MONASH University

Transit Times of Water and Solutes in the Barwon River and Otway Catchments of Southeast Australia

William D. Howcroft

B.Sc. Geology, M.Sc. Geography

A thesis submitted for the degree of *Doctor of Philosophy* at
Monash University in 2018

School of Earth, Atmosphere and Environment

Copyright notice

© *William D. Howcroft (2018)*

I certify that I have made all reasonable efforts to secure copyright permissions for third-party content included in this thesis and have not knowingly added copyright content to my work without the owner's permission.

Abstract

This thesis examines the residence times of water and solutes in the Barwon River and Otway Catchments of Southeast Australia using stable (^{2}H, ^{18}O, ^{13}C) and radioactive (^{3}H, ^{14}C, ^{36}Cl) isotopes, major ion geochemistry, river discharge and water quality data, lumped parameter models (LPMs), catchment attributes and groundwater levels. In a relatively water-scarce region such as this, groundwater and surface water are vitally important resources and, without which, the local economy and natural environment would struggle to survive. This thesis focuses on three main research topics: 1) differences in groundwater and chloride residence times, and the age and origins of highly saline groundwater in the Barwon River Catchment, 2) mean transit times (MTTs) of water in headwater streams within the Otway Ranges, and the uncertainty associated with those MTTs, and 3) the residence times of bank storage and return flow and its influence on water chemistry in the upper Barwon River.

Key conclusions from the first study are that the mean residence times (MRTs) of groundwater within the shallow basalt aquifer in the Barwon River Catchment are up to ~20 ka. However, there is considerable uncertainty in these MRTs, depending on which model is employed to estimate the MRTs, the possibility of carbonate dissolution, and uncertainty in the ^{14}C activity of recharge. Furthermore, chloride residence times are often greater than the groundwater in which it is contained, due to the recycling of chloride within Lake Murdeduke and other regional saline lakes. This finding has broad applications to the use of the widely employed chloride mass balance method of estimating groundwater recharge. Lastly, the elevated groundwater salinity in the region is primarily due to the recycling of solutes in the area's saline lakes with only minor contributions from weathering of halite, silicate and calcite minerals.

The key conclusions from the second study are that mean transit times (MTTs) in six headwater streams in the Otways Catchments vary from approximately 7 to 230 years, which is significantly older than that found in many other headwater streams globally. This difference is likely due to low groundwater recharge in the region and a lack of significant near-river sediments, which would otherwise act to store and later transmit water to the streams during dry times of the year.

As with the first study, the MTTs are subject to considerable uncertainty depending on the LPM employed, the possibility of aggregation error, and uncertainty in the ^{3}H activity in rainfall.

In the third study, key findings are that bank storage and return flow has residence times varying from a few weeks to a few months, if not longer. In addition, the water chemistry data suggest that, while groundwater makes a relatively small contribution to total river discharge, it is nevertheless instrumental in determining river water chemistry.

While this thesis focuses on the Barwon River and Otway Catchments of Australia, it is believed that the results and conclusions of this study can be applied to other regions globally.

Declaration

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.

Signature: [redacted]

Print Name: William D. Howcroft

Date: 04/02/2018

Publications during enrolment

Howcroft, W., Cartwright, I., Fifield, L.K. and D. Cendon, 2017. Difference is groundwater and chloride residence times in saline groundwater: the Barwon River Catchment of Southeast Australia. Chemical Geology, Vol. 451, pp 154-168.

Howcroft, W., Cartwright, I. and U. Morgenstern, 2018. Mean catchment times in headwater catchments: Insights from the Otway Ranges. Hydrol. Earth Syst. Sci., Vol. 33, pp. 635-653, doi: 10.5194/hess-22-635-2018.

Thesis including published works declaration

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 two original papers published in peer reviewed journals and one original paper being prepared for submission for publication. The core theme of the thesis concerns the residence times of water and solutes in groundwater and surface water in the Barwon River and Otway Catchments of Southeast, Australia. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the School of Earth, Atmosphere and Environment under the supervision of Dr 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 Chapters 2, 3 and 4, my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status *(published, in press, accepted or returned for revision, submitted)*	Nature and % of student contribution	Co-author name(s) Nature and % of Co-author's contribution*	Co-author(s), Monash student Y/N*
Chapter 2	*Differences in groundwater and chloride residence times in saline groundwater: the Barwon River Catchment of Southeast Australia*	*Published*	*65%. Concept, collection of groundwater and precipitation samples, lab analysis, and writing and revision of research paper*	*1) Ian Cartwright, input into manuscript 20%* *2) L. Keith Fifield, input into manuscript 10%* *3) Dioni Cendon, input into manuscript 5%*	*No* *No* *No*
Chapter 3	*Mean transit times in headwater catchments: Insights from the Otway Ranges, Australia*	*Published*	*70%. Concept, collection of river water samples, lab analysis, and writing and revision of research paper*	*4) Ian Cartwright, input into manuscript 20%* *5) Uwe Morgenstern, input into manuscript 10%*	*No* *No*
Chapter 4	*Bank storage and return flow: residence times and influence on river water chemistry in the upper Barwon River, Australia*	*Not published (In preparation)*	*65%. Concept, collection of river water samples, lab analysis, and writing and revision of research paper*	*6) Ian Cartwright, input into manuscript 25%* *7) Dioni Cendon, input into manuscript 10%*	*No* *No*

I have renumbered section numbers, figure numbers, table numbers and equation numbers of the submitted or published papers in order to generate a consistent presentation within the thesis.

Student signature: [redacted] **Date:** 04/02/2018

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the authors.

Main Supervisor signature: [redacted] **Date:** 03/02/2018

Acknowledgements

This work would not have been possible without the help and contribution of many people over the past few years.

First and foremost, I would like to thank my faculty advisor, Dr Ian Cartwright, for his tireless support, encouragement, instruction, patience, time in the field and in the laboratory together, and for taking me on as his student. I have learned a tremendous amount at Monash University under Dr Cartwright and, for this reason, will be forever grateful.

I would also like to acknowledge the following people for their help in the field, including Wang Dong, Kwadwo Osei-Bonsu and Lei Chu. Without your assistance, I would never have been able to collect the groundwater, river water and precipitation samples, upon which much of this work is based. The field work wasn't always easy, and sometimes involved some very long days, but I really enjoyed our time together in the Otways region and hope that you did as well.

A special thank you goes out to Massimo Raveggi and Rachelle Pearson for their assistance in the laboratory - teaching me how to prep and run the samples and assessing the accuracy, precision and reproducibility of the results. I wasn't always patient but you were always there to help me. Additional thanks go out to the many staff in the School of Earth, Atmosphere and Environment who have assisted me out in so many ways. This includes Sasha Wilson, Roberto Weinberg, Andrew Tomkins, Xuan Zhu, Robert Oakley, Yuzhou Lin, Silvana Cifaratti, Robin Armit, Katie Tran, Emily Tran, Caroline Venn and Junnel Alegado; you've all been incredibly kind and helpful. Hopefully I haven't missed anyone! A deserved thanks is also due to my fellow students and sometimes office-mates – Alex Atkinson, David Moore, and Nasim Kharazizadeh, especially, for your friendship, support, and encouragement.

Last, but certainly not least, I want to give a very special thank you to Wang Dong, my best friend and partner, for her never ending support, encouragement, and patience while I pursued this degree. For a whole lot of reasons, it wasn't always easy but, without your help, I never would have completed this dissertation. You helped me fulfil a dream of mine that I've had for so much of life – thank you so much for everything!

Table of Contents

Chapter 1 Introduction

1.1. Introduction 1
1.2. Objectives 6
1.3. Thesis Structure and Overview of Research 7
1.4. References 9

Chapter 2 Differences in Groundwater and Chloride Residence Times in Saline Groundwater: the Barwon River Catchment of Southeast Australia

2.1. Introduction 15
2.2. Setting 16
2.3. Methods 20
2.3.1. Sampling 20
2.3.2. Analytical Techniques 21
2.3.3. Groundwater Residence Times 25
2.3.4. Chloride Residence Times 25
2.4. Results 26
2.4.1. Groundwater Elevations and Head Gradients 26
2.4.2. Major Ion Geochemistry 29
2.4.2.1. Precipitation 29
2.4.2.2. Lake Murdeduke and Salt Crust 29
2.4.2.3 Groundwater 31
2.4.3. Stable Isotopes ($\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$) 31
2.4.4. Radioisotopes (^{14}C, ^{3}H, ^{36}Cl) 32
2.5 Discussion 37
2.5.1. Groundwater Flow 37
2.5.2. Geochemical Processes 38
2.5.3. Climatic Controls 39
2.5.4. Groundwater Residence Times 40
2.5.5. $R^{36}Cl$ and Chloride Residence Times 45
2.5.6. Chloride Accession Times 47
2.6. Conclusions 48
2.7. Acknowledgements 49
2.8. References 51

Chapter 3 Mean Transit Times in Headwater Streams: Insights from the Otway Ranges, Australia

3.1. Introduction 59
3.1.1. Estimating Mean Transit Times (MTTs) 60
3.1.2. Predicting Mean Transit Times 62
3.2. Objectives 63
3.3. Study Area 63
3.4. Methods 67
3.4.1. Sampling and Streamflow 67
3.4.2. Geochemical Analyses 68
3.4.3. Catchment Attributes 69
3.4.4. Calculating Mean Transit Times 70
3.4.5. Groundwater Volume 72
3.5. Results 72
3.5.1. Streamflow 72
3.5.2. Tritium Activities 75
3.5.3. Major Ion Geochemistry 76
3.6. Discussion 79
3.6.1. Sources of River Inflows 79
3.6.2. Mean Transit Times 80
3.6.3. Uncertainties in MTT Estimates 81
3.6.4. Predicting Mean Transit Times 87
3.7. Summary and Conclusions 89
3.8. Data Availability 91
3.9. Author Contributions 92
3.10. Acknowledgements 92
3.11. References 93

Chapter 4 Bank Storage and Return Flow: Residence Times and Influence on River Water Chemistry in the upper Barwon River, Australia

4.1. Introduction 102
4.1.1. The Importance of Bank Storage and Return Flow 102
4.1.2. Hysteresis 103
4.1.3. Evaluating the Residence Times of Water 104
4.1.4. Objectives 104
4.2. Setting 105
4.3. Methodology 109
4.3.1. River Water and Precipitation Sampling 109
4.3.2. Analytical Techniques 110
4.4. Results 112
4.4.1. River Discharge 112
4.4.2. Major Ion Geochemistry 113
4.4.3. Stable Isotopes ($\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$) 114
4.4.4. Radioisotopes (^{3}H, ^{36}Cl) 115
4.5. Discussion 120
4.5.1. Seasonal Variation in Bank Storage and Return Flow 120
4.5.2. Short Duration Bank Storage and Return Flow 122
4.5.3. Residence Times at Forrest 122
4.5.4. Residence Times of Solutes 125
4.5.5. Controls on River Water Chemistry 126
4.6. Conclusions 127
4.7. Acknowledgements 129
4.8. References 130

Chapter 5 Conclusions

5.1. Key Research Findings 137
5.2. Review of Research Objectives 140
5.3. Broad Implications of Research 143
5.4. Suggestions for Further Study 144

List of Tables (Abbreviated Titles)

Table 2-1.	**Construction details and groundwater levels for monitoring bores**	**23**
Table 2-2.	**Geochemistry results of groundwater, precipitation and Lake Murdeduke water and salt crust**	**27**
Table 2-3.	**Groundwater and chloride residence times**	**43**
Table 2-4.	**Hydraulic conductivity estimates for the New Volcanics basalt**	**45**
Table 3-1.	**Summary of Gellibrand River catchment attributes**	**67**
Table 3-2.	**Summary of Calculated Mean Transit Times**	**82**
Table 3-3.	**Estimates of the Difference between Mean Transit Times**	**86**
Table 4-1.	**Geochemistry of the upper Barwon River and rainfall**	**116**
Tabl3 4-2.	**MTTs (years) at Forrest**	**125**

List of Figures (Abbreviated Titles)

Figure 2-1.	**Map of the Barwon River Catchment near Lake Murdeduke**	**17**
Figure 2-2.	**Geologic cross section through the study area**	**22**
Figure 2-3.	**Geochemistry results**	**30**
Figure 2-4.	**Stable isotope results**	**34**
Figure 2-5.	**a^{14}C in groundwater**	**35**
Figure 2-6.	**Tritium activity as a function of a^{14}C in groundwater**	**36**
Figure 2-7.	**R^{36}Cl as a function of a^{14}C in groundwater**	**36**
Figure 2-8.	**R^{36}Cl in groundwater and precipitation as a function of Cl^{-}**	**37**
Figure 2-9.	**Mean residence times (MRTs) for groundwater**	**42**
Figure 3-1.	**Map of study area**	**65**
Figure 3-2.	**Streamflows at which samples were collected**	**73**
Figure 3-3.	**Hydrographs at timing of sample collection**	**74**

Figure 3-4. ^{3}H activity as a function of streamflow **76**

Figure 3-5. ^{3}H activities as a function of TDS **77**

Figure 3-6. ^{3}H activities as a function of nitrate and sulphate **78**

Figure 3-7. Variation in MTTs for ^{3}H activities **83**

Figure 3-8. MTTs calculated using the EPM Model **84**

Figure 3-9. Impact of varying ^{3}H rainfall inputs **85**

Figure 3-10. ^{3}H activities vs. runoff coefficient for March 2015 samples **88**

Figure 3-11. Variation in MTT as a function of streamflow at Porcupine Creek **89**

Figure 4-1. Map of the study area showing generalised geology **107**

Figure 4-2. Discharge and EC at Kildean, Winchelsea and Inverleigh **111**

Figure 4-3. Piper diagram of river water, precipitation and groundwater **114**

Figure 4-4. Downstream variation in TDS, $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, ^{3}H and $R^{36}Cl$ **118**

Figure 4-5. Stable isotope ratios **119**

Figure 4-6. $R^{36}Cl$ as a function of chloride concentration **120**

Figure 4-7. Normalised EC-discharge hysteresis loops for storm events **124**

Supplement (to Chapter 3)

Chapter 1

Introduction

1.1. Background

Fresh water is one of Earth's most important natural resources and is used extensively for potable water supply, agriculture, industry, and recreation. In addition, its availability is critically important for the health and maintenance of all ecosystems. Yet, at the same time, fresh water is a finite resource. Less than 5% of the total volume of water on Earth is comprised of fresh water (Shiklamanov, 1993; Oki and Kanae, 2006;, Odlare, 2014). Of this, most is locked up in the polar ice caps and as glaciers and, for this reason, is largely unavailable for use. The remainder consists of groundwater and, to a lesser extent, surface water such as rivers and lakes. Once considered to be separate entities, groundwater and surface are now widely viewed as a single resource (Winter et al., 1998). This is because groundwater discharges to surface water and, in some cases, surface water recharges groundwater systems. As interconnected systems, protecting and managing fresh water resources requires detailed understanding of both groundwater and surface water, as well as their interaction.

One measure of groundwater-surface water interaction is the concept of residence time, which is broadly defined as the amount of time that water spends within an aquifer before discharging to ground surface, such as a surface water body or a spring. Understanding the residence times of water is important in a number of ways. For example, groundwater having long residence times may become increasingly impacted by contaminants over time, which may then affect the water quality of the receiving surface water body (Modica et al., 1998). In addition, the residence time of water can be important to groundwater dependent ecosystems, as variations in residence time may affect water salinity, temperature, microbial activity and organic matter decomposition (Boulton and Hancock, 2006). Lastly, increased residence times can result in the attenuation and dispersion of nutrients and other solutes (Kirchner et al., 2000). Evaluating residence times, however, is

not straight forward due to a number of factors, which include hydrogeochemical reactions, recycling of solutes as a result of precipitation and dissolution, climatic factors including evaporation and climate variability, complex geologic environments, and flow paths that vary in both time and space. Nevertheless, determining the residence times of water and the solutes that it contains is critical if fresh water environments are to be protected.

