 – shown in red) and at the river mouth (235224 – shown in blue).

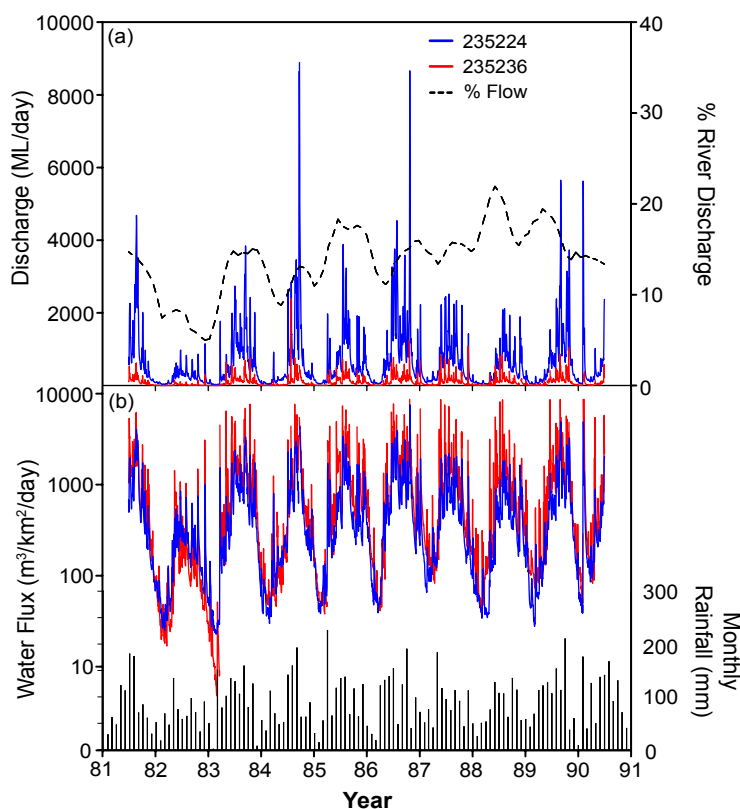
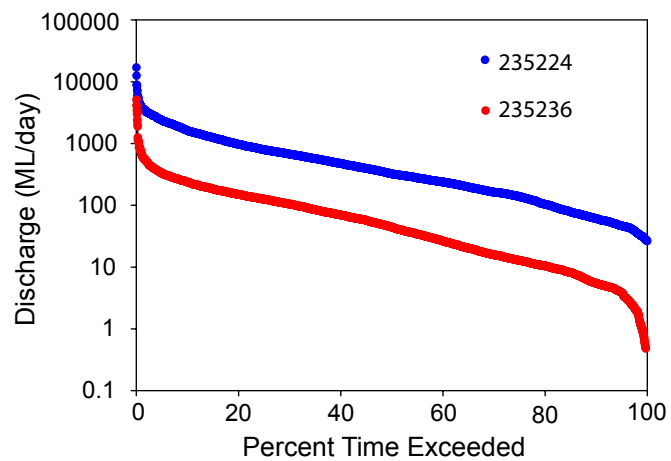


Figure 4.4 (a) Contribution of the upper catchment as a percentage of total river flow

(b) Water flux per km² calculated for the Upper Gellibrand and Gellibrand Catchment.

The importance of streamflow generated in the upper catchment can be assessed by its contribution to annual river flow. The upper Gellibrand catchment constitutes less than 10% of the total river catchment yet provides 5 to 22 % of total flow at gauge 235224. Contributions from the Upper catchment follow an annual cycle which follows rainfall distribution (Figure 4.4a), contributing a higher proportion of river flow during winter months (15 to 22 %) than summer months (5 to 15 %). Specific fluxes are relatively uniform across the catchment during low flows ($\sim 100 \text{ m}^3/\text{km}^2/\text{day}$), with the exception of 1983, where fluxes from the upper catchment drop below $10 \text{ m}^3/\text{km}^2/\text{day}$ following a period of no rainfall (Figure 4.4b). During winter months with high flow, greater fluxes per unit area are observed from the upper catchment ($3000 - 5000 \text{ m}^3/\text{km}^2/\text{day}$) in comparison to the catchment as a whole ($1000 - 2000 \text{ m}^3/\text{km}^2/\text{day}$).

4.4.2 Continuous Electrical Conductivity

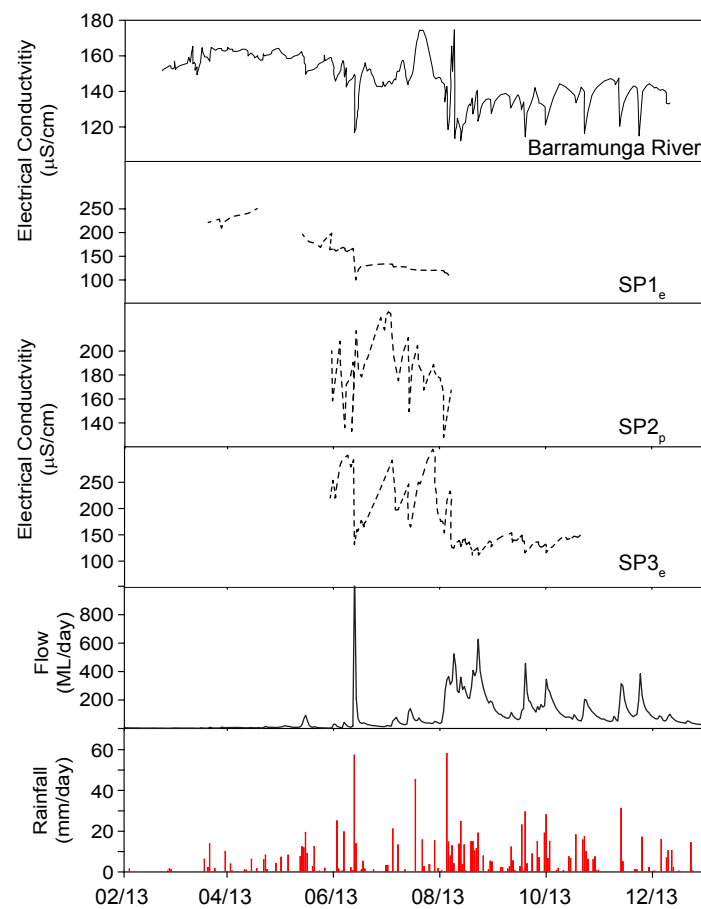


Figure 4.5 – Records of continuous electrical conductivity monitoring from Barramunga River and surrounding soil pipes.

The EC of river water from the upper catchment ranges between 120 – 180 $\mu\text{S}/\text{cm}$ with EC values $> 150 \mu\text{S}/\text{cm}$ occurring during periods of low flow and values $< 150 \mu\text{S}/\text{cm}$ occurring during high flow (Figure 4.5). This is particularly evident between the summer months of February and May 2013, where low discharges in the upper catchment ($< 50 \text{ ML}/\text{Day}$) correlate with high EC values. Increased river discharge during the following winter months is associated with a reduction in EC which remained constant through August to November 2013. High flow events such as that in June 2013 are associated with a rapid drop in river EC. These are well correlated to rainfall falling in the upper catchment.

Continuous EC in the soil pipe waters fluctuate between 120 and 300 $\mu\text{S}/\text{cm}$ (Figure 4.5) and again EC is inversely correlated with discharge, fluctuating in line with the rainfall events. The EC of water from Soil Pipe 1 was $> 200 \mu\text{S}/\text{cm}$ during low flow in April prior to a period between April and May where flow in the pipe ceased. The pipe was reactivated following a small rainfall event in May 2012, and for the remaining period where rainfall was relatively consistent, maintains an EC of $\sim 140 \mu\text{S}/\text{cm}$. A drop in EC is observed during high rainfall events such as in June 2013. Pipes 2 and 3 follow a similar pattern with fluctuations in the EC record largely correlating to increased rainfall and river discharge.

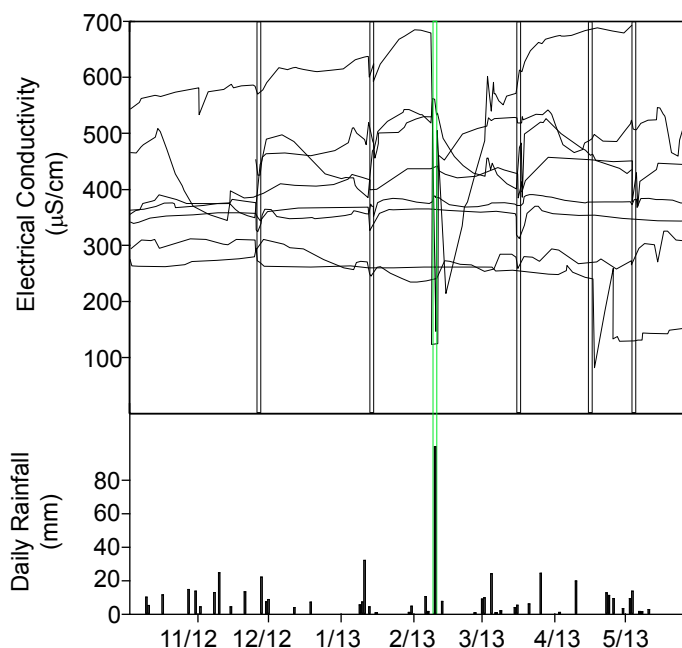


Figure 4.6 – Continuous EC monitoring from 8 riparian piezometers located in the near-river riparian zone.

Continuous EC values in the riparian zone waters are two to three times higher than that of river and soil pipe waters, ranging from 280 to 700 $\mu\text{S}/\text{cm}$ (Figure 4.6). EC remains constant in the majority of riparian zone piezometers with slight increases in EC observed after sampling periods and short-lived dilutions correlating to rainfall events.

4.4.3 Soil Moisture

Soil moisture content exhibits temporal and spatial variation between 0.2 and 0.4 m^3/m^3 (Figure 4.7). The lowest values of soil moisture are observed at shallow depths ($< 0.20\text{m}$), and soil moisture increases with depth, with maximum values of up to 0.38 m^3/m^3 at 0.8m. Soil moisture values are highest during winter months (June 2012 to September 2012) and are lowest during summer months (January to April 2012). Sharp increases in moisture content correlate to rainfall in the catchment with soil moisture response attenuated at depth. During winter months soil moisture content at 0.40 m depth rises to a constant value of 0.37 m^3/m^3 .

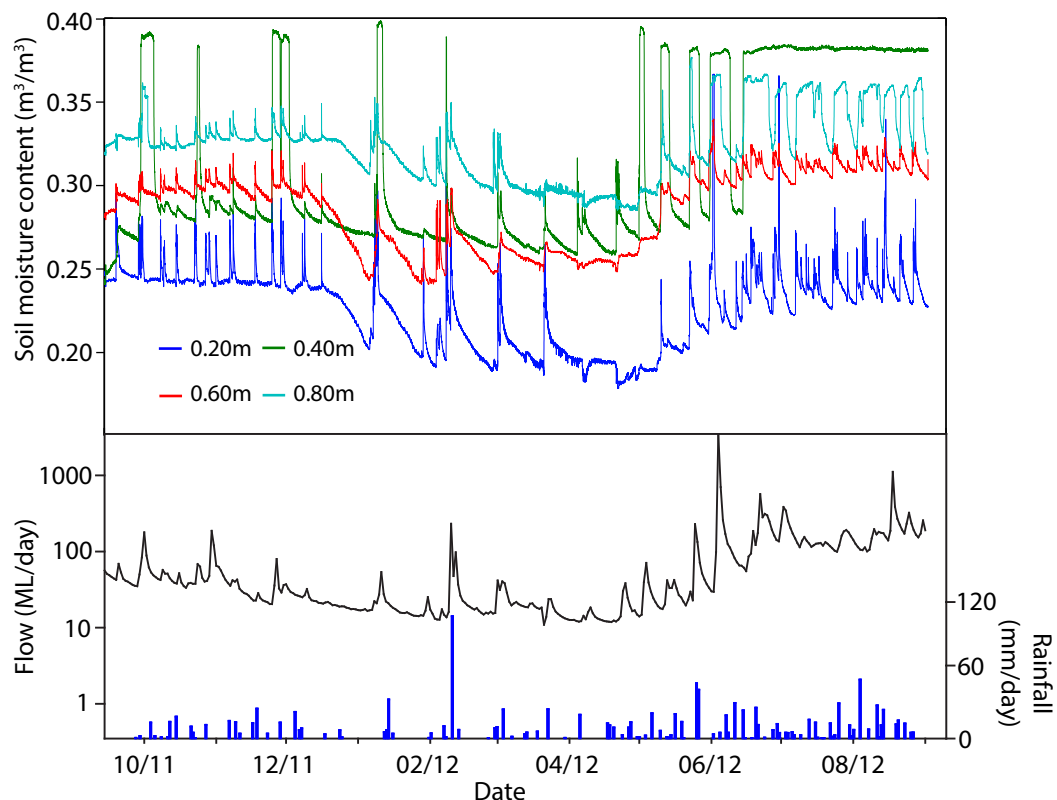


Figure 4.7 – Variations in soil moisture content and upper catchment river flow (Gauge 235202) between September 2011 and September 2012

4.4.4 Soil Pipe Discharge

Measured discharges from the V-Notch weir and from the gauging station at the upper Gellibrand River are shown in Figure 4.8. Discharge in the soil pipe mirrors that of upper catchment and is highly responsive to rainfall events, with flow initially initiated by rain events between 10 – 20 mm/day. Daily discharge rates from the soil pipe range from 1 m³/day during low flow up to 400 m³/day during high flow events. With measured river discharges between 1000 to 10 000 m³/day, a discharge of 50m³/day from the soil pipe amounts to between 0.5 – 5% of river flow.

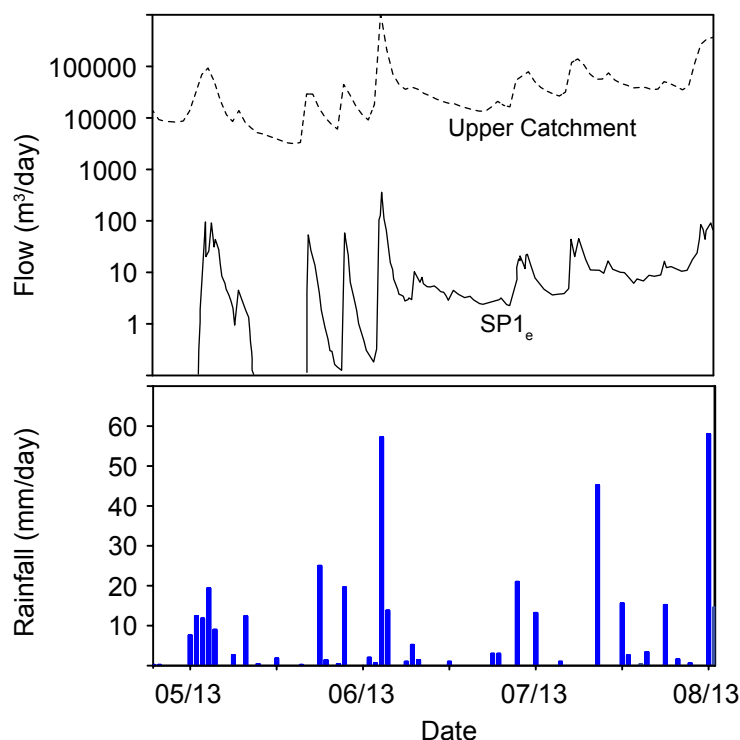


Figure 4.8 – Estimated Pipe Discharge and Flow from the Upper Catchment (Gauge 235202)

4.4.5 Geochemistry

The major ion geochemistry of water samples are summarised in Table 4.1. In river water, riparian zone water and water from the soil pipes, Na, Cl and HCO₃⁻ constitute between 75 and 90% of the major ions. Cl concentrations are broadly similar in river water, soil pipes and unsaturated zone samples. These range from 17 to 27 mg/L in river water (mean = 21 mg/L), 17 to 38 mg/L in water from the soil pipes (mean = 24 mg/L) and 10 to 32 mg/L in the unsaturated zone waters (mean = 19 mg/L). By contrast, Cl concentrations from water in the riparian zone range from 20 to 82 mg/L (mean = 50mg/L). The observation that the soil pipe and river water have similar geochemistry that

is different to the geochemistry of the riparian zone water is true for other major ions. Na vs Cl (Figure 4.9b), Mg vs Cl (Figure 4.9c), K vs Cl (Figure 4.9d) and Ca vs Cl (Figure 4.9e) trends for the Barramunga and Gellibrand Rivers are similar to those of the soil pipes; however the riparian zone waters define different major ion trends with much broader ranges of concentrations (Figure 4.9).