This study focuses primarily on the interaction between groundwater and rivers. Water within a river may be derived from a multitude of potential sources, including groundwater, bank storage and return flow, overland flow, soil water, interflow, and perched aquifers, each of which may have differing residence times. Of these potential inputs, bank storage and return flow is increasingly being viewed as important (e.g. Squillace, 1996; Claxton et al., 2003). Despite this importance, however, relatively little is known about its residence time.

Water within a river system begins its journey when it falls to the earth in the form of precipitation. A portion of that rainfall infiltrates through the ground surface as recharge, travels through the unsaturated (vadose) zone and enters an aquifer system. From there, the water (groundwater) travels to discharge areas such as river, lakes, or springs. The time that it takes for water to travel from the recharge area to a discharge point is known as its transit time. However, because water takes a myriad of pathways along its journey (some long, others short), water sampled from a discharge point will not have a distinct transit time but will instead have a distribution of transit times that can be characterised by its mean or, simply, its mean transit time (MTT). Mean residence time (MRT) is a term that is also used frequently within the scientific literature and refers to the time that groundwater has resided in the aquifers before being sampled. While strictly MRTs should be 50% of the MTT (McDonnell et al., 2010), these terms are commonly used interchangeably.

MTTs and MRTs are commonly evaluated using natural cosmogenic radioactive tracers such as ^{3}H, ^{14}C, and ^{36}Cl (Clark and Fritz 1997), which are present in small but measurable quantities in precipitation. Thus, as rainfall infiltrates into the ground surface, the tracers are carried with it. Once isolated from the atmosphere, the tracers begin to undergo

radioactive decay. With half-lives of 12.32 years (^{3}H), 5,730 years (^{14}C) and 301,000 years (^{36}Cl), these tracers may be used to determine residence times of up to approximately 150 years, 40,000 years, and 1 Ma years, respectively.

In its simplest derivation, the residence time of a water sample collected from a bore, river or spring can be determined from the concentration of a given tracer in the sample, the initial concentration of that tracer in precipitation and the radioactive decay formula (Cook and Herczeg, 2000):

$$t = \frac{1}{\lambda} * \ln \frac{A_0}{A}$$

where t is the residence time, λ is the tracer decay constant, A_0 is the initial concentration of tracer in precipitation, and A is the concentration of the tracer in the sample. Use of the above formula to determine residence times carries a number of important and often invalid assumptions however. Firstly, it is assumed that the initial tracer concentration, A_0, has remained constant over time. Secondly, it assumes that the sampled water has taken a direct flow path from the recharge area to the sampling location with no mixing or dispersion (commonly referred to as "piston flow"). However, neither of these two assumptions generally hold true. For example, during the 1950s and 1960s, above-ground thermonuclear weapons testing released a large amount of radionuclides into the atmosphere, including ^{3}H, ^{14}C, and ^{36}Cl, which were subsequently transported to the Earth's surface with precipitation (the so-called 'bomb-pulse'). Additionally, tracer concentrations in rainfall, ^{14}C in particular, have varied significantly over time (Stuiver, 1961, 1965). Lastly, piston-flow almost never exists in nature, except in the rare cases where dispersion is low, average linear velocity is high, or flow paths are very short (Jurgens et al., 2012). Nonetheless, this approach, particularly in ^{14}C studies, has seen frequent use, e.g. Plummer et al., 2012; Kwicklis and Farnham, 2014.

In recognition of the fact that water does not have a distinct age, but instead has a distribution of ages, residence times are increasingly being estimated through use of Lumped Parameter Models (LPMs), which are mathematical models of fluid transport based

upon idealised aquifer geometries and flow configurations (Maloszewski and Zuber, 1982; 1996). Utilisation of LPMs to determine residence times requires knowledge of the flow system being modelled (to determine the best LPM to employ), the concentration of a tracer within a sample, and the input history of the tracer in precipitation. Residence times are then evaluated by comparing the input history of the tracer in precipitation to the measured concentration of that tracer within the river or in groundwater using the convolution integral (Maloszewski and Zuber, 1982, 1996; Maloszewski et al., 1983):

$$C_0(t) = \int_0^\infty C_i\,(t - \mathrm{T})\; g\;(\mathrm{T}) e^{-\lambda \mathrm{T}} d\mathrm{T}$$

where T is the transit time, t – T is the time that the groundwater entered the flow system, λ is the radioactive decay constant and g (T) is the exit age distribution function, for which closed form analytical solutions have been derived for many LPMs, e.g. Maloszewski and Zuber, 1982, 1996; Kinzelbach et al., 2002.

Two of the most commonly used LPMs in transit time modelling are the Exponential Piston Flow Model (EPM) and the Dispersion Model (McGuire and McDonnell, 2006). The EPM describes aquifers with two segments of flow: a portion with an exponential age distribution and a piston-flow portion. Utilisation of the EPM model requires defining a value for the EPM ratio, which represents the relative contribution of the exponential and piston flow components. In contrast, the DM allows for hydrodynamic dispersion and requires defining a value of the dispersion parameter, D_p, which is the ratio of dispersion to advection.

Use of LPMs to evaluate residence time carries a number of uncertainties, including aggregation error and uncertainty in the tracer input history. Aggregation errors arise when two or more water inputs having different residence time distributions mix (Kirchner, 2016a, 2016b; Stewart et al., 2016). Residence times estimated using geochemical tracers in the mixed (aggregated) water tends to underestimate the actual MTT (i.e. that which would be calculated using the weighted average of each store). This is due to the non-linearity of the tracer input functions and, to my knowledge, has not been quantified in the field. Likewise,

uncertainty in the tracer input history can also lead to error in residence time estimations. Tritium (^{3}H) and ^{14}C activities (concentrations) within rainfall have been measured globally for some decades (IAEA, 2016), including in southeast Australia. However, these measurements are typically limited to specific locations, such as Melbourne. Investigations conducted outside of these locations thus introduces uncertainty in the residence time estimations, as tracer data specific to these regions are generally unavailable. Despite these uncertainties, when used in combination with major ion geochemistry data, groundwater levels and/or river discharge data, LPMs have been successfully used to assess background groundwater quality (e.g. Morgenstern and Daughney, 2012), evaluate sources of water contributing to rivers (e.g. Cartwright and Morgenstern, 2016; Duvert et al., 2016), and assess the role of catchment characteristics, such as runoff, land use, and size on catchment functioning (e.g. Cartwright and Morgenstern, 2015).

The residence times of solutes are more difficult to evaluate. However, if the solute in question behaves conservatively (i.e. it has not been recycled due to precipitation and subsequent dissolution and has not been retarded as a result of isotopic exchange with the rock matrix), then its residence time is generally equivalent to that of the water in which it is contained. Chloride is a solute that is largely viewed as behaving conservatively. In fact, this assumption serves as the basic premise for the widely employed chloride mass balance (CMB) method for estimating groundwater recharge (e.g. Allison and Hughes, 1978; Wood and Sanford, 1995; Scanlon et al., 2006). If chloride was not to behave conservatively, then recharge estimated in this manner will underestimate the true value. In theory, very long chloride residence times can be determined using ^{36}Cl. However, the input history of ^{36}Cl is far less well known. Lastly, solute residence times can also be estimated through computation of their accession time, which is defined as the amount of time required to accumulate a given mass of solute within a known aquifer volume as a result of input by precipitation (only). Estimating residence times in this manner is relatively straightforward as it utilises parameters that are commonly known or which can be reasonably estimated.

However, the solute deposition rate in rainfall must be assumed to have remained constant with time, which may not always hold true.

1.2. Objectives

Using the Barwon River and Otway Catchments of southeast Australia as a study area, the broad objective of this study is to employ residence times as a means of gaining further understanding of river catchment functioning and groundwater-surface water interaction. More specifically, major ion, stable and radioactive isotope geochemistry, river discharge data, and groundwater level data are used to help address the following research questions:

1. Are water and chloride residence time equivalent? If not, this has broad implications for utilisation of the chloride mass balance method for estimating groundwater recharge.
2. What are the sources of water contributing to river discharge? Are these sources the same in headwater streams as they are in lowland rivers?
3. What is the residence time of bank storage and return flow?
4. Are residence times in headwater catchments similar to those of lowland rivers? If not, why?
5. What are the effects of using different models to estimate residence times? Do different models provide different results, how significant are those differences, and when do they occur?

Located in a largely semi-arid region of southeast Australia, the Barwon River and Otway catchments of Victoria suffer from water scarcity. For this reason, the communities within them depend strongly on groundwater and surface water resources for their water needs, which include agriculture, potable water supply and industry. Yet, at the same time, both surface water and groundwater are, in many cases, highly saline (Coram, 1996; Roderick, 1988; Gill, 1989), which places limitations on their use. The region and, in particular the Otway Ranges, also hold significant historical, ecological, and recreational significance. Thus, protecting these environments and its water resources are of utmost importance. It is

hoped that the results of these investigations will not only facilitate understanding and protection of the Barwon River and Otway Catchments, but similar catchments globally.

1.3. Thesis Structure and Overview of Research

In addition to this introductory chapter, this thesis is comprised of four additional chapters:

Chapter 2: Differences in groundwater and chloride residence times in saline groundwater: The Barwon River Catchment of Southeast Australia. Addresses research questions No. 1 and 5.

Chapter 3: Mean Transit Times in Headwater Catchments: Insights from the Otway Ranges, Australia. Addresses research questions No. 2 and 4.

Chapter 4: Bank Storage and Return Flow: Residence Times and Influence of River Water Chemistry in the upper Barwon River, Australia. Addresses research questions No. 2 and 3.

Chapter 5: Conclusions. Addresses research question No. 1, 2, 3, 4 and 5.

In Chapter 2, the processes and timescales leading to the development of highly saline groundwater in the Barwon River Catchment are examined using major ion, stable isotope ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$), and radioactive isotope (^{3}H, ^{14}C, ^{36}Cl) geochemistry. Various geochemical and physical processes are evaluated, including halite dissolution, mineral weathering, evaporation and through-flow from the area's numerous saline lakes. Mean residence times (MRTs) of groundwater are evaluated using the radioactive isotope data, the radioactive decay formula and lumped parameter models (LPMs). The question of whether groundwater and chloride residence times are equivalent is additionally addressed through comparison of chloride accession times with the residence times of groundwater. Lastly, this study documents environmental change within the study area over the past 20 Ka.

In Chapter 3, mean transit times (MTTs) and the sources of baseflow in six headwater catchments in the Otway Basin are evaluated using ^{3}H, major ion geochemistry, river discharge data and LPMs. Uncertainties in the MTT estimates, including the choice of LPM

employed, uncertainty in the ^{3}H rainfall record, aggregation error and analytical uncertainty are evaluated in detail. In addition, catchment controls on MTTs and existing water quality impacts are assessed, and a new method for estimating groundwater recharge rates is proposed.

In Chapter 4, the residence times of water and solutes in the upper Barwon River are evaluated using river discharge and water quality data in combination with major ion, stable isotope ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$), and radioactive isotope (^{3}H, ^{36}Cl) geochemistry. The role of bank storage and return flow in maintaining river discharge and determining river water chemistry is evaluated. Seasonal and short duration residence times of bank storage and return flow are estimated and retention of bomb-pulse ^{36}Cl in the environment is demonstrated.

In Chapter 5, key findings from Chapters 2, 3 and 4 are summarised. In addition, the broad implications of these findings are discussed, along with their relevance to understanding groundwater-surface water interaction in the Barwon River and Otway Catchments, and in river catchments globally.

1.4. References

Allison, G.B. and M.W. Hughes, 1978. The use of environmental chloride and tritium to estimate total recharge to an unconfined aquifer. Australian Journal of Soil Research, Vol. 16, pp. 181-195.

Boulton, A.J. and P.J. Hancock, 2006. Rivers as groundwater-dependent ecosystems: a review of degrees of dependency, riverine processes and management implications. Austr. Jour. of Botany, Vol. 54, pp. 133-144.

Cartwright, I., and U. Morgenstern, 2015. Transit times from rainfall to baseflow in headwater catchments using tritium: the Ovens River, Australia. Hydrol. Earth Syst. Sci., Vol. 19, pp. 3771-3785.

Cartwright, I., and U. Morgenstern, 2016. Using tritium to document the mean transit time and source of water contributing to a chain-of-ponds river system: Implications for resource protection, Appl. Geochem., Vol. 75, pp. 9-19.

Clark, I.D. and P. Fritz, 1997. Environmental Isotopes in Hydrogeology. CRC Press/Lewis Publishers, Boca Raton.

Claxton, A.J., Bates, P.D. and H.L. Cloke, 2003. Mixing of hillslope, river, and alluvial ground waters in lowland floodplains. Ground Water, Vol. 41, No. 7, pp. 926-936.

Cook, P.G. and A.L. Herczeg, 2000. Editors in: Environmental Tracers in Subsurface Hydrology. Springer Science, New York.

Coram, J.E., 1996. Groundwater-surface water interactions around shallow lakes of the Western District Plains, Victoria. Master of Science, University of Melbourne.

Duvert, C., Stewart, M.K., Cendon, D.I., and M. Raiber, 2016. Time series of tritium, stable isotopes and chloride reveal short-term variation in groundwater contribution to a stream. Hydrol. Earth Syst. Sci., Vol. 20, pp. 257-277.

Gill, B., 1989. Hydrogeological review of salinity problems in the Barwon/Corangamite region. Investigations Branch Report No. 1988/16. Rural Water Commission of Victoria. April 1989, 68 p.

International Atomic Energy Association (IAEA): Global Network of Isotopes in Precipitation, available at: http://www.iaea.org/water, last access: March, 2016.

Jurgens, B.C., Bohlke, J.K. and S.M. Eberts, 2012. TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data: U.S. Geological Survey Techniques and Methods Report 4-F3, 60 p.

Kinzelbach, W., Aeschbach, W., Alberich, C., Goni, I.B., Beyerle, U., Brunner, P., Chiang, W.H., Rueedi, J. and K. Zoellmann, 2002. A survey of methods for groundwater recharge in arid and semi-arid regions: early warning and assessment report series: Nairobi, Kenya. Division of Early Warning and Assessment, United Nations Environment Programme, 101 pp.

Kirchner, J.W., Feng, X. and C. Neal, 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. Nature, Vol. 403, pp. 524-527.

Kirchner, J.W., 2016a. Aggregation in environmental systems – Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. Hydrol. Earth Syst. Sci., Vol. 20, pp. 279-297.

Kirchner, J.W., 2016b. Aggregation in environmental systems – Part 2: Catchment mean transit times and young water fractions under hydrologic nonstationarity. Hydrol. Earth Syst. Sci., Vol. 20, pp. 299-328.

Kwicklis, E. and I. Farnham, 2014. Testing the 14C ages and conservative behaviour of dissolved 14C in a carbonate aquifer in Yucca Flat, Nevada (USA), using 36Cl from groundwater and packrat middens. Hydrogeol. Journ., Vol. 22, pp. 1359-1381.

Maloszewski, P. and A. Zuber, 1996. Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability, J. Hydrol., Vol. 57, No. 3-4, pp. 207-231.

Maloszewski, P. and A. Zuber, 1996. Lumped parameter models for the interpretation of environmental tracer data, in: International Atomic Energy Agency, Manual on mathematical models in isotope hydrogeology, TECDOC-910: Vienna, Austria, International Atomic Energy Agency Publishing Section, 9-58.

Maloszewski, P., Rauert, W., Stichler, W., and A. Herrmann, 1983. Application of flow models in an alpine catchment area using tritium and deuterium data, J. Hydrol., Vol. 66, pp. 319-330.

McDonnell, J.J., McGuire, K., Aggarwal, P., Beven, J., Biondi, D., Destouni, G., Dunn, S., James, A., Kirchner, J., Kraft, P., Lyon, S., Maloszewski, P., Newman, B., Pfister, L., Rinaldo, A., Rodhe, A., Sayama, T., Seibert, J., Solomon, K., Soulsby, C., Stewart, M., Tetzlaff, D., Tobin, C., Troch, P., Weiler, M., Western, A., Worman, A., and S. Wrede, 2010. How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis, Hydrol. Process., Vol. 24, pp. 1745-1754.

McGuire, K.J., and J.J. McDonnell, 2006. A review and evaluation of catchment transit time modelling, J. Hydrol., Vol. 330, pp. 543-563.