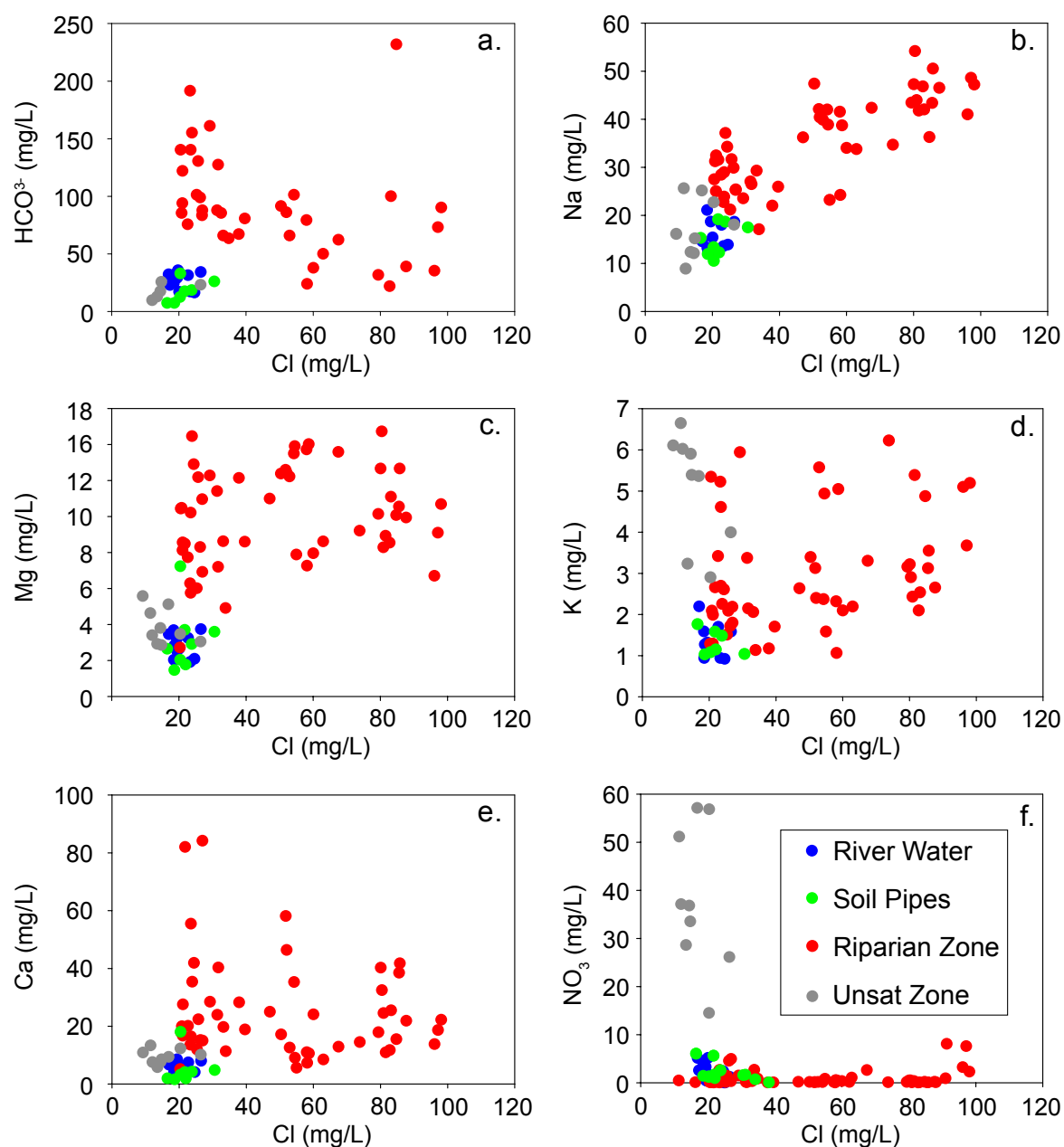


Figure 4.9 – Major Ion geochemistry plots of water from the Barramunga River, Soil pipes, Unsaturated and saturated Riparian Zone sampled between September 2011 and September 2013.

Table 4.1 – Chemistry of sampled waters from the Barramunga River (BR), Upper Gellibrand River (GR), Riparian Zone (RZ), Soil Pipes (SP) and unsaturated zone (UZ). RZ_(1,2,3) indicates samples from piezometers at different sampling sites.

Sample	Date	EC ($\mu\text{S}/\text{cm}$)	Cl (mg/L)	HCO ₃ (mg/L)	NO ₃ (mg/L)	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	K (mg/L)	³ H (TU)
BR1	03/12	154	19.4	29.1	2.1	13	2.5	5.7	1.3	2.06
BR2	03/12	155	19.6	27.4	1.91	13	2.7	5.8	1.3	1.84
BR2	04/12	147	17	32.2	5.1	14.6	3.5	6.7	2.2	2.01
BR1	10/12	140	23.8	26.6	2.12	21	3.7	7.2	1.6	1.95
BR2	10/12	143	25	29.2	1.6	18.7	3.4	7.2	1.3	1.90
BR2	08/13	141	20.1	17	5.1	15.4	2.7	4	1.3	2.036
GR	03/12	160	26	39	0.1	14.7	3.0	5.0	1.5	1.80
GR	04/12	161	27.2	27	0.4	16.6	3.8	6.0	1.4	1.90
GR	10/12	157	32.2	22.2	1.6	22.2	2.7	5.0	1.5	1.87
RZ ₁	04/12	268	23.3	191	0.5	22.8	6.3	13.6	5.2	1.61
RZ ₁	04/12	305	20.5	140	0.11	27.5	10.4	17.9	5.3	1.35
RZ ₂	04/12	334	58.7	65.9	0.4	38.8	14	10.6	5	2.32
RZ ₂	04/12	350	54.5	91.5	0.4	38.7	13.9	9.1	4.9	2.39
RZ ₃	10/12	172	33	65.9	0.3	29.3	8.6	19.7	2	1.94
RZ ₃	10/12	205	23.5	93.9	0.1	25	8.1	16.7	1.3	1.60
RZ ₄	10/12	500	79.4	31.8	0.1	43.5	10.1	17.9	3.2	1.85
SP _e 1	10/12	115	34	21.5	0.7	13	2.7	5.2	1.3	2.09
SP _p 2	10/12	170	22.1	12.5	0.9	13.4	2.0	3.2	1.1	1.80
SP _e 3	10/12	180	31.7	26.1	1.6	17.5	3.6	4.8	1	2.03
SP _e 1	08/13	111	16.5	7.3	6.0	15.3	2.6	1.9	1.8	2.185
SP _e 3	08/13	135	21.7	31.2	5.6	19.2	3.7	4.1	1.6	2.25
UZ	10/12	220	13.4	13.4	34.2	11.1	3.4	7.0	5.1	2.22

There is significant variability in the geochemistry of the riparian zone water between sampling sites whilst riparian zone waters from the same site display a similar chemistry. HCO_3^- concentrations are also similar in river, soil pipes and unsaturated zone waters (10 to 35 mg/L); however, the riparian zone waters have higher HCO_3^- concentrations (mean = 98 mg/L). Although generally similar in chemistry to river water, waters from the unsaturated zone are characterised by high NO_3^- concentrations (26 to 75 mg/L) and are enriched in K (3 – 7 mg/L) relative to river water (1- 2 mg/L).

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of river water, soil pipes and riparian zone water define an overlapping field between $\delta^{18}\text{O} = -4$ to -6 ‰ and $\delta^2\text{H} = -25$ to -35 ‰, with values displaced to the left of the LMWL (Figure 4.10). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of unsaturated zone waters and some soil of the soil pipes waters are lower ($\delta^{18}\text{O} = -5.5$ to -6 ‰, $\delta^2\text{H} = -32$ to -37 ‰).

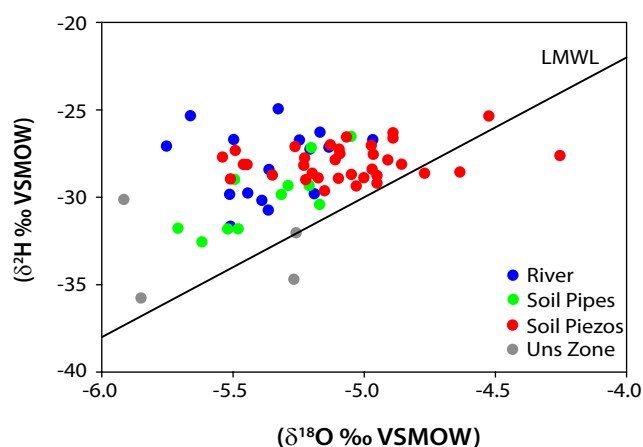


Figure 4.10 – $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ values of the Barramunga River, soil pipes, unsaturated zone and riparian zone waters between September 2011 and September 2013. LMWL = Local Meteoric Water Line for Melbourne, derived from Hughes and Crawford, 2012)

^3H activities in the Barramunga and Gellibrand River range from 1.84 to 2.06 TU and 1.8 to 1.9 TU respectively, with ^3H activities in soil pipes ranging between 1.80 and 2.2 TU. The riparian zone waters have more variable ^3H activities (1.35 to 2.39 TU) while one sample of water in the unsaturated zone has a ^3H activity of 2.2 TU (Table 4.1).

4.5 Discussion

4.5.1 Upper Catchment Water Sources: Soil Pipes and Riparian Contribution

The Barramunga River and upper catchment of the Gellibrand River maintain a constant flux of low EC water, with flow highly dependent on rainfall. Periods of high rainfall, particularly during winter months, are linked to increased discharges from the upper catchment, whereas during dry periods the upper catchment experiences low discharges, with discharge during prolonged drought periods falling to < 5ML/day. This response to rainfall is also observed in continuous electrical conductivity records, soil pipe discharge and soil moisture contents.

The rapid increase in discharge and associated input of low EC water during rainfall events in the upper catchment likely represents the input of event water which has undergone little change in chemical composition since falling as rainfall. That a number of soil pipes have been observed discharging into the river provides a mechanism by which large amounts of water may be transported from the hillslope to the river during rainfall events. The response times of river and soil pipe EC to rainfall demonstrates this event water mobilisation (Figure 4.11). Although a number of events require a rainfall pattern that is not captured by rain gauges, rainfall events are generally associated with the transport of low EC water in both the river and soil pipes. That low EC water is recorded in soil pipes before (Events 1 and 2) and after low EC water is recorded in the river (Event 4) indicates event water is channelled not only through observed soil pipes but through soil pipes/water sources upstream of the sampling locations. With three soil pipes observed over a stream length of < 1 km, a number of unobserved soil pipes may be present along the entire stream length and combined, these are likely to contribute significant amounts of event water into the river channel. These may drain hillslope water sources with minor variations in chemistry, producing a EC response in the river that is different to that in observed soil pipes (Event 3). With rainfall channelled into a number of soil pipes distributed across the catchment, there are likely dynamic controls which determine whether they are switched on or off. This may include antecedent moisture conditions surrounding the pipe channel and rainfall intensity. The potential of soil pipes to provide substantial amounts of water to sustain the river during low flow conditions is unknown; however given that the pipe waters have similar concentrations of Cl, K, Na, Mg, C and HCO_3^- to the river throughout the year, they may act as pathways for older hillslope stores to enter the river.

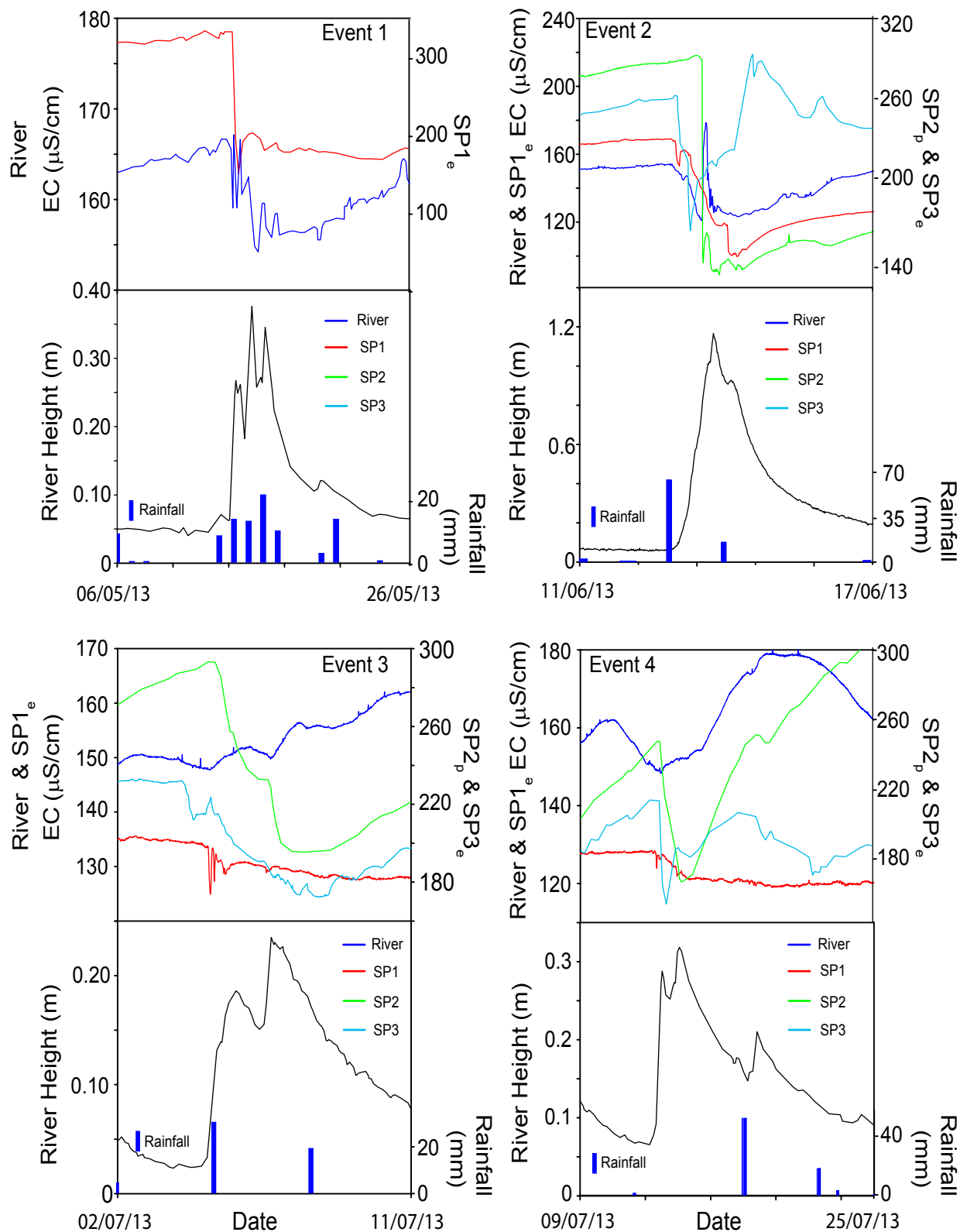


Figure 4.11 – Variable Electrical Conductivity (EC) response in soil pipes and river water over rainfall events.

That the riparian zone is saturated throughout the year indicates that it is a potential store of water. However, the majority of samples from the riparian zone have major ion concentrations that are higher than those in the river and EC values are also 2-3 times that of the river during baseflow conditions. Hence, it is unlikely the riparian zone contributes substantial water to the river. Rather, the riparian zone may be in connection with the stream over discrete areas. Some riparian zone waters have a similar chemistry to river water (RZ_1 , RZ_3) and may play a role in baseflow generation. This connection is likely controlled by soil permeability (in particular the presence of dense clays) and the position of the water table in the riparian zone relative to the stream.

4.5.2 Mean Residence Times of Upper Catchment Water

The mean residence time of water samples were evaluated from ^3H activities using the TracerLPM workbook (Jurgens *et al.*, 2012). ^3H activities in the river, soil pipes and riparian zone waters are related to ^3H activities of recharge by:

$$C_{out}(t) = \int_{-\infty}^t C_{in}(t') e^{-\lambda(t-t')} g(t-t') dt' \quad (1)$$

where $C_{out}(t)$ is the ^3H activity of the sample at time t , $C_{in}(t')$ is the activity of ^3H of recharge at time t' , t is the sample date, $t - t'$ is the age of the water parcel, λ is the ^3H decay constant (0.056 yr^{-1}) and $g(t-t')$ is the transmit time distribution. The mean residence time is the time that water has spent in the catchment since falling as rainfall. Mean residence times are calculated for waters from the Bar-ramunga and Gellibrand Rivers, soil pipes and riparian zone. Exponential flow (EFM), piston flow (PFM) and dispersion flow models (DFM) were run as these transmit time distributions span a range of scenarios and together provide the likely minimum and maximum range of mean residence times. These calculations assume that the pre-atmospheric nuclear test (bomb pulse) precipitation had the same ^3H activity as modern precipitation in Melbourne. A value of 2.7 TU was used to represent modern and pre-bomb pulse rainfall. This is based on the ^3H activity of rainfall measured at Monash University and expected ^3H values in Southern Victoria (Tadros *et al.*, 2014). For intervening years, the mean weighted average of ^3H activities in precipitation in Melbourne was extracted from the International Atomic Energy Agency Melbourne record (International Atomic Energy Association,

2014). The mean residence times for ^3H activities between 1.0 and 3.0 for each of these transit time distributions are shown in Figure 4.12. Comparison between the three models show that mean residence times calculated by exponential/dispersion models and piston flow begin to diverge after mean residence times of 5 years, whereas exponential and dispersion models diverge with residence times > 10 years (Figure 4.12). The exponential flow and dispersion models produce unique residence times. By contrast, as the piston flow model does not involve mixing or dispersion within the flow system, the high ^3H activities from the bomb pulse remain and this model does not produce unique ages.

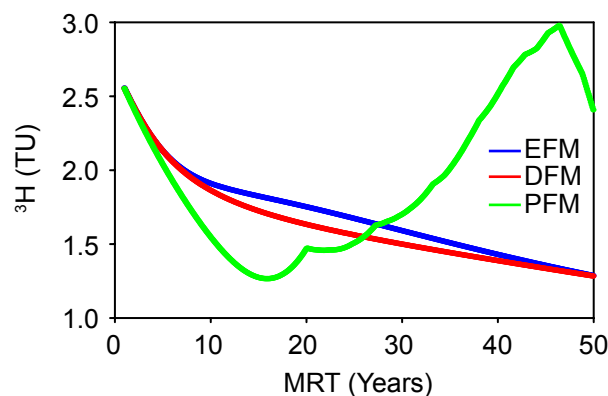


Figure 4.12 – Mean Residence Time (MRT) of ^3H outputs between 1.0 and 3.0 TU calculated for:

Exponential Flow (EFM)
 Dispersion Flow (DFM) where $D/vx = 0.5$
 and Piston Flow (PFM)

In the Upper Catchment, mechanical dispersion in soils, varying downslope velocities and preferential flowpaths indicate that piston flow is unlikely to be a good representation of the flow system. Mean residence times of water were calculated using the EFM and DFM flow models (Table 4.2). These are generally used to represent shallow groundwater flow (Kirchner *et al.*, 2001; Kim & Jung, 2013). In the DFM a D/vx of 0.5 (the ratio of dispersive to advective flow) is utilised to represent short, dispersed flowpaths. During baseflow conditions in March 2012 (18.5 ML/Day) the mean residence time of water from the Barramunga River ranges from 10.6 to 13.9 years, with the Upper Gellibrand River having a mean residence time between 11.9 to 16.6 years. During high flow in October 2012 (82 ML/Day) the mean residence time of water in the Barramunga and Upper Gellibrand River drops to 9.1 to 10.4 years, and 9.8 to 12.0 years respectively. This further decreases to 6.3 to 6.4 years in the Barramunga River during storm sampling in August 2013. Water from soil pipes 1 and 3 (the ephemeral pipes) have mean residence times of 5.6 and 6.5 to 6.6 years respectively, while water from soil pipe 2 (the perennial pipe) has a mean residence time of 12.0 to 16.7 years. In August 2013 the mean residence times of water in soil pipe 1 and soil pipe 3 drop to 4.3 years and 3.6 years respectively.

Table 4.2 – Calculated mean residence times of waters from different sources in the Barramunga and Upper Gellibrand River Catchments where; EFM = Exponential Flow Model. DFM = Dispersion Flow Model where $D/\nu x = 0.5$.

Sample	Date	³ H (TU)	Flow (ML/Day)	Mean Residence Time (Years)	
				EM	DM
<i>BR1</i>	14/03/2012	2.06	18.5	6.1	6.0
<i>BR2</i>	14/03/2012	1.84	18.5	13.9	10.6
<i>BR2</i>	24/04/2012	2.01	30.4	7.0	6.8
<i>BR1</i>	15/10/2012	1.95	82	8.6	7.9
<i>BR2</i>	15/10/2012	1.90	82	10.4	9.1
<i>BR2</i>	7/08/2013	2.04	308	6.4	6.3
<i>GR</i>	14/03/2012	1.80	18.5	16.6	11.9
<i>GR</i>	24/04/2012	1.90	30.4	10.4	9.1
<i>GR</i>	15/10/2012	1.87	82	12.0	9.8
<i>SW 1</i>	26/04/2012	1.61	-	28.9	21.5
<i>SW 2</i>	26/04/2012	1.35	-	45.3	43.6
<i>SW 3</i>	26/04/2012	2.32	-	2.9	2.9
<i>SW 4</i>	26/04/2012	2.39	-	2.3	2.3
<i>SW 2</i>	15/10/2012	1.94	-	8.9	8.1
<i>SW 5</i>	15/10/2012	1.60	-	29.4	22.2
<i>SW 6</i>	15/10/2012	1.85	-	13.2	10.4
<i>SP 1</i>	15/10/2012	2.09	82	5.6	5.6
<i>SP 2</i>	15/10/2012	1.80	82	16.7	12.0
<i>SP 3</i>	15/10/2012	2.03	82	6.6	6.5
<i>SP 1</i>	7/08/2013	2.185	308	4.3	4.3
<i>SP 3</i>	7/08/2013	2.25	308	3.6	3.6
<i>Uns SW</i>	15/10/2012	2.22	-	3.9	2.9

That all sampled soil pipes have mean residence times which are similar to river water further consolidates the hypothesis that they contribute to river flow. The variation in ages between ephemeral pipes and perennial pipes also indicates that water reservoirs from which flow in these pipes is derived also have unique mean residence times. Mean residence times of up to 16.7 years indicates they may play a role in baseflow generation and have the potential to act as longer term water stores. That mean residence times of water in the riparian zone vary by an order of magnitude 2.3 – 45.3 years.

This suggests the riparian zone has the potential to store water over varying timescales which may or may not feed into the river.

With increasing flow, the mean residence times of river water and soil pipes draining the upper catchment decrease, with the exception of sampling during April 2012 (Figure 4.13a). Here mean residence times in both the Barramunga and Gellibrand River are younger than sampling during October 2012 which took place in higher flow conditions (82 ML/Day). Ages were further assessed relative to the pre-event (baseflow) to event water (quickflow) components derived from recursive digital filtering. Hydrograph separation of baseflow and quickflow rations was carried out via the Eckhardt filter (Eckhardt, 2005), with a BFI_{max} of 0.25 selected to represent a perennial stream on a hard rock aquifer. Hydrograph separation shows that the baseflow to quickflow ratio is directly related to the age of water draining in the Barramunga and Gellibrand Rivers. Ratios approaching 1 are characterised by older mean water ages whilst ratios tending toward 0 are characterised by younger mean water ages (Figure 4.13b).

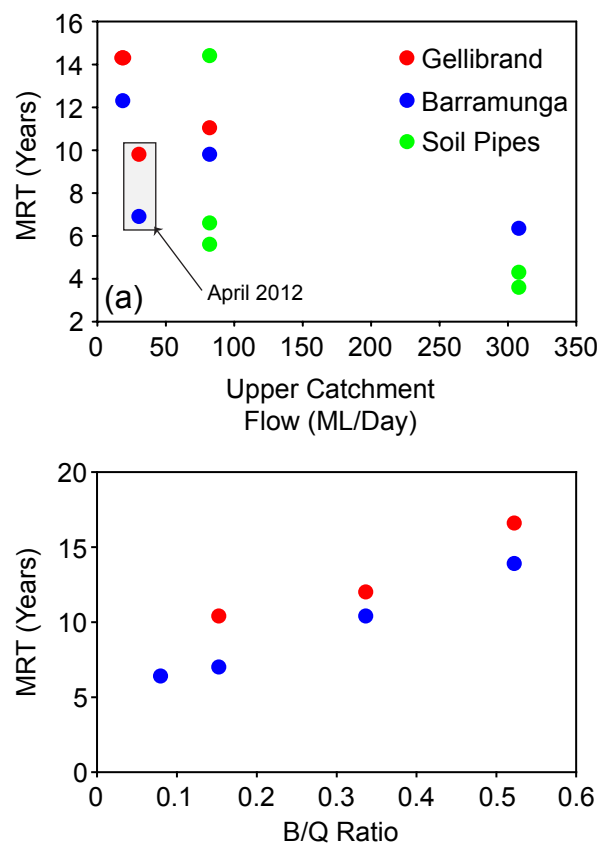


Figure 4.13 (a) Mean Residence Time (MRT) of waters assuming EFM and flow in the upper catchment (Gauge 235202). Sampling during April 2012 is highlighted in grey (b) The relationship of MRT to Baseflow/Quickflow ratio.

4.5.3 Pipeflow Mechanism and First Order Controls On Pipeflow Formation

That the soil pipes show a similar response to rainfall and have identical chemistry and mean residence times to the rivers indicate they play an important role in streamflow generation, channelling event-water into the river and draining older stores present on the hillslope. The presence of pipeflow has previously been described as gulley and tunnel formations in Victoria (Boucher & Powell, 1994) and parts of New South Wales (Crouch *et al.*, 1976) and is linked to the presence of sodic soils with increased clay content in the B-horizon. In the Upper Gellibrand catchment the formation of soil pipes along the hillslope appears to be controlled by soil properties, with field observations showing that erodible top-soils overlie a clay-rich and largely impermeable B horizon. Although the exact mechanism is unknown, saturated soil zones that have developed along the hillslope likely provide connection between soil pipes (Sidle *et al.*, 1995), with pipeflow generated by vertical infiltration into the soil pipe network and rising phreatic surfaces associated with rainfall infiltration. This may explain the strong linkage between soil moisture and river flow and the presence of high NO_3^- concentrations in the unsaturated zone indicating that saturation must be occurring on the hillslope in order for denitrification of water passing through the unsaturated zone to occur. Over time saturated soil areas drain into the pipe network with a resultant drop in the water table resulting in ephemeral or perennial pipeflow regimes dependent on the area of soil saturation surrounding the pipe. Variable water ages (3.2 to 16.7 years) indicate that old water stores with considerable residence times are present in the upper catchment. However, river gauge data show these old water stores to be highly susceptible to long periods of drought, with diminishing flows seen during periods of low rainfall.

4.6 Conclusion

Soil piping has been documented across a broad range of climatic zones, from tropical rainforest to periglacial environments, with a large proportion of literature relating to catchments in humid temperate climates. The Upper Gellibrand catchment, located in a temperate rainforest, Southeast Australia, adds to the body of literature describing pipeflow in these environments. Although the role of riparian and bedrock water is unknown, we propose that pipeflow exerts a strong control on river discharge and chemistry, particularly following rainfall events through which water can be rapidly transmitted from the hillslope to the stream. Limited gauging and monitoring of pipes performed in this study suggests that a network of pipes transmit rainfall into the river channel with rapid response times. In

addition we propose that the first order control on pipeflow development is the presence of an impermeable clay rich layer in the soil profile, above which soil pipes form by erosion of overlying layers. Finally, we provide some of the first estimates of the mean residence times of water draining in headwater streams in Australia, with ^3H ages ranging between 5 – 17 years depending on flow conditions. Further work is required in establishing the occurrence of pipeflow locally (throughout the Otways) and globally as well as utilising mean residence times in other catchments to understand headwater functioning.

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Chapter 5

Conclusion

5.1 Catchment management implications and further research

The Gellibrand River and surrounding groundwater in the Eastern View Formation represent a significant quantity of high quality water with electrical conductivity values of $< 600 \mu\text{S/cm}$. The research presented in this thesis improves our understanding of riverine systems and may aid future catchment management decisions regarding groundwater abstraction, as well as helping to assess the vulnerability to upland river systems to climate and land-use change. Together, chapters 2, 3 and 4 address the sources of water which contribute to discharge in the Gellibrand River, the residence time and origins of groundwater in the upland plain and the sources and residence times of water draining the upper catchment.

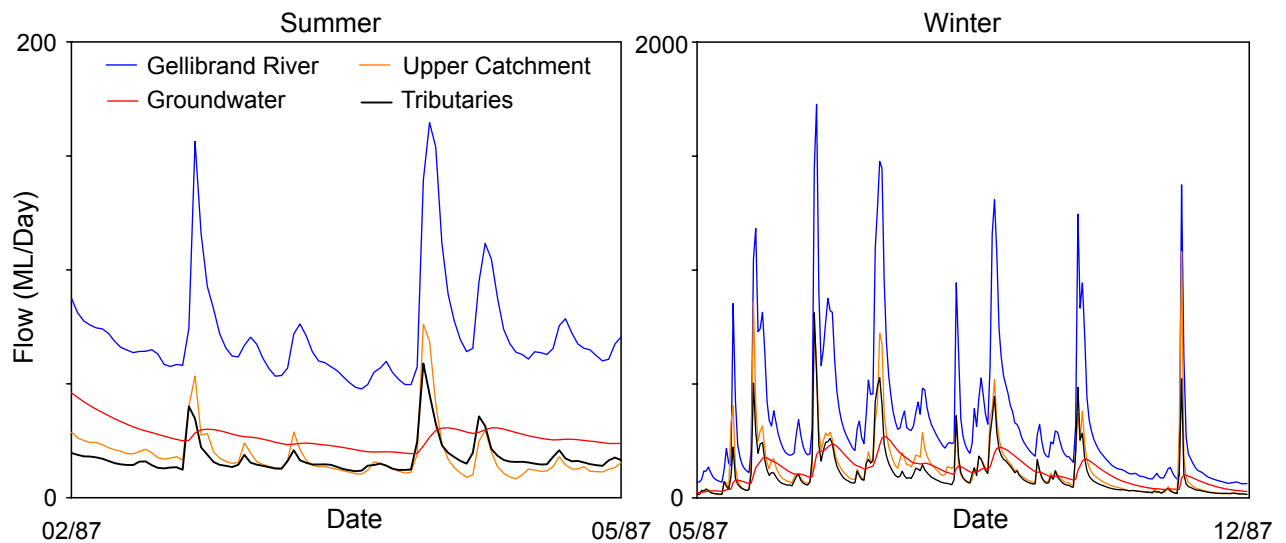


Figure 5.1 - Water sources in the upland plain of the Gellibrand River at Bunkers Hill (Gauge 235227). Dominant water sources are groundwater inflows (calculated using the Echardt Filter and a BFI_{max} of 0.4), discharge from the upper catchment (Gauge 235236) and contribution from surrounding tributaries (Lardners Creek: Gauge 235210 and Love Creek: Gauge 235234). Relative contributions from these sources over summer and winter months can be seen.

Chemical mass balances using environmental tracers (Cl, ^{222}Rn and ^3H) confirm that the upland plain of the Gellibrand River is highly connected to groundwater from the Eastern View Formation. The Gellibrand River is gaining throughout the year, with groundwater discharge accounting for up to 50% of river discharge in summer (Figure 5.1). Between 50 to 90% of total groundwater discharge occurs along a narrow length of river which intersects the Eastern View Formation (18 to 22 km downstream from James Access).

Groundwater residence times determined via ^{14}C and ^3H of between 100 and 10,000 years imply the Gellibrand River Valley acts as a discharge zone for groundwater originating on the Barongarook High, a regional recharge zone (Figure 5.2). A local groundwater system which recharges on outcropping sediments in the upland plain is also present. Recharge rates on the upland plain calculated from bore hydrograph fluctuations are between 90 and 372 mm/year (amounting to 10 to 30% of rainfall). However, ^3H activities between 0.02 and 0.09 TU in the shallow groundwater show that the regional groundwater discharge limits the infiltration of local groundwater to depths of < 10 metres. At the valley margins locally-recharged groundwater exists at greater depths (> 25 metres), however the extent to which the local groundwater system extends is unknown. The proportion of the groundwater resource which is composed of regional to local groundwater may be important in understanding contaminant transport from agricultural land in the upland plain as well as the age of water discharging into the river. The decrease in ^3H activities downstream (1.8 to 1.2 TU) implies the river receives regional groundwater during summer months. It is likely however that locally recharged groundwater in the upland plain also contributes to river flow, especially following winter rains that cause a rise in the water table.