Modica, E., Buxton, H.T. and L.N. Plummer, 1998. Evaluating the source and residence times of groundwater seepage to streams, New Jersey Coastal Plain. Water Resour. Res., Vol. 34, No. 11, pp. 2797-2810.

Morgenstern, U., and C.J. Daughney, 2012. Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand, J. Hydrol., Vol. 456-457, pp. 79-93.

Odlare, M., 2014. Introductory Chapter for Water Resources. In: Reference Module for Earth Systems and Environmental Sciences, Ed. S.A. Elias, Elsevier.

Oki, T. and S. Kanae, 2006. Global Hydrological Cycles and World Water Resources, Science, Vol. 313, pp. 1068-1072.

Plummer, L.N., Eggleston, J.R., Andreasen, D.C., Raffensperger, J.P., Hunt, A.G. and G.C Casile, 2012. Old groundwater in parts of the upper Patapsco aquifer, Atlantic Coastal Plain, Maryland, USA: evidence from radiocarbon, chlorine-36 and helium-4. Hydrogeol. Journ., Vol. 20, pp. 1269-1294.

Roderick, P., 1988. Investigation of highly saline groundwater inflows between Winchelsea and Inverleigh. Investigations Branch Report No. 1988/7. Rural Water Commission of Victoria. August 1989, 27 p.

Scanlon, B.R., Keese, K.E., Flint, A.L., Flint, L.E., Gaye, C.B., Edmunds, W.M. and I. Simmers, 2006. Global synthesis of groundwater recharge in semiarid regions. Hydrologic Processes, Vol. 20, pp. 3335-3370.

Shiklamanov, I., 1993. World Fresh Water Resources, in: Water in crisis: a guide to the world's freshwater resources. Peter H. Gleick (ed.). Oxford University Press, New York.

Stewart, M.K., Morgenstern, U., Gusyev, M.A. and P. Maloszewski, 2016. Aggregation effects on tritium-based mean transit times and young water fractions in spatially heterogeneous catchments and groundwater systems, and implications for past and future applications of tritium. Hydrol. Earth Syst. Sci. Discuss. (in review), doi: 10.5194/hess-2016-532.

Stuiver, M., 1961. Variations in radiocarbon concentration and sunspot activity. Journ. Of Geophys. Res., Vol. 66, No. 1, pp. 273-276.

Stuiver, M., 1965. Carbon-14 content of the 18th and 19th century wood: variations correlated with sunspot activity. Science, Vol. 149, No. 3683, pp. 533-535.

Winter, T.C., Harvey, J.W., Franke, O.L. and W.M. Alley, 1998. Ground water and surface water, a single resource. U.S. Geological Survey Circular 1139. U.S. Department of the Interior, Denver, Colorado.

Wood, W.W. and W.E. Sanford, 1995. Chemical and isotopic methods for quantifying ground-water recharge in a regional, semiarid environment. Ground Water, Vol. 33, pp. 459-468.

Chapter 2

Differences in Groundwater and Chloride Residence Times in Saline Groundwater: the Barwon River Catchment of Southeast Australia

William Howcroft[a], Ian Cartwright[a], L. Keith Fifield[b], and D.I. Cendón[c, d]

[a]School of Earth, Atmosphere and Environment (SEAE), 9 Rainforest Walk (Building 28), Monash University, Clayton Campus, Clayton, VIC, 3800, Australia. Corresponding author: [redacted]

[b]Research School of Physics and Engineering. The Australian National University, Canberra, ACT, 2601, Australia

[c]Australian Nuclear Science and Technology Organisation, Menai, NSW, 2232, Australia

[d]Connected Water Initiative, School of Biological, Earth and Environmental Sciences, University of New South Wales (UNSW), Sydney, Australia

Keywords: groundwater, residence times, salinity, chlorine-36, carbon-14, LPM.

Abstract

The residence times of groundwater and chloride and the processes contributing to the development of saline (total dissolved solids (TDS) up to 45,379 mg/L) groundwater within the Barwon River Catchment of southeast Australia were investigated using major ion, stable isotope ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C$) and radioactive isotope (^{3}H, ^{14}C, ^{36}Cl) geochemistry. The elevated groundwater salinity in the region is primarily due to evapotranspiration and recycling of solutes in saline lakes with minor contributions from weathering of halite, silicate and calcite minerals. Groundwater residence times estimated from ^{14}C vary from modern to ~20 ka; for groundwater with lower ^{14}C activities, the estimated residence times vary significantly depending on the assumed flow model and the ^{14}C activity of recharge. Chloride residence times downgradient of Lake Murdeduke (a saline through-flow lake in the centre of the catchment) are greater than the corresponding groundwater residence

times due to the recycling of Cl within the lake. Precise estimates of chloride residence time could not be determined using ^{36}Cl due to $R^{36}Cl$ in precipitation being lower than that of groundwater. This is most likely due to $R^{36}Cl$ values in rainfall having been higher in the past than they are at present due to climate variability. $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C$ values also suggest that the region has experienced increasingly more evaporative conditions with time. The results of this study demonstrate that, while Cl is a useful tracer of hydrological processes, it must be applied carefully in arid and semi-arid regions of the world. In particular, recharge rates calculated using chloride mass balance may be underestimated where recycling of Cl has occurred.

2.1. Introduction

Understanding groundwater systems requires being able to account for the behaviour of both the water and the solutes (Edmunds, 2009). Chloride is probably the most widely studied solute as it is one of the most abundant ions in groundwater and its concentration is readily measured. Because its concentration is not significantly impacted by biogeochemical reactions, ion exchange or decay, and because it forms minerals only at very high concentrations, chloride is commonly used to estimate groundwater recharge rates and residence times (e.g., Allison and Hughes, 1978; Wood and Sanford, 1995; Scanlon et. al., 2006). Use of Cl in this way makes the explicit assumption that its residence time is equivalent to that of the groundwater in which it is contained. However, this assumption may not always hold true. For example, in arid and semi-arid regions, Cl may be recycled over long timescales within saline lakes. Secondly, diffusion of old Cl from clays into adjacent aquifers may occur. Thirdly, if halite dissolution within an aquifer occurs, the halite represents a source of potentially very old Cl. Each of these scenarios results in Cl having a longer residence time than the water in which it is contained. If chloride residence times are significantly older than groundwater residence times, the use of Cl to estimate recharge rates or groundwater residence times will produce erroneous results. The implications of this are significant in terms of managing groundwater resources, protecting ecosystems, and assessing salinity impacts.

Chloride residence times can be estimated from chloride concentrations within the groundwater, knowledge of aquifer thickness and porosity, and an estimate of the amount of chloride delivered annually via rainfall. As an independent measure, chloride residence times can also be estimated using ^{36}Cl. With a half-life of 301,000 years, ^{36}Cl can be used to determine chloride residence times within the range of approximately 100 ka to 1 Ma (e.g. Bentley et. al., 1986a; Phillips et. al., 1986). Groundwater residence times up to approximately 35 ka are frequently estimated in regional aquifers using ^{14}C. While ^{14}C has been widely used as a tracer, most studies have not taken into account long-term variations in the a^{14}C of the water that recharges the aquifer nor processes such as dispersion, which can impact calculated residence times.

In this study, we use ^{14}C, ^{36}Cl, and ^{3}H in combination with major ion geochemistry and stable isotopes to understand the timescales and processes responsible for the development of saline groundwater within the Barwon River Catchment in southeast, Australia. In addition, we examine whether groundwater residence times and chloride residence times within the catchment are equivalent. While there have been a number of studies that have utilised both ^{36}Cl and ^{14}C (e.g. Bird et al., 1989; Love et al., 2000; Kulongoski et al., 2008; Plummer et al., 2012; Scheiber et al., 2015), this is the first application of these tracers that we know of that specifically addresses the potential differences between groundwater and chloride residence times. The outcomes of this study will help understand the timescales and processes by which chloride is stored and exported from similar catchments globally, and will better inform the use of Cl as a tracer in saline groundwater.

2.2. Setting

The Barwon River Catchment is located in southwestern Victoria, Australia. Comprising an area of approximately 3,900 km^2 (DataSearch Victoria, 2015), the catchment is utilised primarily for grazing, cropping and forestry. Settlements within the catchment include the major population centres of Geelong and Ballarat, as well as numerous rural communities. This investigation focuses primarily on that portion of the catchment located in the vicinity of Winchelsea and Inverleigh (Fig. 2-1a).

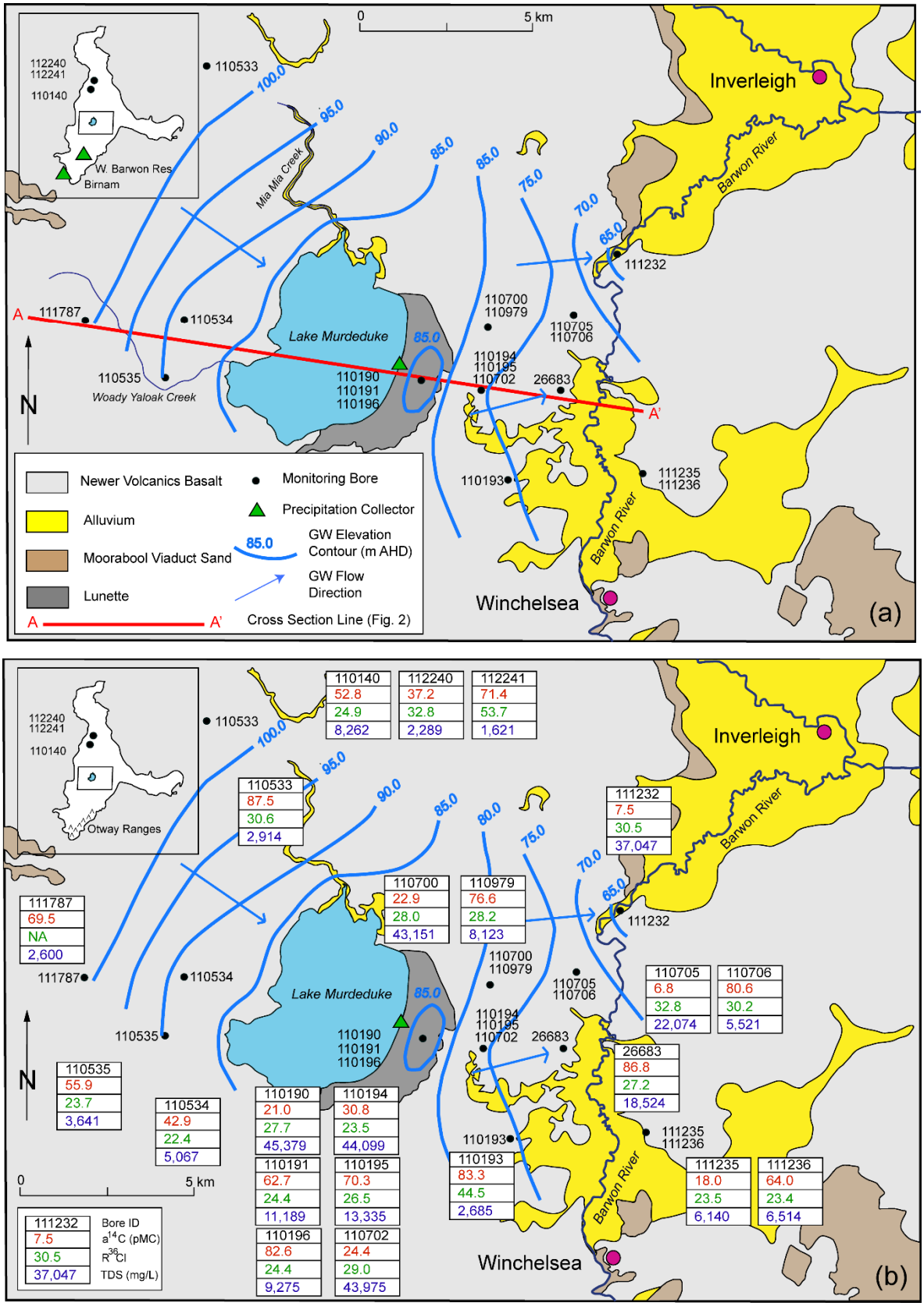

Figure 2-1. Map of the Barwon River Catchment near Lake Murdeduke showing a) lithology (DataSearch Victoria, 2015), groundwater flow and sampling locations and b) groundwater $a^{14}C$, $R^{36}Cl$ and TDS.

The catchment has a temperate climate, with average annual rainfall ranging from approximately 430 mm near Inverleigh to approximately 1,600 mm in the Otway Ranges (Department of Environment, Land, Water and Planning, 2015). The majority of rainfall occurs during the austral winter months (July to September) and, during the summer months, potential evaporation exceeds precipitation (Bureau of Meteorology, 2016). The Barwon River is perennial (Department of Environment, Land, Water and Planning, 2015) and flows northwards from the Otway Ranges, which reach a maximum elevation of approximately 650 metres above sea level. There are a number of permanent and semi-permanent brackish to hyper-saline lakes within the study area (Tweed et al., 2011). The largest of these is Lake Murdeduke, which has an area of approximately 16.6 km^2, a depth of approximately 5 m and a mineral ('salt') crust that periodically forms along its shores. From an analysis of regional groundwater flow paths, salt and water balances, and geochemistry, Coram (1996) concluded that Lake Murdeduke was a through-flow lake, with groundwater entering the lake along its west shore and discharging along its east shore.

The basement of the catchment comprises the early-Cretaceous Otway Group, which consists primarily of volcanogenic sandstone and mudstone with minor amounts of shale, siltstone, and coal (Tickell et al., 1991). The Otway Group is overlain by Tertiary sediments comprising (in ascending order) the Eastern View Formation, the Demons Bluff Formation, the Clifton Formation, the Gellibrand Marl and the Moorabool Viaduct Sand. The Tertiary sediments are in turn overlain by the Quaternary Newer Volcanics, which crop out over approximately 40% of the catchment. This study is based on groundwater sampled primarily from the Newer Volcanics and the Moorabool Viaduct Sand (Fig. 2-1a).

The Moorabool Viaduct Sand is a thin (generally less than 10 m thick), discontinuous unit of clayey sand that crops out at various locations across the catchment, including to the west of Lake Murdeduke and near Winchelsea and Inverleigh. Coram (1996) estimated that the hydraulic conductivity of this unit was approximately 4.3 m/day. The Newer Volcanics have been broadly grouped into "older-" and "younger-phase" deposits. The older-phase Newer Volcanics, which are comprised mainly of weathered olivine basalt, are considered to be a

poor aquifer, with groundwater generally only occurring within joints, vesicles, and poorly-connected interflow layers. Gill (1989) estimated that the older-phase Newer Volcanics have an average transmissivity of approximately 200 m^2/day (which assuming an average thickness of 15 m equates to a hydraulic conductivity of 13.3 m/day). The younger-phase Newer Volcanics consist of basalt, scoria, undifferentiated pyroclastics, pyroclastic surge deposits and pyroclastic fall deposits (Tickell et al., 1991). They are less weathered and have a higher degree of fracturing than the older phase volcanics. Coram (1996) estimated that the younger-phase Newer Volcanics have an average hydraulic conductivity of 8.6 m/day. Together, the older- and younger-phase Newer Volcanics have an average thickness of approximately 30 m in the study area. Also present are Quaternary lunette deposits along the east shore of Lake Murdeduke and alluvium along the Barwon River (Fig. 2-1a).

Regional groundwater in the lower Tertiary units flows from recharge areas in the Otway Ranges to the north or northeast (Witebsky et al., 1995; Petrides and Cartwright, 2006). Flow direction within the Newer Volcanics and underlying Moorabool Viaduct Sand is more variable and is influenced by local topography. Recharge occurs across the basin and groundwater discharges into the Barwon River (Cartwright et al., 2013a). Shallow groundwater in the headwaters of the catchment generally has low (<500 mg/L) total dissolved solids (TDS) concentrations but in the centre of the catchment, near Lake Murdeduke, TDS concentrations in excess of 10,000 mg/L are common (Coram, 1996). TDS concentrations as high as 1,200 mg/L have also been reported within the Barwon River (Cartwright et al., 2013a), which is interpreted to be the result of highly saline groundwater inflow (Roderick, 1988; Gill, 1989).