The lack of change in electrical conductivity records and the negligible ^3H activities in groundwater from adjacent to the Gellibrand River imply that there is little recharge from the river even during high flow events and also limits the extent of bank exchange processes to distances of < 5 m from the river and depths of < 10 m. That environmental tracers and baseflow filtering give similar estimates of groundwater inflows (chapter 2) place further limits on bank storage. Estimates of baseflow using digital filtering techniques include all delayed water, as opposed to just groundwater inflows (Nathan and McMahon, 1990; Brodie *et al.*, 2007; Cartwright *et al.*, 2014). Assuming that delayed water sources

such as bank storage are likely to have a similar geochemical signal to surface water, mass balances using solutes such as Cl are likely to be dominated by the groundwater component of baseflow. This results in chemical mass balances and digital filtering giving different estimates of baseflow. Here this is not the case implying that both may dominantly reflect the groundwater inflows. The lack of significant storage within or recharge through the banks is probably due to the clay-rich nature of the river bed and banks. Additionally the close agreement between ^{222}Rn , which is affected by parafluvial and hyporheic flow (Cook *et al.*, 2006) and Cl which is not, suggests that hyporheic exchange is limited in the study area and does not significantly impact calculated groundwater inflows made using ^{222}Rn . Again the clay-rich river bed would inhibit flow through the hyporheic zone. In the upland plain of the Gellibrand catchment, these processes have minimal impact on calculated groundwater discharge.

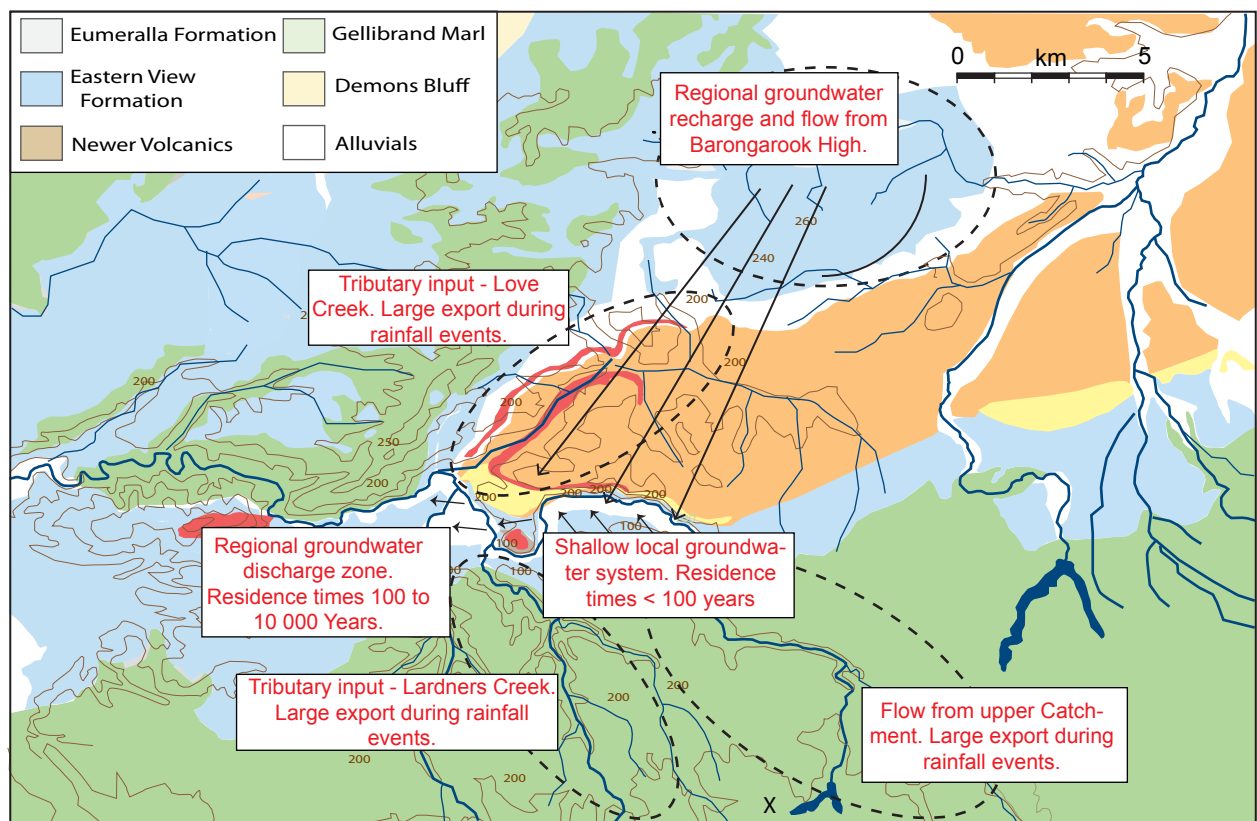


Figure 5.2 – Sources of river flow in the upland area of the Gellibrand River.

The upper catchment represents a significant source of water to the Gellibrand River and its rapid response to rainfall controls high flow events (Figure 5.2). During summer 10 – 20 % of river water in the upland plain is derived from the upper catchment, increasing to between 40 to 60 % during winter months (Fig 5.1). The dramatic recession in flow during periods of low rainfall indicate the

upper catchment is sensitive to periods of drought. This response to rainfall is largely controlled by preferential flow through soil pipes. Although these rapidly transmit rainfall falling on hillslopes into the stream, mean residence times in the pipes of 3.6 to 16.7 years indicate they drain old water sources. Mean residence times in the river between 6 and 16.6 years also suggest that old water stores contribute to streamflow over a range of flow conditions. With a major ion geochemistry largely different to that of river water, the Riparian Zone is unlikely to provide much of the water in the stream (possibly due to clay rich soils in these areas) and suggests groundwater in the bedrock and zones of saturation in soils may act as long term stores.

The remaining proportion of river flow is provided by tributaries, namely Lardners Creek and Love Creek (Figure 5.2). These behave in a similar manner to the upper catchment of the Gellibrand River, with a higher contribution to discharge during winter than summer months (Figure 5.1). The headwaters of Love Creek have undergone significant land clearing and provide a contrast to the native eucalypt forest through which Lardners Creek drains.

Groundwater extraction, climate variability and changes in land-use are likely to influence hydrological processes in the upland area of the Gellibrand Catchment. Although groundwater is currently not abstracted from the Eastern View Formation in the study area, it represents a viable source of water which may be used in the future. In the adjacent Barwon River Catchment, groundwater from the Dilwyn Formation (equivalent to the Eastern View Formation) has been abstracted for water supply during drought periods. This has been linked to drawdown on the Barongarook High (Petrides & Cartwright, 2006) and diminished flows in rivers that are connected to the Eastern View Formation. The high connectivity between the Gellibrand River and Eastern View Formation in the Gellibrand River Valley suggests that groundwater abstraction in the Gellibrand Catchment would have an effect on river flow. The current water abstraction is also likely to impact groundwater flow paths from the Barongarook High; this may impact groundwater flow in the Gellibrand River Valley and may also eventually impact on the Gellibrand River where it is connected to the Eastern View Formation. A better understanding of recharge rates and groundwater flowpaths on the Barongarook High may aid in constraining sustainable extraction in both the Barwon River Valley and the Gellibrand River Valley. Changes in climate through variable rainfall patterns and evapotranspiration rates are also likely

to impact recharge rates on the Barongarook High and the export of water from the upper catchment. Both these areas may be highly susceptible to periods of drought. Changes in land-use on the Barongarook High and the upper catchment must also be carefully considered regarding the impact on recharge rates and run-off processes which contribute to streamflow.

5.2 Wider Scientific Implications

Environmental tracers are widely applied in surface water – groundwater studies. Their use requires proper application as well as an understanding of the limitations which may influence results. Although ^{222}Rn has proven a powerful tool in predicting groundwater influxes into surface water bodies (Mullinger *et al.*, 2007; Cartwright *et al.*, 2011 ; Unland *et al.*, 2013) its use is complicated by uncertainties in the rate of degassing and the flux of ^{222}Rn from the hyporheic zone (Cook *et al.*, 2006; Cook *et al.*, 2012). Here we demonstrate that in catchments where groundwater ^{222}Rn activities and Cl concentrations are spatially heterogeneous, groundwater discharge calculations can also be significantly affected by the assumed ^{222}Rn activity or Cl concentration of the groundwater end-member. This is likely to be true for any environmental tracer which relies on differences between surface water and groundwater chemistry.

A representative value of the ^{222}Rn activities and Cl concentrations was achieved by measurement of a number of groundwater samples, capturing the spatial heterogeneity in groundwater chemistry. This study also validates the use of empirical models in estimating ^{222}Rn degassing (O'Connor & Dobbins, 1958; Negulescu & Rojanski, 1969). These can be used to obtain realistic groundwater discharge values in rivers which experience relatively low turbulence. When combined, it is also shown that evidence from ^{222}Rn , ^3H and Cl can be used to delineate short to medium term storage processes such as bank storage and hyporheic and parafluvial flux from regional groundwater discharge.

The research presented in this thesis also highlights the use of ^3H as a powerful tracer of surface water - groundwater processes. In Chapter 2 we demonstrate the ability of ^3H to reveal whether older and younger reservoirs feed into rivers and use end member mixing analysis to quantify groundwater discharge. In Chapter 3 ^3H is used to give insights into recharge processes and bank exchange that

cannot be seen using traditional water table fluctuation methods. In Chapter 4 ^3H is used to provide the first age estimates of headwater streams in Australia. Generally, mean residence times calculated using stable isotopes and major ion chemistry require high frequency rainfall and stream data and may be ineffective where residence times are > 5 years. By contrast, ^3H differs in that the decay process is the basis for dating. With the distribution of ^3H in precipitation in Australia well documented (Tadros *et al.*, 2014), single ^3H measurements can yield non-unique ages and be used to assess residence times of several years that may be too long for stable isotope tracers. Future research on headwater streams should assess the influence of controls such as catchment size, rainfall and land-use on mean residence times, and the potential threat of climate change on river flows. Where possible, measurement of ^3H in precipitation in specific catchments would allow for tighter constraint on the calculation of water residence times.

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Investigating the spatio-temporal variability in groundwater and surface water interactions: a multi-technique approach

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Abstract. The interaction between groundwater and surface water along the Tambo and Nicholson rivers, south-east Australia, was investigated using ^{222}Rn , Cl, differential flow gauging, head gradients, electrical conductivity (EC) and temperature profiles. Head gradients, temperature profiles, Cl concentrations and ^{222}Rn activities all indicate higher groundwater fluxes to the Tambo River in areas of increased topographic variation where the potential to form large groundwater–surface water gradients is greater. Groundwater discharge to the Tambo River calculated by Cl mass balance was significantly lower (1.48×10^4 to $1.41 \times 10^3 \text{ m}^3 \text{ day}^{-1}$) than discharge estimated by ^{222}Rn mass balance (5.35×10^5 to $9.56 \times 10^3 \text{ m}^3 \text{ day}^{-1}$) and differential flow gauging (5.41×10^5 to $6.30 \times 10^3 \text{ m}^3 \text{ day}^{-1}$) due to bank return waters. While groundwater sampling from the bank of the Tambo River was intended to account for changes in groundwater chemistry associated with bank infiltration, variations in bank infiltration between sample sites remain unaccounted for, limiting the use of Cl as an effective tracer. Groundwater discharge to both the Tambo and Nicholson rivers was the highest under high-flow conditions in the days to weeks following significant rainfall, indicating that the rivers are well connected to a groundwater system that is responsive to rainfall. Groundwater constituted the lowest proportion of river discharge during times of increased rainfall that followed dry periods, while groundwater constituted the highest proportion of river discharge under baseflow conditions (21.4 % of the Tambo in April 2010 and 18.9 % of the Nicholson in September 2010).

1 Introduction

Constraining the interaction between groundwater and rivers is important for calculating water balances and sustainable levels of water extraction (Tsur and Graham-Tomasi, 1991), maintaining healthy river ecology (Boulton, 1993; Krause et al., 2007; Lambs, 2004), understanding biogeochemical reactions at the groundwater–surface water interface (Peyrard et al., 2011; Sophocleous, 2002; Woessner, 2000) and determining the source and fluxes of nutrients and solutes carried by rivers. In order to estimate groundwater discharge to rivers and to define gaining and losing reaches, a number of physical, chemical and numerical methods have been developed (Kalbus et al., 2006).

Differential flow gauging uses the difference in river discharge at two points along a reach in order to calculate net gains or losses along that stretch (Cey et al., 1998; Harte and Kiah, 2009; McCallum et al., 2012; Ruehl et al., 2006). Discharge is usually measured under baseflow conditions where runoff is negligible, allowing the net groundwater discharge or recharge to be calculated once evaporative losses are accounted for. While gauging stations are usually spaced far apart and often overlook variations at smaller spatial scales, long time series of measurements are commonly available, allowing for analysis of temporal trends and comparison with other methods (McCallum et al., 2013).

As groundwater temperature is commonly higher than that of surface water in winter and lower in summer (Anibas et al., 2009), measurement of temperature in rivers and streambeds can be used to identify the gaining and losing

reaches (Anderson, 2005; Andersen and Acworth, 2009; Anibas et al., 2011; Rau et al., 2010; Silliman and Booth, 1993). While quantification of water fluxes using temperature requires detailed subsurface temperature measurements over time, temperature mapping of rivers is a simple and effective method of identifying gaining and losing reaches (Becker et al., 2004). Similarly, if groundwater has a significantly different electrical conductivity (EC) to surface water, changes in river EC can be used to quantify the influx of groundwater (Cartwright et al., 2011; Cey et al., 1998; McCallum et al., 2012). The advantage of along-river temperature/EC surveying is that it allows data to be obtained at a higher spatial resolution than flow gauging or discrete sampling for chemical analysis.

Geochemical tracers including major ions, stable isotopes and radiogenic isotopes have been used to estimate groundwater fluxes in gaining rivers (Cartwright et al., 2008, 2010, 2011; Cook, 2012; Cook et al., 2003, 2006; Durand et al., 1993; Genereux et al., 1993; Genereux and Hemond, 1990; Lamontagne et al., 2005, 2008; Lamontagne and Cook, 2007; Mullinger et al., 2007, 2009; Négrel et al., 2003; Rhode, 1981; Ribolzi et al., 2000; Stellato et al., 2008). The utility of each of these tracers depends on a variety of factors including the difference between the concentration of the tracer in groundwater compared to surface water, its spatial and temporal variability, the accurate characterisation of its sources and sinks, and the potential for it to change by processes such as evaporation, precipitation, radioactive decay, degassing, or biogeochemical reactions. However after such processes are accounted for, chemical tracers are useful in assessing groundwater fluxes, as runoff does not impact flux estimates and spatial analyses are only limited by sampling frequency.

^{222}Rn is produced by the decay of ^{226}Ra in the ^{238}U to ^{206}Pb decay series. Since ^{226}Ra activities are high in minerals, ^{222}Rn activities in groundwater increase as it achieves secular equilibrium with the ^{226}Ra in minerals over periods of approximately 2–3 weeks (Cook, 2012). After groundwater discharges to a surface water body, degassing and radioactive decay will reduce ^{222}Rn activities, resulting in surface water activities that are usually 2 to 3 orders of magnitude lower than those in groundwater (e.g. Cook, 2012; Cook et al., 2006). The use of ^{222}Rn as a groundwater tracer has increased over the last two decades as methods for its measurement in the field have improved (Burnett et al., 2010; Cartwright et al., 2011; Cook et al., 2003; Ellins et al., 1990; Genereux and Hemond, 1990; Gilfedder et al., 2012; Hofmann et al., 2011; Mullinger et al., 2007, 2009; Santos and Eyre, 2011). The short half-life (3.82 days) and degassing of ^{222}Rn from surface water makes it a particularly valuable groundwater tracer, as elevated ^{222}Rn activities will only occur close to zones of groundwater discharge.

The effectiveness of ^{222}Rn as a groundwater tracer can be limited by poorly defined groundwater end members and low surface water concentrations which can lead to high analytical uncertainties. The uncertainties associated with

groundwater end members can be reduced by combining groundwater measurements with laboratory experiments in which the ^{222}Rn activity of water in equilibrium with the river sediments is determined (Burnett et al., 2008; Cook et al., 2006; Corbett et al., 1998; Martens et al., 1980; Peterson et al., 2010). Recent studies have also focussed on better quantifying processes such as hyporheic exchange and gas transfer, making the use of ^{222}Rn more reliable (Cook et al., 2006; Lamontagne and Cook, 2007; Mullinger et al., 2007).

This study uses major ion chemistry, differential flow gauging, and ^{222}Rn activities to calculate groundwater fluxes to the Nicholson and Tambo rivers and assess how groundwater fluxes vary in response to seasonal changes in rainfall and river discharge. These techniques are combined with EC and temperature mapping to evaluate the detailed spatial variability of groundwater discharge. By combining differential flow gauging with chemical mass balance, errors in groundwater estimates due to the presence of losing reaches or runoff during periods of rainfall can be accounted for. By combining these techniques with temperature and EC surveys, the applicability of each technique can be evaluated, and the variability in groundwater–surface water interaction on a fine spatial scale can be investigated. Furthermore, by conducting the study on two rivers in the same catchment, controls on the gaining and losing behaviour of neighbouring rivers can be investigated. Studies that employ multiple techniques for such investigations have been historically less common than research focussed on one or two methods, and can provide additional and more robust information for groundwater–surface water studies (Cox et al., 2007).

Study area

The Tambo and Nicholson rivers occur within the Tambo River Basin (Fig. 1), which has a total surface area of $\sim 4200 \text{ km}^2$. These are perennial rivers that drain southwards from the Eastern Victorian Uplands across the Gippsland Basin to Lake King (a saline coastal lake connected to the Tasman Sea). The lake system is affected by tidal forcing which propagates into the lower sections of both the Nicholson and the Tambo rivers, forming estuarine sections that extend $\sim 15 \text{ km}$ upstream from the lake during low-flow conditions. The river sections do not contain significant tributaries, and minor creeks were not flowing during the sampling campaigns.

Average annual precipitation in the catchment is $\sim 705 \text{ mm}$, increasing from 655 mm in the upper catchment to 777 mm in the mid- to lower reaches. Precipitation is relatively evenly distributed throughout the year, with slightly higher than average monthly rainfall during October to December (Bureau of Meteorology, 2012). Annual evapotranspiration rates decrease from 600 to 700 mm in the upper catchment to 500 to 600 mm in the lower catchment. During the study period, evaporation ranged from $6.7 \times 10^{-3} \text{ m day}^{-1}$ in April 2011 to $3.6 \times 10^{-3} \text{ m day}^{-1}$

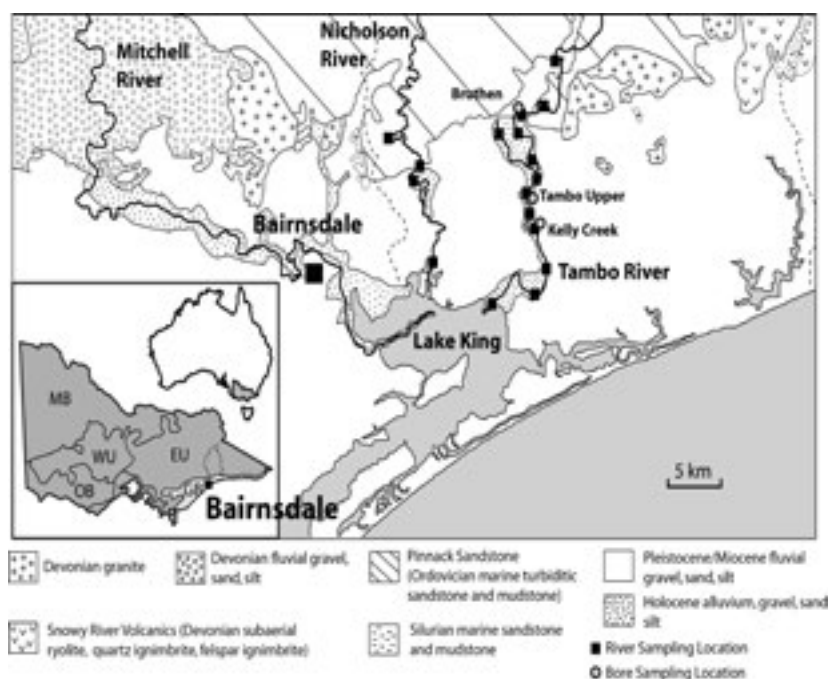


Fig. 1. Map of the Tambo River Basin (dashed line) with sampling locations on Tambo and Nicholson rivers, and local surface geology (modified from Jolly, 1997). GB = Gippsland Basin, EU = Eastern Victorian Uplands, WU = Western Victorian Uplands, OB = Otway Basin, MB = Murray Basin.

during August 2011 (Bureau of Meteorology, 2012). Approximately 80 % of the catchment area is covered by forest and woodland, with the remainder dominated by cattle grazing on river floodplains (Department of Agriculture, Fisheries and Forestry, 2006).

The geology of the northern region of the Tambo River Basin is dominated by Ordovician gneisses and schists and Silurian–Devonian granites that form a fractured rock aquifer (Chaplin, 1995; Jolly, 1997; Vandenberg and Stewart, 1992). The southern section of the basin is dominated by Tertiary sands and gravels (of the Haunted Hills Gravels and Baxter Sandstone) and Quaternary sands, silts, and calcareous sands of the Shepparton Formation (Fig. 1). Various dune/beach deposits, alluvium and colluvium are locally present with the Tertiary and Quaternary units. While very little is known about the bedrock aquifers in the area, the Tambo and Nicholson rivers flow through an Upper Tertiary aquifer of sands, gravels and clays in the lower catchment. In the study area, the Upper Tertiary aquifer contains groundwater with a total dissolved solids (TDS) content of 500 to 1000 mg L⁻¹. The aquifer overlies middle and lower Tertiary aquifers that are dominated by calcareous sands, gravels, coal and basalt that contain groundwater with a TDS of 1000 to 3000 mg L⁻¹.

2 Methods

2.1 River surveys and flow gauging

River discharge is measured at Sarsfield on the Nicholson River and at Ramrod Creek and Battens Landing on the Tambo River (Victorian Water Resource Warehouse, 2012). In the absence of runoff, significant tributary inflows or changes in the storage of a river channel, the net groundwater flux to a river (I_N) can be calculated from (Lerner et al., 1990)

$$I_N = Q_d + E - Q_u - P, \quad (1)$$

where Q_d is the river discharge at the downstream site, Q_u is the river discharge at an upstream site, E is direct evaporation and P is direct precipitation (all terms have units of m³ day⁻¹).

The groundwater flux to the Tambo River was calculated using Eq. (1) and the difference in river discharge between Battens Landing and Ramrod Creek flow gauging stations. The difference in the timing of discharge events between the two stations was accounted for by time shifting the discharge of data of the Ramrod Creek gauging station so that discharge events matched (McCallum et al., 2013). When discharge events did not occur during sampling periods (i.e. baseflow conditions), the Ramrod Creek data were time-shifted using the distance between the stations and the river velocity (calculated using the discharge and river width and depth) to calculate the lag time. I_N estimates were based on the discharge

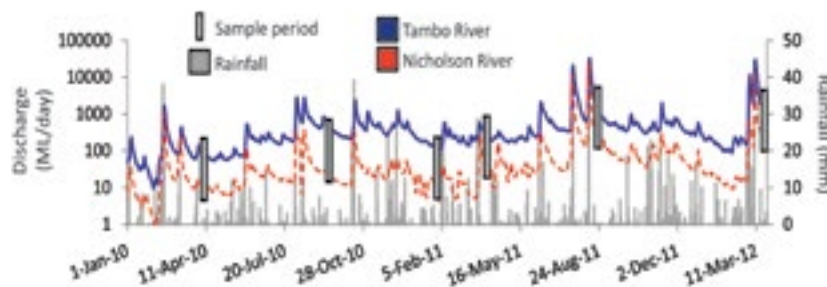


Fig. 2. Sampling frequency superimposed on river hydrographs (Tambo River = Battens Landing station 223209, Nicholson River = Sarsfield gauging station 223210) and rainfall in the Tambo Catchment (Bairnsdale Airport, station 85279).

data for a period of ~ 48 h leading up to and including sampling. Direct evaporation and rainfall were calculated using the surface area of the river and data from the Bairnsdale Airport weather station (Bureau of Meteorology, 2012).

Run-of-the-river continuous surface water EC/temperature surveys were conducted during the February 2011 and March 2012 sampling campaigns using a Schlumberger CTD-Diver and an Aqua TROLL 200 logger with a precision of $\pm 1\%$ (EC) and $\pm 0.1^\circ\text{C}$ (temperature). Elevation and location during the surveys were recorded using a Trimble DGPS with a precision of < 0.02 m. The elevation of bores and the Tambo River adjoining the bores was measured using a Trimble DGPS with a precision of < 0.01 m in February 2011. Elevation of the river in subsequent campaigns was interpolated from river height data at the Battens Landing and Ramrod Creek gauging stations. Groundwater elevations in bores were measured using an electronic water tape during the sampling campaigns. All elevations are reported in metres relative to the Australian Height Datum (AHD). Groundwater–surface water gradients were calculated at Bruthen and Tambo Upper using the measured groundwater elevations of the bore closest to the river and river, with an uncertainty of ± 0.01 m. Gradients were only calculated at Kelly Creek during February 2011 as upstream gauging does not account for the tidal nature of the location and could not be used to interpolate river height in subsequent campaigns. River depth and width in upstream reaches were measured in the field using a tape measure. The width of wider downstream reaches was estimated using Google Earth with an uncertainty of < 1.0 m.

2.2 Sampling

Investigations were carried out between the upper catchment and the coastal plain of the Tambo and Nicholson rivers (Fig. 1). Six sampling campaigns were conducted on a ~ 40 km section of the Tambo River and a ~ 21 km section of the Nicholson River between April 2010 and March 2012. Surface and groundwater sampling took place over a 1- to 2-day period. Sample locations are designated by distance upstream from Lake King. There are 12 sampling locations on the Tambo River and 5 on the Nicholson River. Sampling

in April 2010 was conducted at near-baseflow conditions, while sampling in September 2010 took place during the recession of a minor discharge event (Fig. 2). Sampling in February 2011 occurred during a discharge event, while the April 2011 campaign was conducted during low-flow conditions after a minor discharge event. Sampling campaigns conducted during August 2011 and March 2012 both took place during the recession of major flood events. Groundwater measurement and sampling were conducted in conjunction with river sampling but excluded April 2010 and September 2010 campaigns, as bores were still under construction at these times. Groundwater was sampled at three locations along the Tambo River. Three bores were sampled at Bruthen (28.5 km), two at Tambo Upper (20.2 km) and 1 at Kelly Creek (13.8 km). The bores were installed within 20 m of the river at 6 to 7 m depth below surface, with screened sections 1 to 1.5 m in length. Bores were sampled using an impeller pump set at the screened section, and at least 3 bore volumes were pumped before samples were collected.

2.3 Sample preparation and analysis

EC was measured in the field using a calibrated TPS pH/EC meter. Water samples were preserved in the field by refrigeration in air-tight polyethylene bottles. Anion concentrations were measured on samples that were filtered through $0.45\ \mu\text{m}$ cellulose nitrate filters using a Metrohm ion chromatograph at Monash University, Clayton; precision estimated by replicate analysis is $\pm 2\%$. Cation concentrations were measured on filtered samples that were acidified to $\text{pH} < 2$ using twice-distilled 16 M nitric acid by a Varian Vista ICP-AES (inductively coupled plasma–atomic emission spectroscopy) at the Australian National University or at Monash University, Clayton, using a Thermo Finnigan X series II, quadrupole ICP-MS. Drift during ICP-MS (inductively coupled plasma–mass spectroscopy) analysis was corrected using internal Sc, Y, In and Bi standards, and replicate analyses indicate a precision of $\pm 5\%$. The activity of ^{222}Rn in water samples was measured using a RAD-7 radon-in-air detector by the method outlined in Burnett and Dulaiova (2006) and is reported in Bq m^{-3} . ^{222}Rn was degassed from 500 mL of water for 5 min into an air-tight loop of a known volume. Total counting

times were 2 h for surface water and 40 min for groundwater. Uncertainties based on 4 replicates are less than 15 % for ^{222}Rn activities below 1000 Bq m^{-3} and less than 5 % for ^{222}Rn activities above 1000 Bq m^{-3} . Streambed sediments were sampled at Tambo Upper on the Tambo River for ^{222}Rn ingrowth experiments. Four sediment samples of approximately 1.45 kg were allowed to equilibrate with $\sim 500 \text{ mL}$ of ^{226}Ra free water for 8 weeks in air-tight bottles, before 150 mL of water was sampled for ^{222}Rn analysis using the methods outlined above.

2.4 Mass balance calculations

Assuming that both the concentration of ^{222}Rn in the atmosphere and the ingrowth of ^{222}Rn in river water through the decay of ^{226}Ra in suspended sediment are negligible (Cook et al., 2006; Mullinger et al., 2007), the inflow of groundwater along a reach (I in $\text{m}^3 \text{ m}^{-1} \text{ day}^{-1}$) may be calculated from changes in ^{222}Rn activity in the river c_r (Bq m^{-3}) with distance x (m) by (Cartwright et al., 2011; Cook et al., 2006)

$$I = \left(Q \frac{dc_r}{dx} - w E c_r - F_h + k d w c_r + \lambda d w c_r \right) / (c_i - c_r), \quad (2)$$

where Q is river discharge ($\text{m}^3 \text{ day}^{-1}$), w is stream width (m), E is the evaporation rate (m day^{-1}), F_h is the flux of ^{222}Rn from the hyporheic zone ($\text{Bq m}^{-1} \text{ day}^{-1}$), k is the gas transfer constant (day^{-1}), d is river depth (m), λ is the radon decay constant (0.181 day^{-1}) and c_i is the activity of ^{222}Rn in groundwater (Bq m^{-3}). The hyporheic zone can be defined as the part of the surface aquifer adjacent to the river that exchanges water with the river over relatively short distances (centimetres to tens of centimetres) on timescales of seconds to days (Boano et al., 2007; Kasahara and Wondzell, 2003). The flux of ^{222}Rn from the hyporheic zone can be represented by (Cook et al., 2006)

$$F_h = q_h (c_h - c_r), \quad (3)$$

where q_h is the volumetric flux of water in and out of the hyporheic zone in $\text{m}^3 \text{ day}^{-1}$ (yielding a net flux of $0 \text{ m}^3 \text{ day}^{-1}$ to the river) and c_h is the activity of ^{222}Rn in the hyporheic zone (assuming a single well-mixed reservoir). While c_h is simple to measure in the field, calculating q_h has historically been solved by conducting in-stream tracer injections and modelling breakthrough curves (Runkel, 1998; Wagner and Harvey, 1997), which can be logistically difficult in large river systems. The flux of ^{222}Rn from the hyporheic zone can alternatively be estimated from river stretches that are not receiving groundwater input where there is little change in ^{222}Rn activity (Cartwright et al., 2011). If $dc_r/dx = 0$ and $I = 0$, F_h may be estimated from Eq. (2) as

$$F_h = k d w c_r + \lambda d w c_r - w E c_r. \quad (4)$$

While the degassing of ^{222}Rn to the atmosphere is controlled by wind-driven turbulence in oceans, lakes and estuaries, it has been shown that degassing in upstream rivers

is driven by river flow velocity, depth and width (Genereux and Hemond, 1992). As such, gas transfer rates (k) were estimated using the O'Connor and Dobbins (1958) and Negulescu and Rojanski (1969) gas transfer models as modified by Genereux and Hemond (1992) and Mullinger et al. (2007):

$$k = 9.301 \times 10^{-3} \left(\frac{v^{0.5}}{d^{1.5}} \right) \quad (5)$$

and

$$k = 4.87 \times 10^{-4} \left(\frac{v}{d} \right)^{0.85}, \quad (6)$$

where d is river depth (m) and v is stream velocity (m day^{-1}) calculated from discharge, depth and width data.

A similar mass balance approach may also be used to estimate groundwater inflows from changes in the concentration of major ions, such as Cl. For a conservative ion such as Cl, mass balance calculations are simplified as decay, degassing and hyporheic flux terms are redundant. Thus Eq. (2) reduces to

$$I = \left(Q \frac{dCl_r}{dx} - w E Cl_r \right) / (Cl_i - Cl_r), \quad (7)$$

where Cl_i and Cl_r are the concentrations of Cl in the groundwater and river, respectively.