2.3. Methods

2.3.1. Sampling

Samples of precipitation, groundwater, Lake Murdeduke lake water and Lake Murdeduke salt crust were collected from the study area between September 2014 and November 2015. The EC, pH and temperature of the water samples were measured in the field using a calibrated, TPS® hand-held water quality meter and probes and alkalinity was determined using a Hach® digital titrator and reagents. Sampling locations are shown in Figs. 2-1a, 2-1b and 2-2**.**

Precipitation samples were collected using rainfall collectors located along the east shore of Lake Murdeduke, on the east side of the West Barwon Reservoir and at Birnam in the Otway Ranges (Fig. 2-1a). Precipitation collectors consisted of polyethylene storage containers equipped with funnels positioned approximately one-half metre above ground level. Water within the containers was periodically sampled, the containers rinsed with ultrapure water and then replaced. Precipitation samples were collected on six occasions at Birnam, on two occasions at the West Barwon Reservoir and on one occasion at Lake Murdeduke.

Groundwater samples were collected in March 2015 from 22 groundwater monitoring bores that comprise part of the Victorian State Observation Bore Network (SOBN). All but three of the bores are located within the vicinity of Lake Murdeduke; the remaining bores are located approximately 20 to 30 km to the north of the lake (Fig. 2-1a). The sampled bores are screened within the Newer Volcanics, the Moorabool Viaduct Sand or lunette deposits at depths ranging from approximately 8 to 65 m below ground level. At several locations, adjacent bores are screened at different depths within a single geologic unit and/or between units. Bore details are summarised in Table 2-1. Standing water levels were measured prior to sampling using an electronic water level tape. Groundwater samples were collected using an impeller pump (shallow bores) or a piston pump (deep bores) set within the screened zone, with approximately three bore volumes of groundwater removed prior to sample collection.

Samples of Lake Murdeduke salt crust and lake water were collected along the east shore of the lake in March and June, 2015 respectively. The lake water sample was collected from approximately 0.5 m below the lake water surface.

2.3.2. Analytical Techniques

The groundwater samples were analysed for cations and anions, $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, ^{14}C, ^{36}Cl, and ^{3}H (select samples only). The precipitation and Lake Murdeduke salt crust samples were analysed for cations, anions and ^{36}Cl. The salt crust sample was dissolved in ultrapure water prior to analysis. The Lake Murdeduke lake water sample was analysed for cations, anions, $\delta^{18}O$ and $\delta^{2}H$.

Cation analysis was conducted at Monash University using a ThermoFinnigan ICP-OES on samples that had first been filtered through 0.45 µm cellulose nitrate filters and acidified to pH < 2 using double-distilled 16 M HNO_3. Anions were analysed at Monash University on filtered, un-acidified samples using a Metrohm ion chromatograph (IC). The precision of the cation and anion analyses, based upon replicate sample analysis, is ± 2% while the accuracy, based on analysis of certified water standards, is ± 5%. To assess quality control, duplicate samples were prepared and analysed at a rate of approximately one per every ten primary samples. Total dissolved solids (TDS) concentrations were determined by summing the concentrations of cations and anions.

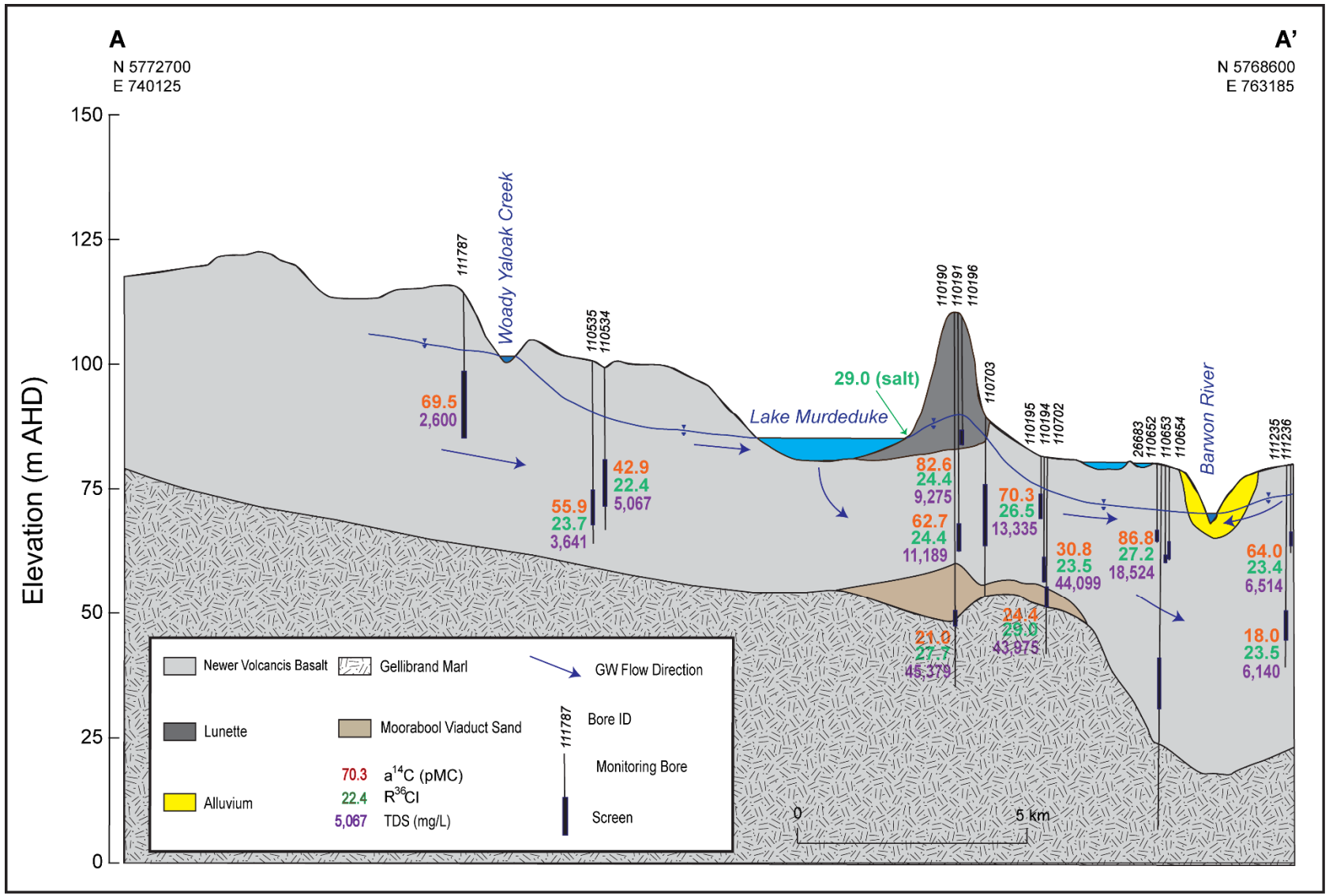

Figure 2-2. Geologic cross section through the study area showing lithology and $a^{14}C$, $R^{36}Cl$ and TDS in groundwater.

Bore ID	Geologic Unit	Bore Depth	Screen Interval	Screen Mid-point	mp	SWL	GW Elevation
		m bgl	m bgl	m bgl	m AHD	m bmp	m AHD
26683	Basalt	8.2	6 - 8	7	72.45	1.89	70.56
110140	Basalt	28.0	22 - 28	25	179.55	17.55	162.00
110190	M. Viaduct Sand	65.0	62 - 65	63.5	113.25	33.80	79.45
110191	Basalt	50.0	45 - 50	47.5	113.51	35.28	78.23
110193	Basalt	9.0	3 - 9	6	77.47	1.68	75.79
110194	Basalt/Clay	21.0	18 - 21	19.5	78.18	2.42	75.76
110195	Basalt	9.0	6 - 9	7.5	78.41	3.07	75.34
110196	Lunette	29.5	26 - 29.5	27.75	113.25	23.43	89.82
110533	Basalt	30.1	9 - 15	12	109.54	5.01	104.53
110534	Basalt	27.0	21 - 27	24	99.10	10.63	88.47
110535	Basalt	27.0	21 - 27	24	95.17	5.47	89.70
110700	Basalt	58.0	40 - 58	49	86.77	8.25	78.52
110702	M. Viaduct Sand	26.5	23 - 26.5	24.75	78.68	3.26	75.42
110705	Basalt	46.0	34 - 46	40	82.81	9.81	73.00
110706	Basalt	12.5	6 - 12.5	9.25	82.60	9.23	73.37
110979	Basalt	13.0	7 - 13	10	86.79	8.16	78.63
111232	Basalt	27.0	21 - 27	24	77.01	13.42	63.59
111235	Basalt/Clay	34.0	28 - 34	31	78.85	6.24	72.61
111236	Basalt	15.0	12 - 15	13.5	79.14	6.05	73.09
111787	Basalt	30.5	20.5 - 30.5	25.5	116.23	14.08	102.15
112240	M. Viaduct Sand	72.0	66 - 72	69	250.24	26.41	223.83
112241	Basalt	25.0	13 - 25	19	250.35	20.23	230.12

Table 2-1. Construction details and groundwater levels for monitoring bores sampled as part of this study. m = metres, bgl = below ground level, mp = measuring point, m AHD = metres Australian Height Datum, SWL = Standing Water Level, GW = Groundwater. SWL for 111787 provided by D. Banfield (pers. comm., 2015).

Stable isotopes were analysed at Monash University using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}O$ values were determined via equilibration with He-CO_2 at 32 °C for 24 to 48 hours in a ThermoFinnigan Gas Bench. $\delta^{2}H$ was measured by reaction with Cr at 850 °C using an automated Finnigan MAT H/Device. $\delta^{18}O$ and $\delta^{2}H$ were measured relative to internal standards calibrated using IAEA, SMOW, GISP and SLAP. Data were normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW. Precision (1σ), based on replicate analysis, is ± 0.1% for $\delta^{18}O$ and ± 1% for $\delta^{2}H$. CO_2 from dissolved inorganic carbon (DIC) was liberated by acidification using H_3PO_4 in a He atmosphere in a ThermoFinnigan Gas Bench. $\delta^{13}C$ values are expressed relative to PDB and the precision, based on replicate samples, is ± 0.2%.

^{36}Cl analysis was conducted at the Australian National University (ANU) using accelerator mass spectrometry (AMS) and techniques described by Fifield (1999) and Fifield et al. (2013). ^{36}Cl activities are expressed as $R^{36}Cl$, where $R^{36}Cl = {}^{36}Cl/Cl \times 10^{-15}$. Uncertainties in the $R^{36}Cl$ values are derived from the counting statistics of the number of ^{36}Cl counts combined in quadrature with a 3% reproducibility uncertainty. Uncertainties for the samples measured range between 5 and 6%.

^{14}C analysis was performed at the Rafter Radiocarbon Laboratory of the Institute of Geological and Nuclear Sciences (GNS) in Lower Hutt, New Zealand. Analysis was conducted by first converting the DIC in the water samples to CO_2 using H_3PO_4, re-combusting the CO_2 with silver wire to remove sulphur, and converting the CO_2 to graphite. ^{14}C activities were then determined on the graphite using AMS. ^{14}C activities ($a^{14}C$) are expressed as pMC (percent modern carbon) where pMC = 100% corresponds to 95% of the ^{14}C activity of the National Bureau of Standards (NBS) oxalic acid standard (Stuiver and Polach, 1977).

^{3}H analysis was conducted at the GNS Water Dating Laboratory in Lower Hutt, New Zealand. The samples were distilled and electrolytically enriched prior to analysis by liquid scintillation counting, as described by Morgenstern and Taylor (2009). ^{3}H activities are expressed in tritium units (TU) with a relative uncertainty and quantification limit of ± 2% and 0.02 TU, respectively.

2.3.3. Groundwater Residence Times

Groundwater residence times were estimated from the measured ^{14}C activities of DIC via:

$$t = \frac{1}{\lambda} * \ln(\frac{q\,A_0}{A}) \qquad (2\text{-}1)$$

(Clark and Fritz, 1997), where λ is the ^{14}C decay constant (1.21 x 10^{-4} yr^{-1}), A is the measured ^{14}C activity, A_0 is the initial ^{14}C activity in the recharging water (assumed to be 100 pMC), and q is the proportion of DIC derived from the recharging water. Use of this approach assumes that q is known, or can be reasonably estimated, and that A_0 has remained constant over time. It is also assumed that the sampled water has taken a direct flow path from the point of recharge to the sampling point with no mixing or dispersion (i.e., piston flow). These are simplifying assumptions; nevertheless, Eq. (2-1) is commonly used to estimate groundwater residence times.

Groundwater residence times were also estimated using TracerLPM (Jurgens et al., 2012), which is an Excel-based program that estimates mean residence times (MRTs) using lumped parameter models (LPMs). Use of this approach readily allows variation in A_0 with time to be accounted for. In addition, it is not necessary to assume piston flow. However, LPMs are based upon simplified aquifer geometries, which may not always strictly apply to a given flow system. Furthermore, tracer input histories are in many cases incomplete and must therefore be interpolated. Nonetheless, the use of LPMs allows the impact of processes such as dispersion on ^{14}C activities to be addressed.

2.3.4. Chloride Residence Times

Chloride residence times may be estimated using measured $R^{36}Cl$ values in groundwater and:

$$t = -\frac{1}{\lambda} * \ln\frac{R - R_{se}}{R_0 - R_{se}} \qquad (2\text{-}2)$$

(Bentley et al., 1986a), where λ is the ^{36}Cl decay constant (2.3 x 10^{-6} yr^{-1}), R is the measured $R^{36}Cl$, R_0 is the initial $R^{36}Cl$ in recharge and R_{se} is the secular $R^{36}Cl$ due to hypogene (subsurface) production. As with ^{14}C, use of Eq. (2-2) assumes that R_0 is both known and

time invariant. R_{se}, which largely depends on the amount of uranium and thorium in the aquifer matrix, matrix porosity, and the Cl content of groundwater, is difficult to determine but only becomes significant after about five half-lives (Clark and Fritz, 1997).

Chloride residence or accession times can also be estimated from:

$$t = \frac{Cl_{gw}}{m_{Cl}} * b * n \qquad (2\text{-}3)$$

where Cl_{gw} is the chloride concentration in groundwater in mg/m^3, m_{Cl} is the chloride deposition rate from precipitation in mg/m^2/year, b is the saturated thickness of the aquifer in m, and n is aquifer porosity. Eq. (2-3) allows estimates of the time required for Cl in groundwater to accumulate using parameters that are commonly known, or which can easily be estimated. However, the Cl deposition rate is implicitly assumed to have remained constant with time, runoff is considered to be negligible and input by precipitation is assumed to be the only source of chloride within the aquifer.

2.4. Results

Groundwater elevations and the geochemistry of precipitation, groundwater, and Lake Murdeduke lake water and salt crust are summarised in Tables 2-1 and 2-2.

2.4.1. Groundwater Elevations and Head Gradients

Groundwater elevations ranged from approximately 63.59 m AHD at bore 111232 to 230.12 m AHD at bore 112241. Shallow groundwater flow direction is generally to the east-southeast, except for an area of groundwater mounding immediately to the east of Lake Murdeduke (Figs. 2-1a, 2-1b and 2-2). Horizontal head gradients ranged from 0.002 to 0.008. Vertical head gradients ranged from 0.003 to 0.586 and were downward except at bore pairs 110190/110191 and 110194/110195, which are located between Lake Murdeduke and the Barwon River, where the gradients were upwards.

Location	Sample Date	Temp.	EC	pH	TDS	HCO_3	Cl	Br	SO_4	Na	Mg	K	Ca	$\delta^{13}C$	$\delta^{18}O$	$\delta^{2}H$	d-excess	$R^{36}Cl$	$a^{14}C$	^{3}H	Cl/Br	Na/Cl	SI Calcite
		°C	µS/cm	S.U.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	‰	‰	‰	‰	x 10^{15}	pMC	TU			
Groundwater																							
26683	12/03/2015	15.0	32,000	7.81	18,524	771	10,074	30.7	729	6,324	448	66.3	50.0	-13.2	-2.8	-24	-1.8	27.2	86.8	0.511	741	0.97	0.55
110140	11/03/2015	17.0	14,770	7.56	8,262	590	4,227	14.6	603	2,193	534	24.2	52.4	-17.3	-5.2	-36	6.0	24.9	52.8	-	653	0.80	0.25
110190	10/03/2015	16.3	53,100	7.31	45,379	468	26,057	95.0	1,532	14,820	2,058	133.9	197	-12.7	-0.7	-16	-10.4	27.7	21.0	-	618	0.88	0.68
110191	10/03/2015	15.4	18,290	7.75	11,189	730	5,892	15.8	472	3,764	267	19.0	7.1	-10.8	-3.4	-28	-0.7	24.4	62.7	-	839	0.99	-0.30
110193	13/03/2015	14.0	4,250	7.64	2,685	712	861	3.3	214	658	103	8.9	28.7	-13.1	-4.9	-34	5.6	44.5	83.3	0.127	588	1.18	0.16
110194	10/03/2015	-	64,100	7.64	44,099	620	25,636	85.4	1,676	13,677	2,048	157.4	181	-12.9	-0.7	-16	-10.7	23.5	30.8	-	677	0.82	1.06
110195	10/03/2015	14.7	21,980	6.29	13,335	359	7,618	22.6	531	4,158	514	45.5	35.8	-14.4	-3.2	-26	0.1	26.5	70.3	-	761	0.84	-1.41
110196	10/03/2015	-	15,990	7.53	9,275	922	4,790	14.8	257	2,846	356	6.1	68.2	-15.6	-3.3	-29	-2.0	24.4	82.6	0.010	729	0.92	0.55
110533	11/03/2015	-	5,300	7.87	2,914	444	1,262	4.9	212	779	114	13.2	64.4	-16.6	-4.7	-31	6.3	30.6	87.5	1.399	581	0.95	0.59
110534	11/03/2015	14.7	8,880	7.73	5,067	612	2,417	9.2	311	1,473	176	1.8	40.6	-15.6	-4.9	-30	9.2	22.4	42.9	0.005	590	0.94	0.41
110535	11/03/2015	15.7	6,470	8.00	3,641	386	1,709	5.9	284	956	191	18.4	70.0	-16.1	-5.0	-33	6.8	23.7	55.9	-	658	0.86	0.66
110700	12/03/2015	16.8	67,900	7.61	43,151	761	24,890	86.4	1,935	13,056	2,057	118.1	214	-13.2	-1.0	-16	-8.1	28.0	22.9	-	649	0.81	1.20
110702	10/03/2015	-	63,300	7.66	43,975	781	25,396	85.3	1,616	13,620	2,028	130.0	282	-12.7	-0.5	-16	-12.4	29.0	24.4	-	671	0.83	1.33
110705	12/03/2015	17.5	36,700	7.86	22,074	293	12,174	40.9	1,395	6,748	894	139.9	329	-15.8	-2.4	-24	-4.5	32.8	6.8	-	671	0.85	0.96
110706	12/03/2015	17.8	10,490	8.33	5,521	503	2,745	11.1	328	1,633	231	18.6	34.8	-17.5	-3.8	-30	0.7	30.2	80.6	0.826	559	0.92	0.85
110979	12/03/2015	15.3	14,370	7.94	8,123	664	3,918	15.4	628	2,457	316	28.4	39.5	-16.4	-4.0	-31	1.7	28.2	76.6	-	574	0.97	0.55
111232	13/03/2015	15.9	59,200	7.37	37,047	583	20,322	72.9	2,530	10,695	2,024	173.7	606	-15.4	-1.6	-20	-6.6	30.5	7.5	-	628	0.81	1.20
111235	12/03/2015	15.7	10,930	7.76	6,140	464	2,940	12.2	459	1,720	213	52.4	269	-14.4	-5.3	-34	8.6	23.5	18.0	-	542	0.90	1.09
111236	12/03/2015	14.8	11,130	7.79	6,514	749	2,950	12.0	481	1,911	222	31.3	139	-12.5	-5.3	-34	8.0	23.4	64.0	-	553	1.00	1.02
111787	20/01/2015	-	4,345	7.81	2,600	447	1,093	3.3	108	776	120	17.5	31.0	-13.8	-5.2	-34	8.0	-	69.5	0.002	741	1.09	0.24
112240	11/03/2015	17.4	3,820	7.56	2,289	737	759	2.8	101	550	101.5	5.1	15.1	-16.0	-5.6	-35	9.4	32.8	37.2	-	620	1.12	-0.10
112241	11/03/2015	16.5	2,530	7.92	1,621	717	364	1.3	48	380	65.5	3.5	10.4	-14.9	-5.6	-36	8.7	53.7	71.4	0.073	618	1.61	0.12
Precipitation																							
Birnam	27/09/2014	22.1	80.3	6.49	25	5.7	8.5	0.02	1.5	5.1	0.7	2.6	0.8	-	-4.4	-22	14.0	13.7	-	2.446	962	0.93	-
Birnam	20/12/2014		-	-	-	-	-	-	-	-	-	-	-	-	-0.8	-10	-3.8	20.1	-	-	-	-	-

Location	Sample Date	Temp.	EC	pH	TDS	HCO_3	Cl	Br	SO_4	Na	Mg	K	Ca	$\delta^{13}C$	$\delta^{18}O$	$\delta^{2}H$	d-excess	$R^{36}Cl$	$a^{14}C$	^{3}H	Cl/Br	Na/Cl	$SI_{Calcite}$
		°C	µS/cm	S.U.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	‰	‰	‰	‰	x 10^{15}	pMC	TU			
Birnam	9/05/2015	-	94.9	5.67	43	11.3	15.7	0.04	2.1	6.5	1.1	5.2	1.3	-	-4.5	-24	12.2	-	-	-	981	0.64	-
Birnam	18/05/2015	12.4	73.6	6.48	30	0.6	15.6	0.05	2.1	7.7	1.0	1.9	0.8	-	-5.4	-30	13.4	-	-	-	712	0.76	-
Birnam	18/07/2015	7.4	64.8	5.44	29	5.7	10.6	0.03	1.4	4.3	0.9	4.3	1.1	-	-5.8	-33	13.9	-	-	-	908	0.63	-
Birnam	5/11/2015	-	67.0	5.88	29	7.3	10.2	0.03	1.8	5.4	0.8	2.8	0.9	-	-3.4	-16	11.1	-	-	-	764	0.81	-
W. Barwon Res.	18/07/2015	8.8	61.9	4.34	25	0.0	14.1	0.04	1.6	5.0	0.8	1.8	0.9	-	-5.6	-30	15.4	19.1	-	-	808	0.55	-
W. Barwon Res.	5/11/2015	-	68.9	4.62	28	2.4	13.5	0.03	1.5	6.3	1.0	2.4	0.9	-	-3.5	-17	11.1	-	-	-	959	0.72	-
L. Murdeduke	18/05/2015	-	77.1	5.76	29	0.2	15.4	0.05	1.4	8.2	1.3	0.4	1.6	-	-3.7	-26	4.1	20.2	-	-	637	0.83	-
Lake Murdeduke																							
Lake Water	20/06/2015	8.2	106,300	8.47	240,480	615	123,658	355	6,162	65,406	7,656	434	98	-	-2.3	-25	-6.2	-	-	-	786	0.82	1.45
Salt Crust	10/03/2015	-	-	-	-	0.0	30.7	0.01	0.2	18.9	0.2	BDL	BDL	-	-	-	-	29.0	-	-	4,841	0.95	-

Table 2-2. Geochemistry results of groundwater, precipitation and Lake Murdeduke lake water and salt crust. Saturation indices for calcite ($SI_{calcite}$) calculated using PHREEQC. Results for 111787 provided by D. Banfield (pers. Comm., 2015). Cl/Br and Na/Cl ratios are molar.

2.4.2. Major Ion Geochemistry

2.4.2.1. Precipitation

The EC of precipitation ranged from 61.9 to 94.9 µS/cm while TDS ranged from 25 to 43 mg/L. Cl concentrations of the precipitation ranged from 8.5 to 15.7 mg/L, which is higher than the mean concentrations reported by Blackburn and McLeod (1983) for Kybybolite (6.6 mg/L) in western Victoria and by Crosbie et al. (2012) for Melbourne (5.36 mg/L). The higher Cl concentrations in rainfall in the Barwon River Catchment may be due to evaporation within the collectors, aeolian transport of salt from Lake Murdeduke and/or addition of salts previously captured by overlying vegetation.

Molar Cl/Br ratios of precipitation ranged from 637 to 981 (Fig. 2-3a), which are slightly higher than the value of ~650 which characterises seawater and coastal rainfall (Drever, 1997; Davis et al. 1998, 2001). Molar Na/Cl ratios (Fig. 2-3b) ranged from 0.55 to 0.93, which are similar to that of both seawater (~0.86) and rainfall in southeast Australia (0.6 to 1.1, Hutton and Leslie, 1958; Blackburn and McLeod, 1983; Crosbie et al., 2012).

2.4.2.2. Lake Murdeduke Water and Salt Crust

The water from Lake Murdeduke had an EC of 106,300 µS/cm, a TDS concentration of 240,480 mg/L, and a Cl concentration of 138,812 mg/L. The TDS concentration is higher than that previously reported by Tweed et al. (2011) for the period 1965 to 2008. The molar Cl/Br ratio of the lake water was 786 while that of the salt crust was 4,841.

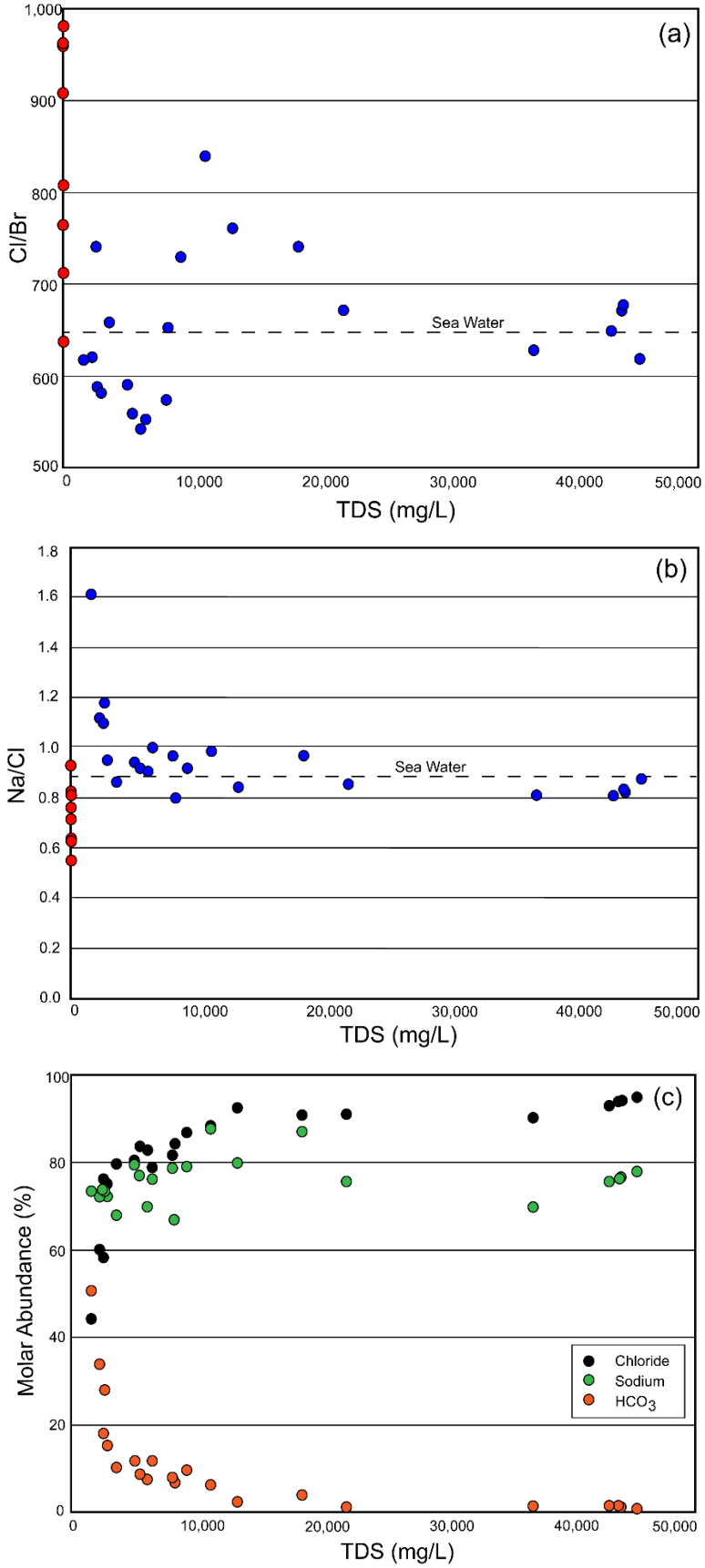

Figure 2-3: Geochemistry results showing: a) Cl/Br ratios and b) Na/Cl in groundwater (blue circles) and in precipitation (red circles), and c) molar abundance (% mass) of chloride, sodium and bicarbonate in groundwater. Cl/Br and Na/Cl ratios are molar.

2.4.2.3. Groundwater

The EC of the groundwater ranged from 2,530 to 67,900 µS/cm while TDS ranged from 1,621 to 45,379 mg/L (Fig. 2-2). Groundwater from four of the observation bores in close proximity to, and immediately downgradient of, Lake Murdeduke (110190, 110194, 110700 and 110702; Figs. 2-1b, 2-2) had TDS concentrations that exceed 40,000 mg/L. Two of these bores (110190 and 110702) are screened within the Moorabool Viaduct Sand while the remaining two (110194 and 110700) are screened within basalt. The lowest TDS concentrations were at bores 112240 and 112241, which are located approximately 30 km to the north of Lake Murdeduke. At locations where two or more bores are screened at different depths, TDS generally increases with depth below ground surface. The one exception to this is bore pair 111235/111236, where TDS varies little with depth.

Cl concentrations in groundwater range from 364 to 26,057 mg/L and the relative molar abundance of Cl increases from 44% of total anions at TDS = 1,621 mg/L to more than 90% at TDS > 12,000 mg/L (Fig. 2-3c). In contrast, HCO_3 decreases in relative abundance from approximately 50% at TDS = 1,621 mg/L to <3% at TDS > 12,000 mg/L. Sulphate concentrations range from 48 to 2,530 mg/L and SO_4 constitutes <5.5% of total anions. Na is the dominant cation (67 to 88% on a molar basis) and its concentration is strongly correlated with TDS. Mg, Ca and K constitute 6 to 15%, <6.5% and <1.5% of total cations, respectively**.**

Molar Cl/Br ratios of the groundwater range from 542 to 839 and do not vary significantly with TDS (Fig. 2-3a). Cl/Br ratios scatter around the ratio of seawater and coastal rainfall and overlap with those of the local precipitation. Molar Na/Cl ratios range from 0.8 to 1.6 and are generally higher in groundwater with TDS < 3,000 mg/L (Fig. 2-3b).

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

δ^2H and $\delta^{18}O$ values of groundwater and Lake Murdeduke lake water are illustrated in Figure 2-4a along with the Melbourne Meteoric Water Line (MMWL) and the Global Meteoric Water Line (GMWL), which are defined as $\delta^2H = 7.43 * \delta^{18}O + 8.6$ (Hughes and

Crawford, 2012) and $\delta^2H = 8.0 * \delta^{18}O + 10$ (Craig, 1961), respectively. The δ^2H and $\delta^{18}O$ values of groundwater define an array with a slope of 3.9 to the right of the MMWL, indicating that evaporation occurred during or prior to recharge (Clark and Fritz, 1997). The array intercepts the MMWL at approximately δ^2H = -38‰ and $\delta^{18}O$ = -6.5‰, which are lower than the weighted average δ^2H and $\delta^{18}O$ values of modern rainfall in Melbourne located 100 km to the east (δ^2H = -28.4‰, $\delta^{18}O$ = -4.98‰; Hughes and Crawford, 2012). The δ^2H and $\delta^{18}O$ values of Lake Murdeduke water lie close to the same trend line as the groundwater samples. Deviation from the GMWL can be expressed as deuterium excess (*d*), where $d = \delta^2H - 8 * \delta^{18}O$ (Dansgaard, 1964) and there is a strong correlation between TDS and deuterium excess (Fig. 2-4b).