3 Results

3.1 ^{222}Rn activities

Figure 3 shows the ^{222}Rn activities from all sampling campaigns on the Tambo River. These range from 52 to 604 Bq m^{-3} and show significant spatial and temporal variation. Average ^{222}Rn activities were highest for the Tambo River during August 2011 ($380 \pm 62 \text{ Bq m}^{-3}$) and lowest during April 2011 ($160 \pm 50 \text{ Bq m}^{-3}$). ^{222}Rn activities were generally higher at 28.5, 16.2 and 13.8 km compared to other locations with average activities of 302 ± 51 , 288 ± 51 and $326 \pm 37 \text{ Bq m}^{-3}$, respectively. ^{222}Rn activities were generally lower at 20.0 and 1.8 km, with average ^{222}Rn activities of $184 \pm 52 \text{ Bq m}^{-3}$ and $105 \pm 37 \text{ Bq m}^{-3}$, respectively. ^{222}Rn activities in the Nicholson River were generally lower than those in the Tambo River, with 16 of the 27 samples yielding activities below 120 Bq m^{-3} . During April and September 2010, ^{222}Rn activities in the Nicholson River were $< 100 \text{ Bq m}^{-3}$ at all sites except 13.6 km, which had activities of 370 and 734 Bq m^{-3} , respectively (Fig. 4). In February 2011 activities were $< 200 \text{ Bq m}^{-3}$ for all sites except at 3.2 km, which had an activity of 856 Bq m^{-3} . Activities varied little during April 2011, with all activities below 120 Bq m^{-3} . In August 2011 and March 2012, activities were $< 200 \text{ Bq m}^{-3}$ at all sites except the uppermost sample point (21.2 km), in which activities were 891 and 292 Bq m^{-3} , respectively.

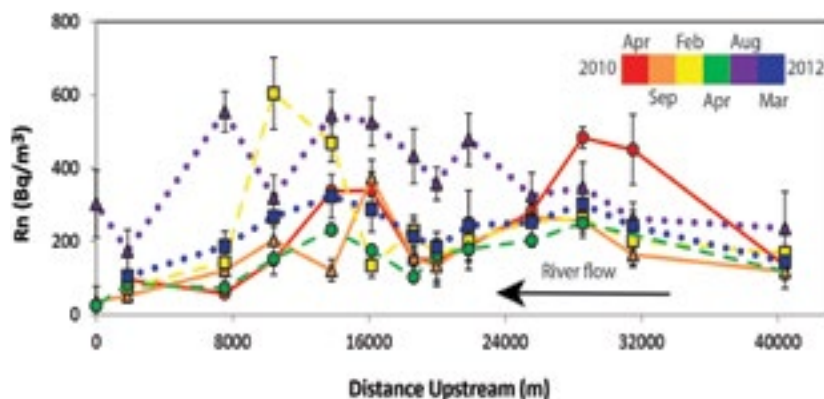


Fig. 3. Distribution of ^{222}Rn activities in water sampled from the Tambo River over the study period. April 2010=solid line with circles, September 2010=solid line with triangles, February 2011=dashed line with squares, April 2011=dashed lines with circles, August 2011=dotted line with triangles, March 2012=dotted line with squares.

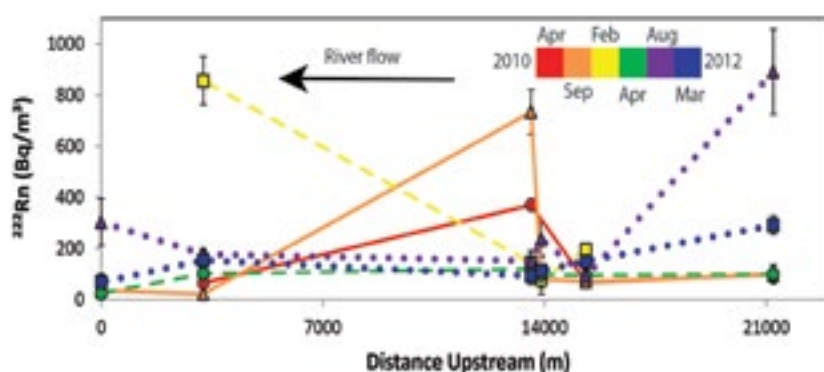


Fig. 4. Distribution of ^{222}Rn activities in water sampled from the Nicholson River over the study period. April 2010=solid line with circles, September 2010=solid line with triangles, February 2011=dashed line with squares, April 2011=dashed lines with circles, August 2011=dotted line with triangles, March 2012=dotted line with squares.

Groundwater ^{222}Rn activities at Bruthen ranged from 2380 to 9130 Bq m^{-3} , with an average activity of $5000 \pm 2340 \text{ Bq m}^{-3}$ over the study period. Average activities at this site were generally higher in February and April 2011 (4620 ± 2750 and $5160 \pm 1970 \text{ Bq m}^{-3}$) and lower during August 2011 and March 2012 (3100 ± 570 and $2150 \pm 440 \text{ Bq m}^{-3}$). Groundwater activities at Tambo Upper were generally lower than at Bruthen, with average activities at the site ranging from $1500 \pm 170 \text{ Bq m}^{-3}$ in March 2012 to $2290 \pm 2770 \text{ Bq m}^{-3}$ in February 2011. Activities at this site were also highly variable, ranging from 330 to 4240 Bq m^{-3} over the study period. Groundwater activities at Kelly Creek were the highest of any site, with an average activity of $8740 \pm 3550 \text{ Bq m}^{-3}$, ranging from 13480 Bq m^{-3} in August 2011 to 5220 Bq m^{-3} in March 2012. The activity of ^{222}Rn in water equilibrated with streambed sediments ranged from 1900 to 3740 Bq m^{-3} , with an average activity of $2640 \pm 880 \text{ Bq m}^{-3}$ (Table 1). This is within the range of the average ^{222}Rn activities of groundwater at Bruthen and Tambo Upper (2320 to 4600 Bq m^{-3}).

Table 1. Activity of water equilibrated with streambed sediments in four samples.

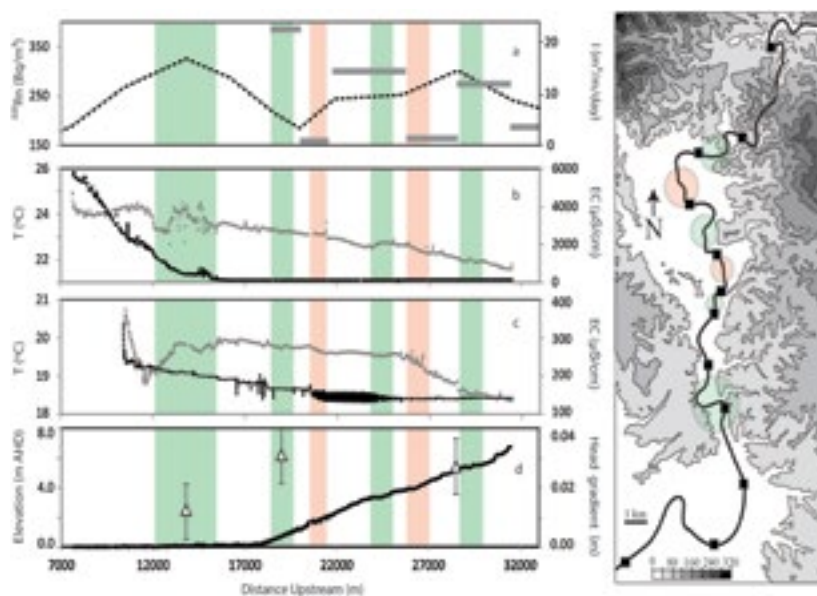
Sample	^{222}Rn	Test 1	Test 2	Test 3	Test 4	Average	Std. deviation 1σ
1	Bq m^{-3}	2540	2980	3300	3010	2960	310
2	Bq m^{-3}	1230	2230	2600	1850	1980	590
3	Bq m^{-3}	1430	2140	1930	2090	1900	320
4	Bq m^{-3}	3170	3830	3970	3990	3740	390

3.2 River gauging and water elevation

The parameters used to calculate net groundwater fluxes I_N using Eq. (1) are listed in Table 2. The discharge of the Tambo River at the Battens Landing station varied by up to two orders of magnitude during the study, ranging from $6.6 \times 10^4 \text{ m}^3 \text{ day}^{-1}$ in April 2010 to $7.9 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ in August 2011. Direct rainfall to the river for the 48 hr period leading up to and including sampling/analysis ranged from 0 to $4093 \text{ m}^3 \text{ day}^{-1}$. Direct evaporative losses for the same periods were on a similar order of magnitude as

Table 2. Parameters used for calculating the net groundwater flux (I) by differential flow gauging using Eq. (1).

Parameter	10 Apr	10 Sep	11 Feb	11 Apr	11 Aug	12 Mar
Q_u (m ³ day ⁻¹)	60 473	305 115	152 516	188 493	7 328 592	1 249 945
Q_d (m ³ day ⁻¹)	65 978	354 034	178 316	201 032	7 869 027	1 393 043
P (m ³ day ⁻¹)	238	0	4093	3378	119	40
E (m ³ day ⁻¹)	1033	1073	1974	636	636	1788
I_N (m ³ day ⁻¹)	6300	49 992	23 681	9797	540 952	144 846

**Fig. 5.** Inferred zones of increased groundwater discharge (green shading) and decreased groundwater discharge (red shading) on the Tambo River as indicated by (a) average ^{222}Rn activities (dashed line) and average groundwater fluxes by ^{222}Rn mass balance (grey bars), temperature (grey dots) and EC (black dots) profiles from February 2011 (b) and March 2012 (c), average groundwater–surface water gradients (triangles) surface water elevation (black line) (d), and local topography (e).

rainfall, ranging from 636 to 1974 m³ day⁻¹ and averaging 1190 m³ day⁻¹.

River elevation during the February 2011 survey decreased from 6.66 to −0.15 m between 31.5 and 18.1 km with a slope of ~ 0.46 m km⁻¹. River slope increased to 1.1 m km⁻¹ between 30.5 and 30.0 km and to 0.79 m km⁻¹ between 29.5 and 29.2 km, but decreased to 0.2 m km⁻¹ between 24.7 and 23.7 km before levelling out to -0.01 ± 0.06 m downstream of 18.1 km. Groundwater elevations neighbouring the Tambo River were the highest in August 2011, ranging from 8.86 m at Bruthen to 3.63 m at Kelly Creek. Elevations were the lowest in April 2011, ranging from 7.51 m at Bruthen to 3.15 m at Kelly Creek. Hydraulic gradients at Bruthen were towards the Tambo River (positive) in all campaigns except August 2011. Hydraulic gradients ranged from −0.018 (August 2011) to 0.112 (March 2012), with an average gradient of 0.027 ± 0.019 (Fig. 5d). Hydraulic gradients at Tambo Upper were towards the river during all campaigns, ranging from 0.001 in August 2011 to 0.075 in March 2012, with an average gradient of 0.033 ± 0.013 . The hydraulic gradient at Kelly Creek in February was 0.013.

3.3 Temperature and EC surveys

Results from the temperature/EC surveys on the Tambo River are illustrated in Fig. 5. The temperature of river water in February increased from 21.6 °C at 31.5 km to 25.0 °C at 7.7 km (Fig. 5b). Groundwater temperatures near the Tambo River at this time were ~ 15.5 °C at Bruthen, increasing to ~ 16.5 °C at Kelly Creek. Temperature increase was generally gradual in the Tambo River between 31.5 and 15.6 km (~ 0.11 °C km⁻¹). River temperature however remained constant at ~ 20.0 °C between 29.9 and 28.7 km. Temperature also remained constant at ~ 23.2 °C between 20.5 and 18.9 km, and declined from 22.8 to 22.5 °C between 24.8 and 24.0 km. Higher rates of temperature increase occurred between 26.6 and 25.8 km (~ 0.5 °C km⁻¹) and between 21.5 and 21.4 km (~ 7 °C km⁻¹). Downstream of 15.6 km the river became estuarine and temperatures more variable, ranging from 23 to 25 °C with a drop in temperature of > 1.0 °C between 13.2 and 11.8 km. River EC values in February ranged from 112 to 9270 $\mu\text{S cm}^{-1}$, with a sharp increase from 120 to 645 $\mu\text{S cm}^{-1}$ between

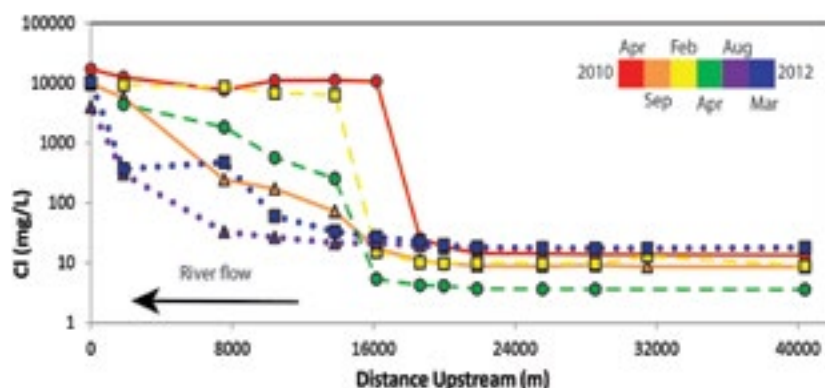


Fig. 6. Distribution of Cl concentrations in water sampled from the Tambo River over the study period. April 2010=solid line with circles, September 2010=solid line with triangles, February 2011=dashed line with squares, April 2011=dashed lines with circles, August 2011=dotted line with triangles, March 2012=dotted line with squares.

16 and 15 km, indicating the mixing of fresh water with estuarine water. ECs changed very little between 31.5 and 15 km (from 114 to $150 \mu\text{S cm}^{-1}$) and increased variably to $> 9270 \mu\text{S cm}^{-1}$ downstream of 15 km. Groundwater EC during February 2011 ranged from 145 to $260 \mu\text{S cm}^{-1}$ at Bruthen, from 2200 to $2400 \mu\text{S cm}^{-1}$ at Tambo Upper and was $7080 \mu\text{S cm}^{-1}$ at Kelly Creek.

Surface and groundwater temperatures were less variable in March 2012, with groundwater increasing from $\sim 15.3^\circ\text{C}$ at Bruthen to $\sim 15.5^\circ\text{C}$ at Kelly Creek and river water ranging from 18.4 to 20.1°C . River temperature remained at $\sim 18.5^\circ\text{C}$ between 30.1 and 29.2 km (Fig. 5c) before increasing irregularly to 19.6°C between 29.2 and 25.5 km. Temperatures then declined to 19.4°C between 25.5 and 24.3 km before stabilising at $19.5 \pm 0.1^\circ\text{C}$ between 24.3 and 21.1 km. River temperature then increased to 19.8°C between 21.1 and 20.3 km before stabilising at $19.8 \pm 0.1^\circ\text{C}$ between 20.3 and 15.8 km. Downstream of 15.8 km temperature increased variably as the river became estuarine, with an initial drop in temperature from 19.8 to 18.8°C between 13.7 and 11.7 km. River EC during March 2012 ranged from 141 to $195 \mu\text{S cm}^{-1}$ between 40.4 and 20.1 km before increasing variably to $338 \mu\text{S cm}^{-1}$ downstream of 16 km. Groundwater EC in March 2012 ranged from 140 to $290 \mu\text{S cm}^{-1}$ at Bruthen, from 1650 to $1850 \mu\text{S cm}^{-1}$ at Tambo Upper and was $3410 \mu\text{S cm}^{-1}$ at Kelly Creek.

3.4 Chloride concentrations

Cl concentrations in the Tambo River follow a similar trend to EC values from EC/temperature surveys (Fig. 6), with lower Cl concentrations increasing gradually in the upstream reaches (between 40.4 and 20.0 km) and more significant increases between 20.0 km and Lake King as the river becomes estuarine. Upstream Cl concentrations were the lowest in April 2011 and the highest in April 2010, with concentration ranges of 3.58 to 4.14 mg L^{-1} and 13.43 to 18.94 mg L^{-1} , respectively. The interface between fresh upstream water and

saline lake water varied considerably in the Tambo River. Under low-flow conditions in April 2010, Cl concentrations increased from 25.5 to 10700 mg L^{-1} between 18.6 and 16.2 km, but under high-flow conditions in August 2011, Cl concentrations were 33.0 mg L^{-1} at 7.5 km and 4030 mg L^{-1} at Lake King. Similar trends were observed on the Nicholson River, with Cl concentrations increasing from 15.1 to 4950 mg L^{-1} between 21.2 and 15.3 km in April 2010, and from 53.2 to 4030 mg L^{-1} between 3.2 km and Lake King in August 2011 (Fig. 7). Upstream Cl concentrations in the Nicholson River were also lower in April 2011 and higher during April 2010, with minimum Cl concentrations of 6.43 and 15.14 mg L^{-1} , respectively.