The $\delta^{13}C$ values of DIC in groundwater range from -17.5‰ to -10.8‰, with an average value of -14.6‰. There is no correlation between $\delta^{13}C$ values and HCO_3, Ca or Mg concentrations, depth below ground surface, or TDS. However, the four samples (bores 110190, 110194, 110700 and 110702) having the highest TDS concentrations (>43,000 mg/L) have relatively similar $\delta^{13}C$ values (-13.2 to -12.7‰).

2.4.4. Radioisotopes (^{14}C, ^{3}H, ^{36}Cl)

^{14}C and ^{36}Cl activities of the groundwater are illustrated in Figs. 2-1b and 2-2 and summarised in Table 2-2. $a^{14}C$ of groundwater range from 6.8 pMC at bore 110705 to 87.5 pMC at bore 110533. West of Lake Murdeduke, there is a decrease in $a^{14}C$ in groundwater eastwards in the direction of flow. Groundwater $a^{14}C$ to the east of, and downgradient of, Lake Murdeduke are higher than those immediately upgradient of the lake; $a^{14}C$ also decrease in the direction of groundwater flow. At locations where two or more bores are screened at different depth intervals, $a^{14}C$ are lower in the deeper bore (Fig. 2-2).

There is generally no correlation between $\delta^{13}C$ values and $a^{14}C$. However, in groundwater with $a^{14}C$ <31 pMC (bores 110190, 110194, 110700, 110702, 110705, 111232 and 111235) there is a trend of decreasing $\delta^{13}C$ values with decreasing $a^{14}C$ (Fig. 2-5a). There is also no

correlation between $a^{14}C$ and TDS; however, the four samples with the highest TDS concentrations (>43,000 mg/L) have relatively similar $a^{14}C$ (21 to 31 pMC).

Aside from one outlier (bore 111235), groundwater may be divided into two populations using deuterium excess and $a^{14}C$ (Fig. 2-5b). The first population is characterised by $a^{14}C$ <31 pMC and d-excess values <-4.5‰. This groundwater is from bores 110190, 110194, 110700, 110702, 110705 and 111232, which also have the highest TDS concentrations (Fig. 2-4b). The second population is characterised by $a^{14}C$ > 37 pMC and d-excess values >-2‰. Both populations demonstrate increasingly negative d-excess values with increasing $a^{14}C$ and, although the data are scattered, the trends have similar slopes.

^{3}H activities of groundwater ranged from below detection at bores 110196, 110534 and 111787 to 1.399 TU at bore 1110533. Bore 1110533 is located approximately seven km to the northwest of Lake Murdeduke and groundwater from this bore also had the highest $a^{14}C$ (87.53 pMC). In general, measurable ^{3}H activities were only present in shallow (<15 m below ground level) groundwater with $a^{14}C$ >80 pMC (Fig. 2-6).

$R^{36}Cl$ values of precipitation ranged from 13.7 to 20.2×10^{-15}. Three of the four samples have $R^{36}Cl$ values of approximately 20×10^{-15}, which are similar to the predicted $R^{36}Cl$ value of rainfall of ~20×10^{-15} for this region (Davie et al., 1989). $R^{36}Cl$ values of groundwater (Figs. 2-1b and 2-2) ranged from 22.4 to 53.7×10^{-15}, with the highest values being recorded in the groundwater from bores 112241 (53.7×10^{-15}) and 110193 (44.5×10^{-15}). Bore 112241 is located approximately 30 km to the north of Lake Murdeduke while bore 110193 is located approximately 5 km to the southeast of the lake. Excluding these two samples, the $R^{36}Cl$ of the groundwater clusters between 22 and 33 $\times 10^{-15}$ with an average value of 27.0×10^{-15}. This average value is similar to that of the Lake Murdeduke salt crust sample (29.0×10^{-15}) but is higher than that of the precipitation samples. $R^{36}Cl$ values do not correlate with $a^{14}C$ (Fig. 2-7) or with Cl concentration (Fig. 2-8).

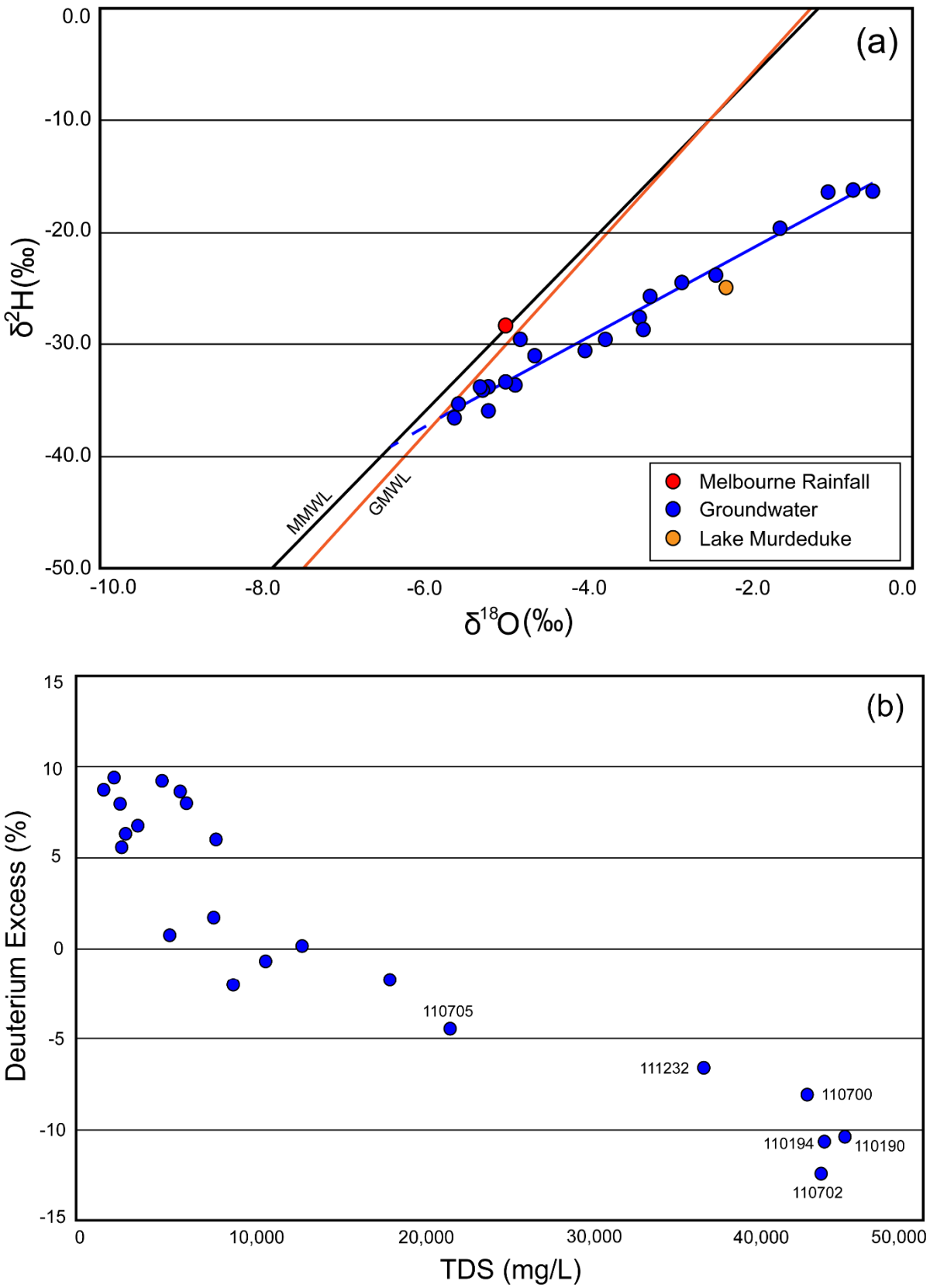

Figure 2-4: Stable isotope results showing: a) δ^2H and $\delta^{18}O$ for groundwater and Lake Murdeduke water relative to the Melbourne Meteoric Water Line (MMWL), the Global Meteoric Water Line (GMWL) and Melbourne rainfall, and b) deuterium excess as a function of TDS for groundwater.

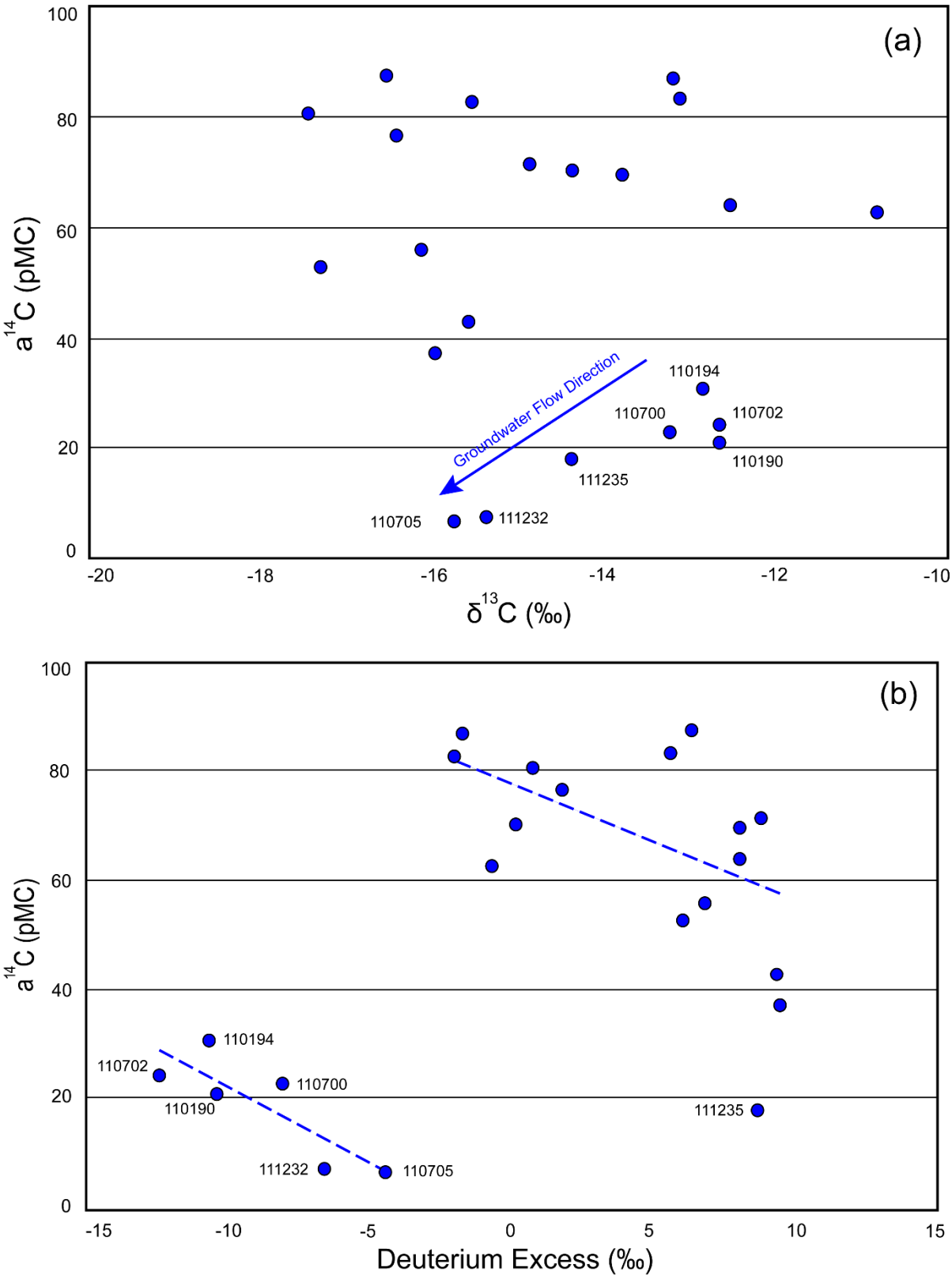

Figure 2-5: a^{14}C in groundwater as a function of: a) δ^{13}C and b) deuterium excess.

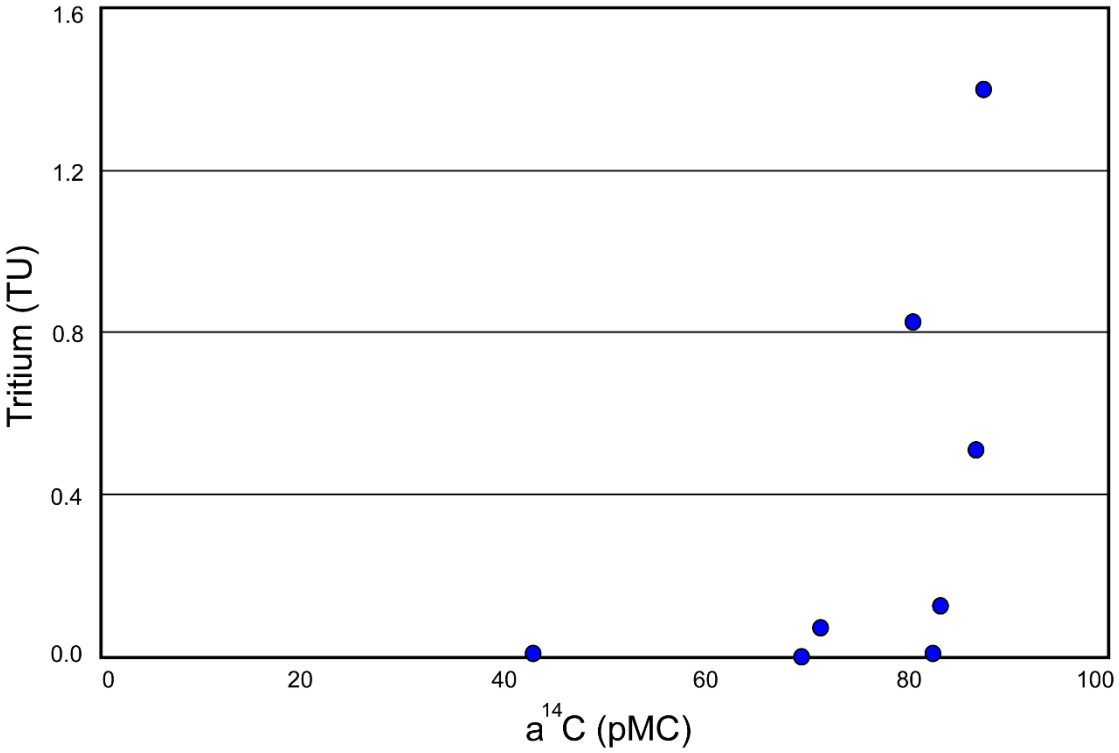

Figure 2-6: Tritium activity as a function of $a^{14}C$ in groundwater

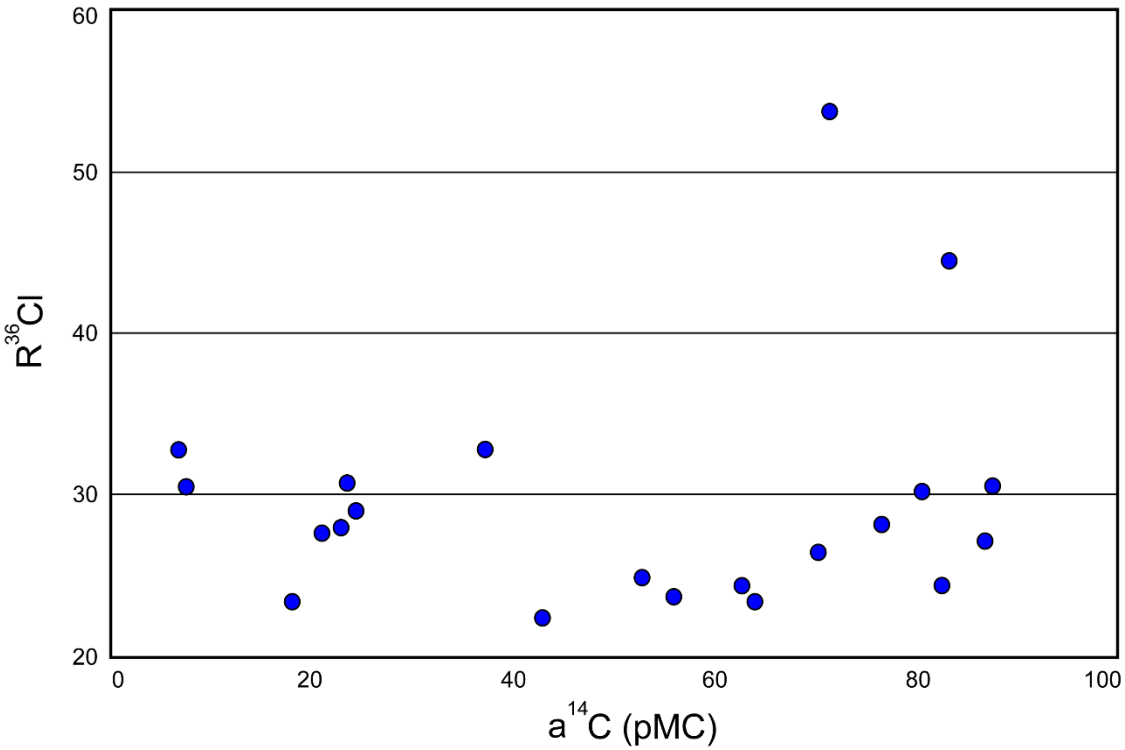

Figure2-7: $R^{36}Cl$ as a function of $a^{14}C$ in groundwater

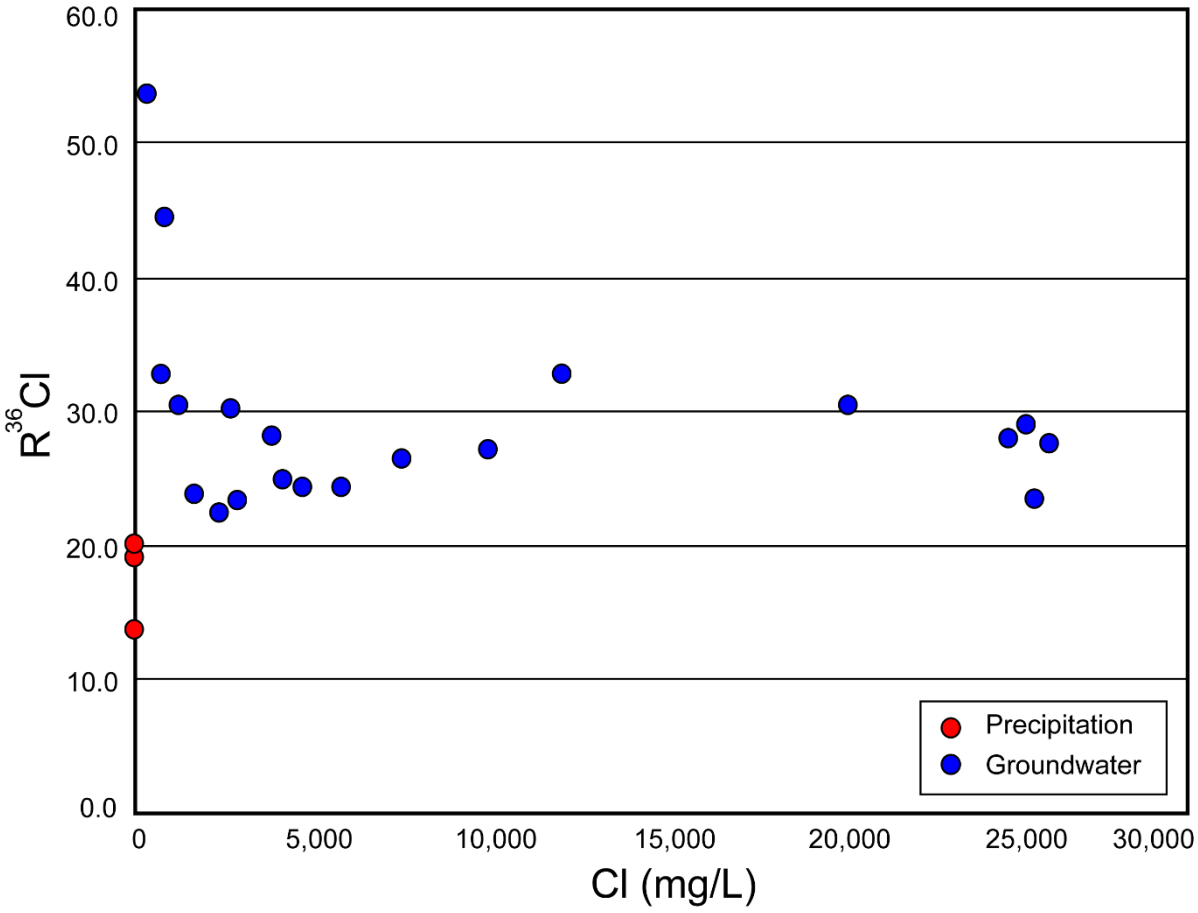

Figure 2-8: $R^{36}Cl$ in groundwater and in precipitation as a function of Cl^- concentration

2.5. Discussion

The major ion and isotope geochemistry of the precipitation, groundwater, Lake Murdeduke water and salt crust samples, in combination with groundwater elevations, allow a comprehensive understanding of hydrogeologic and geochemical processes, groundwater and chloride residence times, and the climatic controls relating to the development of saline groundwater in the Barwon River Catchment.

2.5.1. Groundwater Flow

The distribution of hydraulic heads and a general decline in $a^{14}C$ implies that the groundwater flows from northwest to southeast across the study area. The area to the northwest of Lake Murdeduke is interpreted to be a regional recharge area, while the upward head gradients to the southeast of the lake imply that there is groundwater discharge close to and into the Barwon River. TDS concentrations of groundwater increase

from ≤6,000 mg/L northwest of Lake Murdeduke to >20,000 mg/L southeast of the lake (Fig. 2-1b). ^{14}C activities are also higher in groundwater to the southeast of the lake than to the northwest (Figs. 2-1b, 2-2). This implies that Lake Murdeduke is a through-flow lake, as proposed by Coram (1996), and that shallow groundwater to the east of the lake is recharged by highly saline lake water.

The Moorabool Viaduct Sand appears to play an important role in the distribution of groundwater salinity within the catchment. The highest TDS concentrations occur either within (bores 110190 and 110702) or immediately above (bores 110194, 110700, 110705 and 111232) this unit. As discussed above, this saline groundwater reflects saline through-flow from Lake Murdeduke. The full aerial extent of the unit is not known; however, it may occur below or in close proximity to the lake.

2.5.2. Geochemical Processes

The observations that Cl/Br ratios of groundwater range from 542 to 839, do not vary appreciably with increasing TDS, and are similar to those of both seawater and local precipitation (Fig. 2-3a) indicates that, in common with the majority of groundwater in southeast Australia (Cartwright et al., 2004; Bennetts et al., 2006), halite dissolution is not a significant contributor to groundwater salinity. Because Cl/Br ratios in halite generally exceed 10^4 (McCaffrey et al., 1987; Herczeg and Edmunds, 2000), substantial halite dissolution would be expected to result in much higher Cl/Br ratios than those observed. In addition, other than salt crusts that periodically form along the shores of Lake Murdeduke, there are no known deposits of halite within the study area. The salt crust from Lake Murdeduke had a Cl/Br ratio of approximately 4,800, which is much higher than that of groundwater. While dissolution of salt crust most likely occurs periodically, the lack of elevated Cl/Br ratios implies that this salt is not a major contributor to groundwater salinity.

Molar Na/Cl ratios of groundwater are generally similar to those of both seawater and precipitation and do not vary markedly with increasing TDS (Fig. 2-3b). Only in low TDS groundwater are more elevated Na/Cl ratios (up to 1.6) evident, which suggests that only

minor weathering of silicate minerals occurs. In addition, there is no correlation between $\delta^{13}C$ values and HCO_3, Ca or Mg concentrations, implying that calcite and/or dolomite dissolution are not significant processes. This is consistent with there being no major carbonate deposits in the study area, although calcite minerals may be present as cements, veins or evaporite minerals within the Lake Murdeduke (Tweed et al., 2011). Groundwater $\delta^{13}C$ values are variable (-17.5 to -10.8‰), which is likely the result of minor dissolution of calcite, in combination with a variable $\delta^{13}C$ signature of through-flow from Lake Murdeduke.

Decreasing molar abundance of bicarbonate with increasing TDS (Fig. 2-3c) suggests that precipitation of calcite minerals occurs as a result of evapotranspiration. This hypothesis is supported by the observation that, with but three exceptions (bores 110191, 110195 and 112241), the groundwater is oversaturated with respect to calcite (Table 2-2, saturation indices calculated using PHREEQC: Parkhurst and Appelo, 2013).

2.5.3. Climatic Controls

Both $\delta^{13}C$ values and $a^{14}C$ of groundwater southeast (down gradient) of Lake Murdeduke decrease in the direction of groundwater flow (Fig. 2-5a). In addition, the deuterium excess increases and TDS decreases in the flow direction (Fig. 2-4b), implying that the groundwater close to Lake Murdeduke is more evaporated than water further down the flow path. The decrease in $a^{14}C$ is due to radioactive decay as groundwater moves away from Lake Murdeduke. There are no processes, however, that can decrease the TDS of groundwater along a flow path. Likewise, in the absence of high-temperature water-rock interaction, there are no processes that increase d-excess (Clark and Fritz, 1997). These trends, therefore, most likely represent a progressive increase in evaporation at Lake Murdeduke over time. Similarly, as there are few processes that decrease the $\delta^{13}C$ values of DIC in groundwater (Clark and Fritz, 1997), it is also likely that the variation in groundwater $\delta^{13}C$ values also reflect changes to the $\delta^{13}C$ values of Lake Murdeduke water over time as a result of evaporation. Although enrichment of $\delta^{2}H$ and $\delta^{18}O$ in evaporating water is well documented, comparatively little is known about the effect of evaporation on $\delta^{13}C$ values.

However, in a series of laboratory experiments, Horton et al. (2015) demonstrated that evaporation of lake water can lead to enrichment in $\delta^{13}C$ of dissolved inorganic carbon (DIC) due to equilibrium exchange with atmospheric carbon dioxide. The data from this study may represent the first field scale evidence of variable $\delta^{13}C$ enrichment due to changes in the degree of evaporation of lake water.

2.5.4. Groundwater Residence Times

Determination of groundwater residence times using Eq. (2-1) requires an estimate of q, the proportion of DIC derived from the recharging water. While there are no limestones in the Barwon River Catchment, minor dissolution of calcite from veins, cements, and the soil zone is still possible. Since the $\delta^{13}C$ of such calcite is unknown and can potentially be variable (Quade et al., 1995; Quade and Cerling, 2013), it is not possible to estimate the proportion of DIC contributed from calcite dissolution using isotope mass balance (e.g. Ingersol and Pearson, 1964; Tamers, 1967; Fontes and Garnier, 1979). Additionally, such calculations assume predominantly closed system dissolution of calcite whereas open-system calcite dissolution in the unsaturated zone may also occur and may increase $\delta^{13}C$ values without significantly impacting $a^{14}C$ (Clark & Fritz, 1997; Cartwright et al., 2013b). Similarly, if calcite precipitation has occurred, the major ion geochemistry does not allow the proportion of DIC derived from carbonate dissolution to be estimated.

The highest recorded $a^{14}C$ of 87.53 pMC is from bore 110533, which is in the recharge area northwest of Lake Murdeduke. This groundwater has a ^{3}H activity of ~1.4 TU, which suggests that the groundwater was recently recharged. Assuming that the ^{14}C in this groundwater is modern, this implies that there has been a contribution of ~12% old carbon from the aquifer matrix. Estimates of between 0 and 17% contribution by calcite dissolution to DIC in groundwater (i.e. q values of 0.83 to 1.0) from non-carbonate aquifers in southeast Australia were made by Love et al. (1994), Cartwright et al. (2010, 2012), Atkinson et al. (2014) and Raiber et al. (2015). In keeping with those studies, q values of between 0.85 and 0.95 are adopted here. A q value of 0.85 is frequently cited as typical for non-carbonate

aquifers (e.g., Clark and Fritz, 1997) and the groundwater chemistry data indicate that at least some calcite dissolution is occurring, implying that q is less than 1.0. For these q values, groundwater residence times calculated using Eq. (2-1) vary from modern at bores 26683, 110193 and 110533 to 21,860 years at bore 110705 (Table 2-3).

The mean residence time (MRT) of groundwater was also estimated using the Piston Flow Model (PFM) and the Dispersion Model (DM) within TracerLPM. The PFM, which assumes that no hydrodynamic dispersion occurs between the recharge area and the sampling point, is similar to the use of Eq. (2-1) except that A_0 can be varied with time. In contrast, the DM allows for variable degrees of dispersion through use of the dispersion parameter D_p. The dispersion parameter represents the ratio of dispersion to advection and, as its value approaches zero, advection becomes the dominant process controlling tracer transport. The DM can apply to a variety of aquifer configurations and is considered to best represent the flow system within the study area. In this study, two values of the dispersion parameter were employed, 0.05 and 0.5, as the range defined by these values applies to most flow systems of this scale (Zuber and Maloszewski, 2001; Gelhar et al., 1992). The ^{14}C record for the southern hemisphere in Jurgens et al. (2012) was used for A_0. As with the calculations above, it was assumed that there was a contribution of between 5 and 15% ^{14}C-free carbon to the DIC.

MRTs estimated using the PFM varied from modern at bores 26683, 110193 and 110533 to 25,165 years at bore 110705 (Table 2-3, Fig. 2-9). At most locations, MRTs calculated using the PFM exceeded those determined using Eq. (2-1) by less than 10%, with the relative difference increasing as residence time increased. For groundwater with a^{14}C > ~70 pMC, MRTs calculated using the PFM were shorter than those determined using Eq. (2-1). This is due to the fact that atmospheric a^{14}C (A_0) within the southern hemisphere has often been below 100 pMC, which Eq. (2-1) does not account for. MRTs estimated using the DM varied from modern at bores 26683, 110193 and 110533 to 57,510 years at bore 110705 (Table 2-3, Fig. 2-9). MRTs calculated using the DM were typically longer, but not significantly so, than those determined using Eq. (2-1) or the PFM when D_p was set equal to 0.05. Significant

differences between MRT estimates only become apparent when D_p was set equal to 0.5, leading to relative differences in MRTs as high as 90% (in groundwater with $a^{14}C$ <10 pMC). The variability in groundwater residence times determined using the three methods demonstrates the uncertainties in using radioactive tracers to determine groundwater residence times.