Cl concentrations in groundwater at Bruthen were the highest during March 2012, with a range of 17.8 to 23.4 mg L^{-1} . Average Cl concentrations at this location were the lowest during April 2011, with a range of 6.75 to 10.3 mg L^{-1} . Concentrations at Tambo Upper were significantly higher than Bruthen, with concentrations ranging between 385 and 599 mg L^{-1} over the study period. Concentrations at Tambo Upper were generally higher in February 2011 ($563 \pm 11.7 \text{ mg L}^{-1}$) and lower in March 2012 ($464 \pm 11.2 \text{ mg L}^{-1}$). Concentrations at Kelly Creek were higher than at Tambo Upper, ranging from 474 mg L^{-1} in April 2011 to 598 mg L^{-1} in March 2012.

3.5 Groundwater fluxes

3.5.1 ^{222}Rn mass balance

Groundwater fluxes were calculated using Eq. (2). River discharge (Q) for the Tambo River was based on interpolation between discharge at the Ramrod Creek (40.4 km) and Batens Landing (20 km) flow gauging stations, while Q for the Nicholson River uses the discharge at the Sarsfield gauging station at 15.3 km. As flow gauging did not occur in the river estuaries where river discharge will vary tidally, groundwater fluxes were not calculated where EC data indicate estuarine

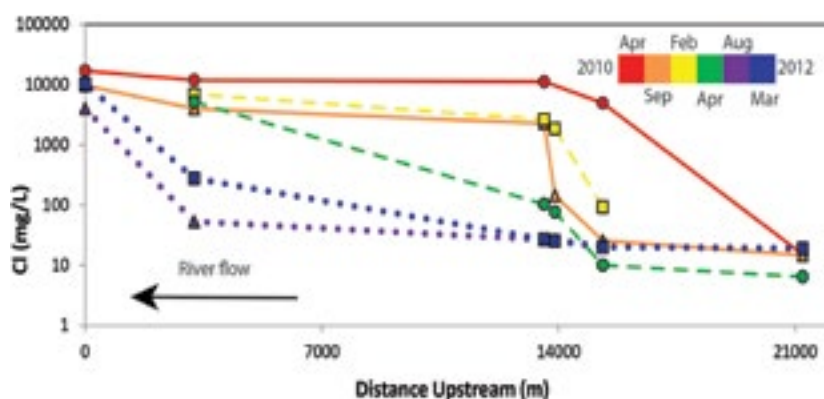


Fig. 7. Distribution of Cl concentrations in water sampled from the Nicholson River over the study period. April 2010=solid line with circles, September 2010=solid line with triangles, February 2011=dashed line with squares, April 2011=dashed lines with circles, August 2011=dotted line with triangles, March 2012=dotted line with squares.

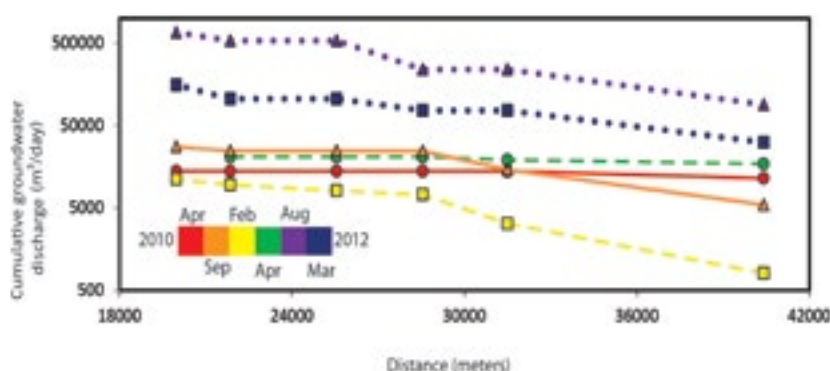


Fig. 8. Cumulative groundwater discharge to the Tambo River from ^{222}Rn mass balance. April 2010=solid line with circles, September 2010=solid line with triangles, February 2011=dashed line with squares, April 2011=dashed lines with circles, August 2011=dotted line with triangles, March 2012=dotted line with squares.

conditions. Calculations are based on the average ^{222}Rn activity of groundwater (C_i) measured in each sampling round at Bruthen and Tambo Upper (total = 5 bores). Groundwater from these bores is located in the upstream reaches for which groundwater fluxes have been calculated and has ^{222}Rn activities that are within 2000 Bq m^{-3} of the average of the sediment ingrowth experiments (Table 1).

Groundwater fluxes for a given reach are calculated using the average depth, width and gas transfer velocities for that reach. The flux of ^{222}Rn from the hyporheic zone (F_h) of the Tambo River is estimated using Eq. (4). Groundwater fluxes (I) of $0 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ were calculated by Cl and ^{222}Rn mass balance between 21.9 and 20.0 km in February 2011 (Figs. 8 and 9). At that time there is little change in ^{222}Rn activities along this stretch of river (i.e. $dc_r/dx \sim 0$). Using $k = 1.16 \text{ day}^{-1}$, $E = 5 \times 10^{-3} \text{ m day}^{-1}$ (Bureau of Meteorology, 2012) and $C_r = 150 \text{ Bq m}^{-3}$ yields $F_h = 5440 \text{ Bq m}^{-1} \text{ day}^{-1}$. A similar calculation was made for the Nicholson River for April 2011. Cl and ^{222}Rn mass balance for the stretch between 13.6 and 3.2 km yielded $I = 0 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$, and again there is little change in ^{222}Rn activities. For $k = 0.1 \text{ m day}^{-1}$, $E = 5 \times 10^{-3} \text{ m day}^{-1}$

and $C_r = 102 \text{ Bq m}^{-3}$, $F_h = 7610 \text{ Bq m}^{-1} \text{ day}^{-1}$. The river morphology and streambed sediment of these sections are representative of the Tambo and Nicholson rivers and likely to accurately represent F_h to the rivers. It is possible however that F_h will vary over time and location as a function of river slope and I . The uncertainties associated with F_h are discussed further in Sect. 4.2.

Total groundwater discharge between 40.4 and 18.6 km on the Tambo River ranged from 9660 to $24\,700 \text{ m}^3 \text{ day}^{-1}$ between April 2010 and April 2011 (Fig. 8). This reflects between 21.4 and 10.5% of river discharge under low-flow conditions (April 2010 and 2011, respectively), and between 6.83 and 7.44% of river discharge under intermediate-flow conditions (September 2010 and February 2011, respectively). Under higher-flow conditions during August 2011 and March 2012, groundwater discharge ranged from $535\,000$ to $105\,000 \text{ m}^3 \text{ day}^{-1}$ (Fig. 8), representing 12.7 and 8.2% of river discharge, respectively. Groundwater fluxes were generally higher, between 31.5 and 28.5 km, in comparison to other reaches. Between April 2010 and April 2011 fluxes to this section ranged from 0 to $3.3 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$, increasing to 50.1 and

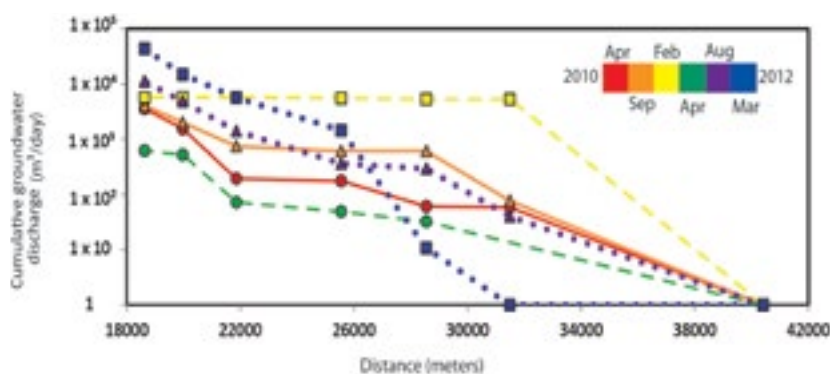


Fig. 9. Cumulative groundwater discharge to the Tambo River from Cl mass balance. April 2010=solid line with circles, September 2010=solid line with triangles, February 2011=dashed line with squares, April 2011=dashed lines with circles, August 2011=dotted line with triangles, March 2012=dotted line with squares.

$15.3 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ during August 2011 and March 2012, respectively. Groundwater fluxes were generally lower between 21.9 and 20.0 km, with fluxes of $0 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ during all periods except February 2011 ($0.78 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$).

Groundwater fluxes were not calculated for the Nicholson River during April 2010 and February 2011 due to tidal forcing in the upper reaches. Total groundwater discharge to the Nicholson River was lower than the Tambo River, ranging from $88.4 \text{ m}^3 \text{ day}^{-1}$ in April 2011 to $32\,900 \text{ m}^3 \text{ day}^{-1}$ in August 2012. Similar to the Tambo River, groundwater reflected a higher proportion of river discharge under low-flow conditions in September 2010 (18.9%), a lower proportion of river discharge under intermediate-flow conditions in April 2011 (< 1%) and an intermediate proportion of river discharge under high-flow conditions in August 2011 and March 2012 (10.9 and 14.9%, respectively).

3.5.2 Cl mass balance

Groundwater fluxes were estimated from Cl concentrations using Eq. (1). Groundwater fluxes were only calculated for the upstream reaches in which estuarine water did not impact Cl concentrations. Cl mass balance calculations for the Tambo River are based on the average Cl concentrations of groundwater from Bruthen and Tambo Upper, which ranged from 228 to 253 mg L^{-1} . For the Nicholson River, Cl mass balance was conducted between 21.2 and 13.5 km for all periods except August 2011. Groundwater sampling near the Nicholson River was not possible; however, the regional groundwater near the Nicholson River has similar TDS concentrations to groundwater at Tambo Upper (Department of Environment and Primary Industries, 2013). Furthermore Cl is the dominant anion in groundwater in this region and its concentration varies regularly with TDS (Victorian Water Resources Data Warehouse, 2012). Thus, the Cl concentrations from Tambo Upper have been used to calculate the fluxes along the Nicholson River.

Groundwater fluxes to the Tambo River from Cl mass balance range from 0 to $4.85 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$. Fluxes were generally higher, between 21.9 and 20.0 km, with an average flux of $1.17 \pm 1.82 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$. Total groundwater discharge was the highest in March 2012 ($14\,800 \text{ m}^3 \text{ day}^{-1}$) and the lowest in April 2011 ($522 \text{ m}^3 \text{ day}^{-1}$) (Fig. 9). Groundwater constituted the highest proportion of river discharge in April 2010 (2.4%) and the lowest under intermediate-flow conditions in September 2010 (0.61%). Groundwater discharge to the Nicholson River was higher during August 2011 ($38\,300 \text{ m}^3 \text{ day}^{-1}$) and September 2011 ($20\,900 \text{ m}^3 \text{ day}^{-1}$), and lower during September 2010 ($4810 \text{ m}^3 \text{ day}^{-1}$) and March 2012 ($3960 \text{ m}^3 \text{ day}^{-1}$). Groundwater discharge represented the highest proportion of river flow under low-flow conditions during September 2010 at 29.4%, compared to high-flow conditions in August 2011 and March 2012 in which groundwater constituted less than 7% of total river discharge.

4 Discussion

This section focusses on combining chemical and physical methods in order to characterise the distribution of gaining and losing reaches along the Tambo and Nicholson rivers. The impact of changing meteorological and hydrological conditions as drivers of groundwater fluxes is also investigated. Finally the discrepancies, strengths and weaknesses of different tracer methods are discussed.

4.1 Spatial variability of groundwater discharge to the Tambo River

As groundwater temperatures near the Tambo River were lower than river temperatures during the temperature surveys, decreases in river temperature are likely to indicate increased groundwater discharge, while increased river temperature is likely to indicate reduced groundwater discharge (e.g. Becker et al., 2004). Temperature along the Tambo

River in both surveys increased steadily between 31.5 and 27.0 km except for a zone at ~ 29 km where water temperature did not increase (Fig. 5), suggesting increased groundwater discharge. Average ^{222}Rn activities at 28.5 km are the second highest ($302 \pm 100 \text{ Bq m}^{-3}$) of any location on the Tambo River, yielding an average groundwater flux of $12.1 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$. Furthermore, groundwater–surface water gradients nearby at Bruthen were towards the river (6.1×10^{-3} to 0.112) during all periods except August 2011, supporting the gaining nature of this stretch. River elevation through this stretch is 5 to 10 m, while land areas within 200 m of the river are over 80 m in elevation (Fig. 5e). Such areas of increased topography will likely result in steep hydraulic gradients towards the river (Sophocleous, 2002) and may account for the higher groundwater fluxes.

A decrease in groundwater discharge between 27.0 and 25.5 km is indicated by a general decline in ^{222}Rn activities (Fig. 3) and an average groundwater flux of $0.89 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ (Fig. 5a). This is supported by an increase in temperature from 22.3 to 22.7 °C between 26.8 and 25.8 km in February 2011, and from 19.1 to 19.6 °C between 26.8 and 25.4 km in March 2012. This stretch of river flows through extensive floodplains that extend for > 2 km from the river (Fig. 5e). Given the subdued topography, it is likely that groundwater head gradients are lower, which will reduce groundwater influxes. A similar trend is observed between ~ 21 and ~ 19 km, where river temperatures increased from 22.9 to 23.6 °C in February 2011, and from 19.5 to 19.8 °C in March 2012, suggesting reduced groundwater discharge (Fig. 5b and c). This is again supported by ^{222}Rn mass balance, which gives an average groundwater flux between 21.9 and 20.2 km of $0.13 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$. This is also an area of low topographic variation, with likely lower head gradients (Fig. 5e).

In contrast to these sections, increased topography near the Tambo River at ~ 25 km correlates with decreased river temperature both in February 2011 (0.3 °C) and March 2012 (0.2 °C), suggesting increased groundwater discharge. The average groundwater flux from ^{222}Rn mass balance between 25.5 and 21.5 km is also relatively high at $14.8 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$. Similarly, the river section between ~ 20 and 19 km is characterised by relatively stable river temperatures and an average groundwater flux of $23.5 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ (between 20 and 18.6 km). These observations support local topographic variation as a driver of groundwater discharge, with reduced groundwater discharge in regions of wider floodplains and increased groundwater discharge in areas of greater topographic variation (Fig. 5e).

Between ~ 16 and 6.5 km, EC values increased to $> 23\,000 \mu\text{S cm}^{-1}$ in February 2011 and $> 300 \mu\text{S cm}^{-1}$ in March 2012, indicating the transition into an estuarine setting. In this zone, mixing with warmer lake water (25 to 30 °C; Arnott and McKinnon, 1985) is expected to cause an increase in river temperature; however river temperature declines between 13.5 and 11.5 km, suggesting a zone of

increased groundwater discharge. Nevertheless, mixing between lake water and river water through the estuarine fringe is not always systematic (e.g. MacKay and Schumann, 1990; Nunes Vaz et al., 1989; Stacey et al., 2008), and the decline in river temperature may be an artefact of measuring different water types as they mix variably through the estuarine fringe. While river discharge is not constrained through this reach preventing mass balance calculations, the average ^{222}Rn activities through this zone are the highest of any location on the Tambo River, supporting an increase in groundwater discharge. At 13.8 km the Tambo River is immediately adjacent to a cliff > 40 m in elevation. This may again facilitate high groundwater gradients toward the river resulting in higher groundwater inputs. While ^{222}Rn activities at 13.8 km were the highest of any sample location on the Tambo River, they were also highly variable (between 135 and 526 Bq m^{-3}). This variability may reflect the transient nature of the interface between river water and lake water as they mix under tidally driven flow conditions. Furthermore, changing river flow in estuaries over tidal cycles may affect the balance of ^{222}Rn at the estuarine fringe (Santos et al., 2010). Constraining such balances requires further work and is beyond the scope of this paper. While the tidal nature of the lower river sections prevents mass balance calculations, a decline in ^{222}Rn activities through these reaches suggests reduced groundwater fluxes in the lower estuaries. Lower topographic variation through these sections (Fig. 5e) will again provide lower potential for the formation of high groundwater gradients. This is consistent with topographic variation as a driver of groundwater discharge to the Tambo River as asserted above.

4.2 Uncertainty analysis

The impact of uncertainties in k on groundwater discharge estimates using ^{222}Rn mass balance calculations was investigated by comparing alternate k values from Eqs. (5) and (6). The Negulescu and Rojanski model generally yields higher k values (and hence results in higher calculated groundwater fluxes) than the O'Connor and Dobbins (1958) model, although this is reversed at low velocities and shallow depths (Fig. 10). This is demonstrated by the cumulative groundwater discharge estimates to the Tambo River, which were higher using Eq. (5) under low-flow conditions during April 2010 and February 2011, but lower during higher-flow conditions from other sampling periods. Systematic trends in k values under changing flow conditions are less apparent on the Nicholson River, as river velocity is less variable and changes in river width and depth downstream have a greater impact on the k values. The difference in the cumulative groundwater discharge to the Nicholson River calculated using Eqs. (5) and (6) ranged from 3.1 to 44 % with an average difference of 20 ± 17 %. For the Tambo River these differences ranged from 2.5 to 48 % with an average difference of 30 ± 16 %. The variability in k is recognised as a source of

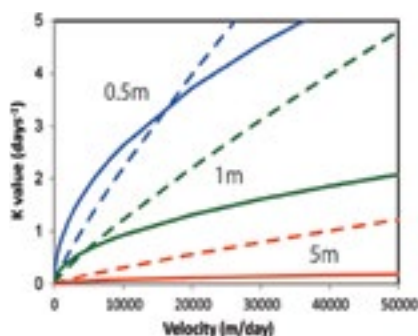


Fig. 10. K values from O'Connor and Dobbins (1958) (solid lines) and Negulescu and Rohanski (1969) (dashed lines) models at 0.5 m (blue), 1 m (green) and 5 m depth (red) with increasing river velocities.

error in ^{222}Rn mass balance calculations; however changes to k have little impact on the distribution of gaining reaches or seasonal trends in groundwater discharge identified by ^{222}Rn mass balance (Fig. 11).

For both the Tambo and Nicholson rivers, F_h estimates were made when dc/dx was 0 (within 1 SD of the equipment precision). As the activity of ^{222}Rn in the Tambo and Nicholson rivers is relatively low, failure to account for F_h will result in overestimations during groundwater flux calculations. On average, failure to account for F_h on the Tambo River resulted in a 104 % increase in groundwater discharge. Excluding April 2011, failure to account for F_h on the Nicholson River results in an average increase in the estimated groundwater discharge by 45 %. As ^{222}Rn activities in the Nicholson are particularly low ($< 120 \text{ Bq m}^{-3}$) at all locations during April 2011, failure to account for F_h at this time results in nearly a 630 % increase in the groundwater discharge estimate. This illustrates the need to account for F_h in streams with lower ^{222}Rn activities where the dc_r/dx term in Eq. (2) is small (cf. Cook et al., 2006).

The variability of C_i represents the greatest source of uncertainty in ^{222}Rn mass balance calculations as C_i values varied by up to 3 orders of magnitude at different locations. As $C_i \gg C_r$ during all sampling periods, a 50 % change in C_i will result in an approximately 50 % change in I . The sensitivity of the model to C_i is demonstrated by calculating I at one standard deviation from the average C_i values used during mass balance calculations. For example, during February 2011 when C_i was the most varied ($4600 \pm 2750 \text{ Bq m}^{-3}$), groundwater discharge to the Tambo River will range from 5860 to $25\,800 \text{ m}^3 \text{ day}^{-1}$ based on C_i values one standard deviation from the mean. This demonstrates the need to accurately assign groundwater end member values. The variability of ^{222}Rn activity in groundwater remains a source of uncertainty when conducting groundwater studies, and further research in characterising such variability both spatially and temporally would be useful to subsequent studies.

The sensitivity of the Cl mass balance model to Cl_i on the Tambo River was tested by assuming the Cl_i end member was a mixture between groundwater from Bruthen and Tambo Upper, and then varying the weighting between each location. Using Tambo Upper concentrations as the end member reduced groundwater discharge estimates for the stretch by between 39 and 40 % during individual sampling periods. Estimates using the Bruthen concentrations as the end member increased estimates by 2 to 4 orders of magnitude during September 2010, February 2011, April 2011 and March 2012 and reduced estimates to 0 during April 2010 and August 2011 periods. Cl_i again represents the greatest source of uncertainty in mass balance calculations given that values vary by up to 3 orders of magnitude between Bruthen and Tambo Upper. Furthermore, C_i is generally similar to C_r in upstream reaches, making Cl mass balance calculations very sensitive to variations in C_i as opposed to ^{222}Rn mass balance calculations where $C_i \gg C_r$. This again highlights the need for accurate characterisation of groundwater end members.

4.3 Method comparison

While similar temporal trends in groundwater discharge to the Tambo River (i.e. increased groundwater discharge under high-flow conditions) were identified by differential flow gauging, Cl mass balance and ^{222}Rn mass balance, estimates from Cl mass balance were generally 1 to 2 orders of magnitude lower than those from ^{222}Rn mass balance or differential flow gauging (Fig. 12). It is likely that some discrepancies between the tracer methods result from uncertainties in groundwater end member characterisation, and the sensitivity of the mass balance models to this parameter. It has been shown that interaction between groundwater and surface water near rivers is likely to increase the variability of groundwater chemistry near rivers, making accurate characterisation of the groundwater end member difficult (Lambs, 2004; McCallum et al., 2010). For example, infiltration of river water into the banks at high river discharges may result in near-river groundwater having lower Cl concentrations than the regional groundwater. This would result in the fluxes from Cl mass balance being too low (McCallum et al., 2012). Bank infiltration will vary as a function of river morphology, aquifer characteristics and changing flow conditions (Chen and Chen, 2003; Chen et al., 2006; Lambs, 2004; McCallum et al., 2010; Woessner, 2000) and is difficult to characterise accurately. While this study sampled near-river groundwater, it is possible that the near-river groundwater along the Tambo River has variable Cl concentrations, resulting in a level of uncertainty in the characterisation of groundwater end members.

Discrepancies between the Cl and ^{222}Rn mass balances may also reflect the discharge of relatively young groundwater that has been stored for a period of weeks, either as recently infiltrated rainfall, bank return flow or parafluvial flow

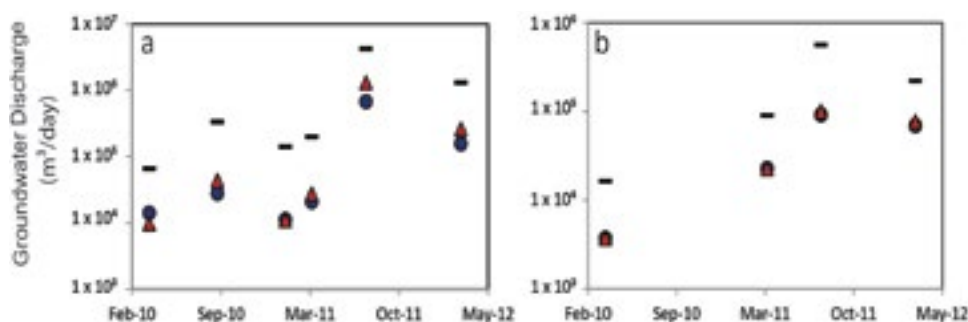


Fig. 11. Temporal variations in river discharge (black lines) and groundwater discharge to the Tambo River (a) and Nicholson River (b) given by ^{222}Rn mass balance using O'Connor and Dobbins (1958) (blue circles) and Negulescu and Rojanski (1969) (red triangles) models of gas transfer.

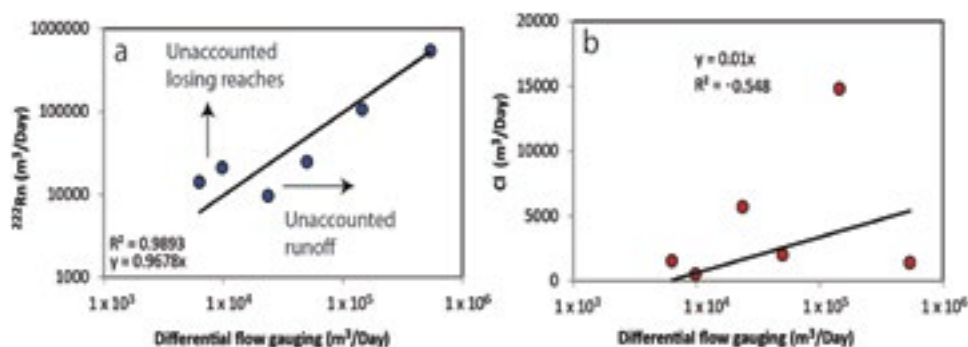


Fig. 12. Groundwater discharge to the Tambo River by differential flow gauging (x axis) versus groundwater discharge given by ^{222}Rn mass balance (a) and Cl mass balance (b).

(McCallum et al., 2010; Woessner, 2000). Chemically, such groundwater would have low Cl concentrations but elevated ^{222}Rn activities through ingrowth (Cartwright et al., 2011). Cook (2012) makes the point that variations in groundwater Cl concentrations will be greater than ^{222}Rn activities as a function of such processes. Under these conditions, groundwater estimates from ^{222}Rn mass balance will more closely reflect the total volume of groundwater entering the river, whereas Cl mass balance will more closely reflect the volume of regional groundwater entering the river. This may account for the agreement between groundwater inflows from differential flow gauging and ^{222}Rn mass balance but the poor agreement between differential flow gauging and Cl mass balance (Fig. 12).

While there is a strong correlation between groundwater discharge estimates from ^{222}Rn mass balance and differential flow gauging, estimates from ^{222}Rn mass balance are greater than those from differential flow gauging during April 2010 and April 2011 (Fig. 12). As ^{222}Rn mass balance will account for the total groundwater discharge, compared to differential flow gauging which accounts for the net groundwater discharge (inflow–outflow), this discrepancy may result from the presence of losing reaches. Sampling during April 2010 and April 2011 occurred after dry periods when the water table was low and losing reaches are more likely to develop (Fig. 13a). In contrast, groundwater discharge

estimates during February 2011 given by differential flow gauging were greater than ^{222}Rn mass balance. This discrepancy is likely to reflect unaccounted runoff during increased rainfall in the catchment in the days leading up to sampling (Fig. 13b).

In contrast to the Tambo River, Cl and ^{222}Rn mass balance give groundwater discharge estimates generally on the same order of magnitude for the Nicholson River, with discharge by Cl mass balance ranging from 654 to 38 300 $\text{m}^3 \text{ day}^{-1}$ and discharge by ^{222}Rn mass balance ranging from 88.4 to 61 100 $\text{m}^3 \text{ day}^{-1}$. While groundwater near the Tambo River was used to characterise groundwater entering the Nicholson River, these results suggest that the groundwater end members used for mass balance calculations on the Nicholson River may reasonably characterise the groundwater entering the Nicholson River. It also implies that groundwater–surface water interaction along the Nicholson River is less variable than the Tambo River. Under such conditions, uncertainties associated with groundwater characterisation will be reduced.

These results not only highlight the importance of accurately characterising groundwater chemistry for mass balance calculations, but also emphasise the need for groundwater characterisation both regionally and at a high spatial resolution proximal to river systems. This is because near-river groundwater (which is the water that enters rivers) may

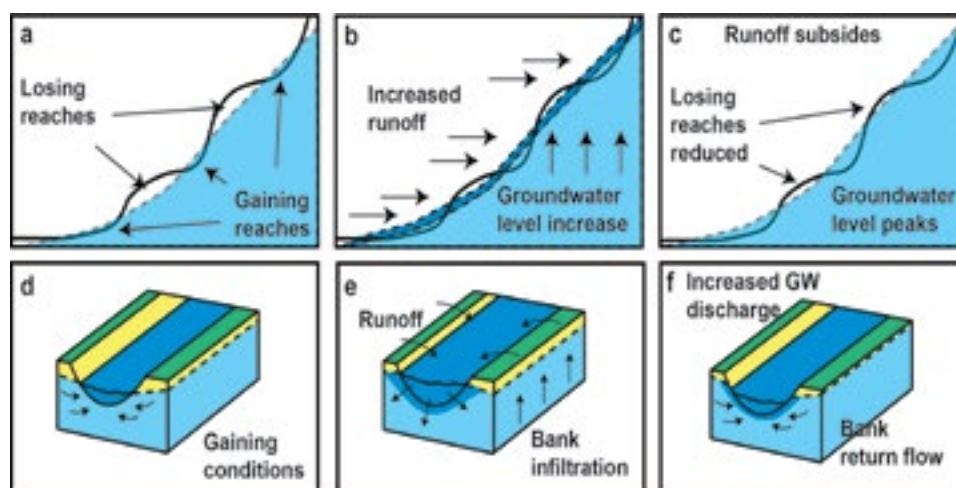


Fig. 13. Schematic representation of the Tambo River profile (solid line), water table (dashed line/light blue shading) and runoff (dark blue shading) under baseflow conditions (a), high-flow conditions (b) and receding conditions (c). River cross sections shown in (d), (e) and (f) for baseflow, high flow and recession, respectively.

have a different and more variable chemistry than regional groundwater.

4.4 Hydrological drivers

Groundwater discharge to both the Tambo and Nicholson rivers increased with river discharge. Sampling during high-flow periods occurred in the days to weeks following peak-flow conditions and is likely to reflect a period in which river discharge is receding while groundwater levels remain high from recharge. Under these conditions high groundwater gradients can form, resulting in increased groundwater discharge (Fig. 13c and f). These results indicate that during high rainfall periods, groundwater levels in the Tambo Catchment can increase quickly enough to maintain a groundwater fraction of $\sim 10\%$ in the Nicholson and Tambo rivers around 1 week after flooding (e.g. Cey et al., 1998). This indicates that the sand-rich Tertiary and Quaternary aquifers of the region are responsive to rainfall.

While the total groundwater discharge to the Tambo and Nicholson rivers was highest under high-flow conditions, groundwater constituted the highest proportion of river flow under low-flow conditions (Fig. 13a and d). For the Tambo River this occurred during April 2010, with groundwater discharge by ^{222}Rn mass balance representing 21.4% of total river flow. For the Nicholson River, this occurred during September 2010, with groundwater discharge by ^{222}Rn mass balance constituting 18.9% of river flow. Conversely, groundwater constituted the lowest proportion of river flow under intermediate-flow conditions. This occurred during February 2011 on the Tambo River, with groundwater discharge by ^{222}Rn mass balance constituting 6.8% of river discharge. For the Nicholson River this occurred during April 2011, with groundwater discharge by ^{222}Rn mass balance constituting $< 1\%$ of river discharge. Both of these

sampling campaigns took place during a time of increased rainfall (~ 35 mm of rainfall in the 4 days leading up to sampling) that followed an extended dry period. As such, it is likely that these periods represent conditions in which the water table was still low while river levels were increasing due to runoff, which would result in reduced groundwater discharge (Fig. 13b and e).

This study shows that, while two rivers within the same aquifer system may vary considerably with respect to discharge volumes, groundwater may still represent a similar proportion of the total river discharge in each case. Further to this, when two rivers occur in the same aquifer system, they are likely to respond similarly under changing rainfall and flow conditions – with relatively low volumes of groundwater providing a high proportion of river discharge under base-flow conditions, rainfall and runoff providing a higher proportion of river discharge during increased rainfall following dry periods, and higher volumes of groundwater representing an intermediate proportion of river flow in the weeks following extensive rainfall in the catchment. This suggests that the lower discharge volumes associated with the Nicholson River are likely to represent the smaller catchment area from which its flow is derived, as opposed to differences in groundwater–surface water interaction.

5 Conclusions

By combining the use of chemical and physical tracer methods on the Tambo River, increased groundwater influxes were identified near areas of increased topographic variation, where the potential for higher groundwater–surface water gradient formation is increased. The highest volume of groundwater discharge occurred in the days to weeks following heavy rainfall, when river levels were receding and

groundwater levels remained high. Groundwater formed the highest proportion of river discharge under baseflow conditions, while rainfall and runoff formed a higher proportion of river flow during periods of increased rainfall that followed from dry periods in the catchment. Discrepancies between ^{222}Rn and Cl mass balance suggest that spatially variable bank exchange processes can amplify the heterogeneity of Cl in groundwater-neighbouring rivers, while the equilibration between ^{222}Rn in aquifer sediments with groundwater can reduce the heterogeneity of ^{222}Rn in groundwater. Under these circumstances, extensive spatial groundwater sampling is required to accurately characterise the groundwater Cl end member. The impact of water exchange between rivers and groundwater on tracers at the bank scale is a process that is still poorly defined, and further investigation into these processes may prove particularly useful in the interpretation of tracer data during future groundwater–surface water studies.

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Appendix B