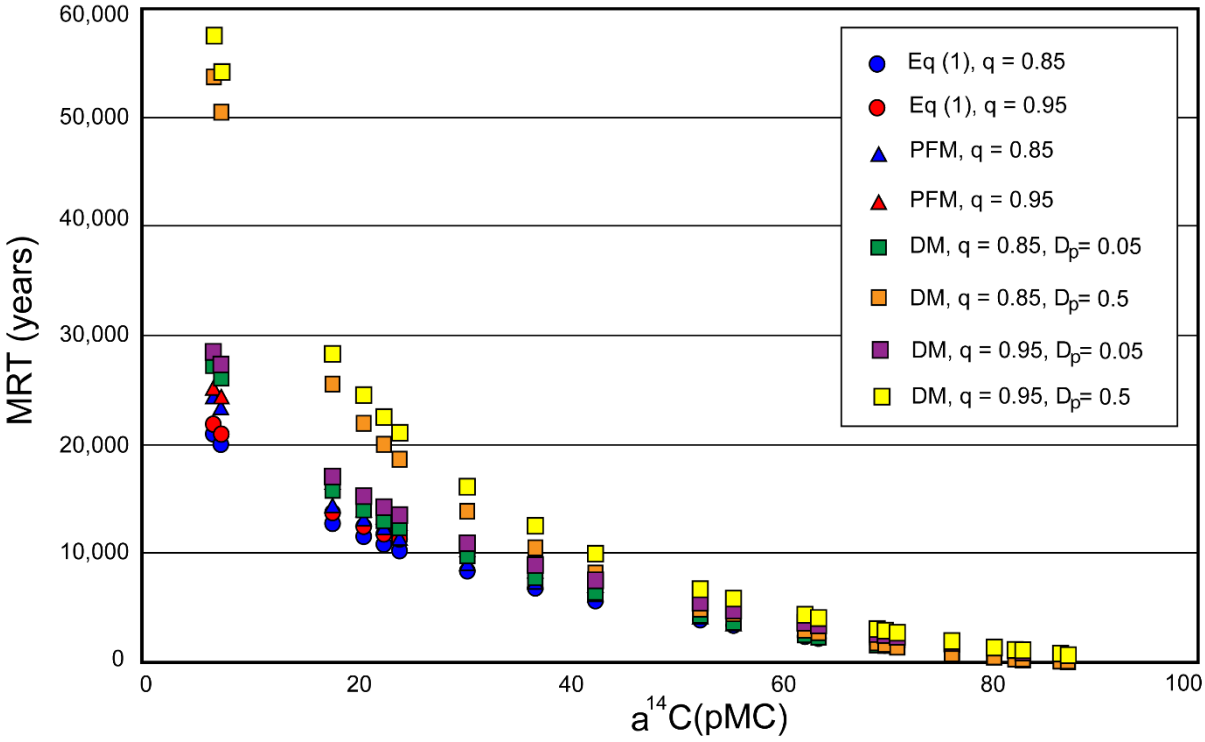

Figure 2-9: Mean residence times (MRTs) for groundwater calculated using Eq. 2-1, the Piston Flow Model (PFM) and the Dispersion Model (DM) for q = 0.85 & 0.95 and D_p = 0.05 & 0.5.

Bore ID	^{3}H	^{14}C	^{14}C Age, Eq. 2-1		PFM		DM				Cl^- Accession Time
			q = 0.85	q = 0.95	q = 0.85	q = 0.95	q = 0.85		q = 0.95		
							D_p = 0.05	D_p = 0.5	D_p = 0.05	D_p = 0.5	
	TU	pMC	years	years	years	years	years	years	years	years	years
26683	0.511	86.84	Modern	742	Modern	720	Modern	202	716	762	6,296
110140	-	52.78	3,939	4,859	4,179	5,478	4,297	5,110	5,439	6,692	2,642
110190	-	20.97	11,570	12,489	13,165	13,964	13,968	21,946	15,256	24,535	16,285
110191	-	62.68	2,518	3,438	2,419	3,540	2,533	2,937	3,667	4,304	3,682
110193	0.127	83.27	Modern	1,089	Modern	990	Modern	305	1,000	1,132	538
110194	-	30.76	8,403	9,322	9,075	10,255	9,746	13,945	10,928	16,123	16,023
110195	-	70.28	1,572	2,491	1,410	2,415	1,468	1,697	2,501	2,900	4,761
110196	0.010	82.55	242	1,161	240	1,025	258	337	1,063	1,211	1,996
110533	1.399	87.53	Modern	677	Modern	662	Modern	Modern	664	693	789
110534	0.005	42.88	5,656	6,576	6,340	7,100	6,407	8,167	7,511	9,986	1,511
110535	-	55.92	3,461	4,381	3,559	4,888	3,704	4,350	4,857	5,864	1,068
110700	-	22.88	10,849	11,769	12,482	13,225	12,979	20,013	14,251	22,509	15,556
110702	-	24.36	10,331	11,250	11,403	12,755	12,266	18,643	13,523	21,071	15,872
110705	-	6.75	20,940	21,860	24,270	25,165	27,193	53,719	28,499	57,510	7,609
110706	0.826	80.57	442	1,362	405	1,293	475	467	1,256	1,445	1,716
110979	-	76.57	863	1,783	750	1,619	806	883	1,689	1,957	2,449
111232	-	7.52	20,047	20,967	23,385	24,379	26,042	50,475	27,348	54,164	12,701
111235	-	18.02	12,823	13,742	14,389	16,554	15,756	25,566	17,059	28,321	1,837
111236	-	63.97	2,350	3,269	2,230	3,420	2,331	2,702	3,454	4,041	1,844
111787	0.002	69.50	1,664	2,584	1,475	2,550	1,566	1,813	2,615	3,034	683
112240	-	37.19	6,833	7,753	7,530	8,390	7,823	10,520	8,945	12,495	474
112241	0.073	71.41	1,440	2,360	1,349	2,290	1,337	1,542	2,349	2,723	227

Table 2-3: Groundwater and chloride residence times. PFM = Piston Flow Model, DM = Dispersion Model.

The residence times of groundwater, in combination with groundwater elevations and distances between the bores, allow the horizontal and vertical hydraulic conductivities of the Newer Volcanics basalt to be estimated using Darcy's Law. In these calculations, an effective porosity of 5% was assumed, which is at the upper end of the range (1-5%) suggested by Finegan (1996) for the Newer Volcanics basalt near Melbourne. Hydraulic conductivity values were calculated using groundwater ages derived from Eq. (2-1). However, these estimates do not change appreciably if MRTs from the Piston Flow Model or Dispersion Model are utilised instead. Horizontal hydraulic conductivities for the basalt range from $2x10^{-2}$ to $5x10^{-2}$ m/day while vertical horizontal conductivities are between $2x10^{-5}$ and $2x10^{-4}$ m/day (Table 2-4). An inherent assumption in these calculations is that the hydraulic gradient has not changed appreciably with time. The calculated horizontal hydraulic conductivity values are more than two orders of magnitude lower than that (8.6 m/day) estimated by Coram (1996) for the younger-phase basalts. However, those estimates were based on slug tests, which typically examine a very small area around a bore, whereas the estimates from this study are regional in scale. In addition, it is possible that the bores were screened across fractures to ensure groundwater entry or that drilling may have disturbed the adjacent basalt. Lastly, lack of detailed geologic mapping in the area does not allow us to distinguish whether these values are representative of the younger or older-phase Newer Volcanic basalts. Due to a lack of bores, hydraulic conductivities could not be calculated for the Moorabool Viaduct Sand or lunette deposits.

Bore Pair	Distance (m)	GW Elevation (m AHD)	Hydraulic. Gradient	Residence Time (years)	K_x (m/day)	K_z (m/day)
111787	2,860	102.15	0.005	1,664	$2x10^{-2}$	-
110534		88.47		5,656		
111787	2,850	102.15	0.004	1,664	$5x10^{-2}$	-
110535		89.70		3,461		
110191	1,760	78.23	0.001	2,518	$3x10^{-2}$	-
110194		75.76		8,403		
110700	2,530	78.52	0.002	10,849	$2x10^{-2}$	-
110705		73.00		20,940		
110979	39	78.63	0.003	863	-	$2x10^{-4}$
110700		78.52		10,849		
110706	31	73.37	0.012	442	-	$2x10^{-5}$
110705		73.00		20,940		

Table 2-4: Hydraulic conductivity estimates for the Newer Volcanic basalt based upon groundwater elevations and distances between bore pairs and groundwater residence times determined using $a^{14}C$ and Equation 2-1. K_x = horizontal hydraulic conductivity, K_z = vertical hydraulic conductivity.

2.5.5. $R^{36}Cl$ and Chloride Residence Times

$R^{36}Cl$ values of groundwater in the Barwon catchment (22.4 to 53.7 x 10^{-15}) are greater than those of both local modern precipitation (13.7 to 20.2 x 10^{-15}) and the predicted rainfall $R^{36}Cl$ value of ~20 x10^{-15} (Davie et al., 1989). Consequently, it is not possible to determine chloride residence times using Eq. (2-2). Possible reasons for the $R^{36}Cl$ values in groundwater being higher than those of modern precipitation are: 1) input of bomb-pulse ^{36}Cl into groundwater during the 1950s and 1960s (Bentley et al. 1982); 2) $R^{36}Cl$ values in rainfall in the past have been higher than at present; 3) deep, subsurface (hypogene) production of ^{36}Cl through nuclear reactions involving uranium, thorium and/or their daughter products (Andrews et al., 1986); and/or 4) shallow, near-surface (epigene) production of ^{36}Cl as a result of cosmic ray spallation of potassium and calcium and/or neutron capture by ^{35}Cl (Phillips et al., 1983). Each of these possibilities is discussed briefly below.

The elevated $R^{36}Cl$ values at bores 112241 ($53.7x10^{-15}$) and 110193 ($44.5x10^{-15}$) likely reflect the input of bomb-pulse ^{36}Cl. Both waters have measurable tritium, as well as ^{14}C activities that are close to the maximum observed, which suggests that some fraction of the water is derived from recharge 50 to 60 years ago during the nuclear testing era.

A strong indication that $R^{36}Cl$ values of rainfall during the past were different than they are presently is provided by the salt crust sample collected from Lake Murdeduke. Its $R^{36}Cl$ of $29x10^{-15}$ is significantly higher that the value of ~$20x10^{-15}$ measured in present day rainfall. As the $R^{36}Cl$ value is a function of both ^{36}Cl fallout and Cl deposition, a change in either of the two parameters will cause the ratio to vary. Chloride deposition is sensitive to distance from the coast (Bentley et al., 1986b; Keywood et al., 1997, 1998), especially in areas relatively close to the coast such as the present study location. During the last glacial maximum, the coast line would have been much further away; thus, chloride deposition would have been lower, resulting in higher $R^{36}Cl$ values in rainfall. Since the chloride in Lake Murdeduke must represent at least tens of thousands of years of accumulation, its $R^{36}Cl$ value will represent an average over a period of time during which the coastline has moved substantially. Hence, it is not surprising that the salt crust sample's $R^{36}Cl$ value is nearly 50% higher than that of modern rainfall.

Deep, hypogene production of ^{36}Cl by nuclear reactions only becomes significant after 1 ma or more. As discussed below, it is unlikely that the residence time of Cl in the catchment is that long. Similarly, significant epigene production of ^{36}Cl requires long exposure at or close to the surface and again is unlikely to make an important contribution.

While it is not possible to determine precise residence times from the $R^{36}Cl$ values, some broad constraints may be made. Excluding bores 112241 and 110193, where bomb pulse input is suspected, the $R^{36}Cl$ values of the groundwater are relatively similar and do not decrease along the groundwater flow paths or with depth. In addition, there are no correlations between $R^{36}Cl$ values and $a^{14}C$ or Cl concentrations. These observations suggest that limited decay of ^{36}Cl has occurred. In turn, this implies that the residence time

of Cl in the Barwon catchment may be a few thousand to tens-of thousand years old but not hundreds of thousands of years.

2.5.6. Chloride Accession Times

Chloride accession times for the Newer Volcanics basalt, Moorabool Viaduct Sand and lunette deposits were estimated using Eq. (2-3), measured chloride concentrations in groundwater (Table 2-2), estimates of average aquifer thicknesses and porosity, and a Cl deposition rate of 2,400 mg/year. The Cl deposition rate is based upon an average chloride concentration in rainfall of 6 mg/L, derived from Blackburn and McLeod (1983) and Crosbie et al. (2012), and an average annual rainfall of 400 mm/year, which is approximately that of Inverleigh. The porosities of the Newer Volcanics basalt, the Moorabool Viaduct Sand and lunette deposits are unknown but, for the purposes of these calculations, are assumed to be 5%, 15% and 10%, respectively. Likewise, the average saturated thickness of these units is assumed to be 30 m, 10 m and 10 m, respectively. Chloride accession times range from approximately 225 years at bore 112241 to approximately 16,000 years at bores 110190 and 110194 (Table 2-3). The accession times listed in Table 2-3 are conservative estimates, as increases in either porosity or aquifer thickness would increase the accession times. Likewise, in keeping with the interpretation of the $R^{36}Cl$, if this region was further inland in the past Cl deposition rates would likely be lower (based on modern distribution of Cl concentrations in rainfall (Blackburn and McLeod, 1987)), which would also increase the estimated accession times. At around half of the localities, the chloride accession time exceeds the groundwater residence time calculated using $a^{14}C$. In general, chloride accession times in groundwater immediately downgradient of Lake Murdeduke are greater than the groundwater residence times calculated using ^{14}C, while groundwater upgradient or far from the lake have similar (or lower) Cl accession and residence times. Chloride residence times calculated in this manner are at best broad estimates; nonetheless, these results suggest that chloride is being recycled within the study area and is locally older than the groundwater in which it is contained. This in turn suggests that any estimate of aquifer recharge based upon groundwater Cl concentrations would be underestimated.

A key assumption in estimating recharge via the chloride mass balance method, as well as determining chloride accession times, is that runoff is negligible so that all chloride delivered via rainfall enters the subsurface. If significant runoff occurs, some of the chloride delivered by rainfall is diverted away from the recharge area, which in turn results in lower chloride concentrations in groundwater. To test the assumption of negligible runoff, the annual volume of water exported by Mia Mia Creek (Fig. 2-1) was compared to that of average annual rainfall. Except for flood events in 2001, 2003 and 2005, average flow within Mia Mia Creek during the period 1997 to 2009 was approximately 3.3×10^5 m^3/year (DELWP, 2015). In comparison, based upon a catchment area of 1.1×10^8 m^2 (Milne, 2008) and an average annual rainfall of 0.4 m (Bureau of Meteorology, 2016), approximately 4.4×10^7 m^3 of rainfall is delivered to the catchment each year. The volume of water exported by Mia Mia Creek is thus less than 1% of that delivered by rainfall. In addition, much of the water in the rivers in the Barwon River Catchment is derived from groundwater inflows rather than from direct runoff (Cartwright et al., 2013b). Overall, these observations suggest that export of Cl via runoff is minimal.

2.6. Conclusions

Elevated groundwater salinity in the Barwon River Catchment is primarily the result of the inflow of highly saline water from Lake Murdeduke, a through flow lake located in the centre portion of the catchment. Highly saline lake water enters the shallow groundwater system, is transported eastward through the Moorabool Viaduct Sand and the Newer Volcanics basalt, and then discharges into the Barwon River. Groundwater residence times estimated from $a^{14}C$ are up to ~20 ka. Significant differences in estimated residence times in groundwater with low $a^{14}C$ result from adoption of different flow models and the use of different input functions for ^{14}C in rainfall. While studies of ^{14}C in groundwater commonly consider corrections for ^{14}C-free carbon inputs, there have been few studies that have looked at the impacts of adopting different flow models or varying ^{14}C in recharge. This study shows that, especially in groundwater with long residence times, varying these conditions can produce significantly different results.

Even using conservative assumptions, chloride accession times downgradient of Lake Murdeduke are greater than the residence times of the groundwater in which it is contained. This study is one of only a few to attempt to estimate the residence time of solutes and groundwater and while it was not possible to calculate Cl residence times using ^{36}Cl, the lack of significant ^{36}Cl decay implies that the residence time of Cl is on the order of tens of thousands of years not longer. Based upon a ^{14}C in groundwater, the horizontal hydraulic conductivity of the Newer Volcanics basalt is approximately 10^{-2} m/day while vertical horizontal conductivities range from approximately 10^{-5} to 10^{-4} m/day.

Other saline lakes elsewhere in this and adjacent catchments operate in a similar way and produce high salinity groundwater throughout the Newer Volcanics Province (Bennetts et al., 2007). In these and other semi-arid catchments globally, similar decoupling of solutes and water is likely and this must be taken into account in using Cl to understand hydrological processes. Specifically, Cl concentrations will underestimate recharge rates calculated using chloride mass balance. This study also illustrates the utility of isotope tracers in assessing environmental change. While the use of oxygen and hydrogen isotopes in this regard is well established, the variation in $R^{36}Cl$ and $\delta^{13}C$ values in the Barwon River groundwater also reflect environmental change. The observation that $R^{36}C$ values in rainfall were likely higher in the past than they are at present is most probably related to sea level changes and consequently the distance of this area from the coast. The increase in $\delta^{13}C$ values in groundwater downgradient of the Lake Murdeduke suggest that the region has experienced increasingly more evaporative conditions with time.

2.7. Acknowledgements

Field work and laboratory analyses were conducted with the help of Massimo Raveggi, Rachelle Pearson, Kwadwo Osei-Bonsu, Wang Dong and Lei Chu. We also thank Steve Tims, Anton Wallner and Michaela Froehlich for assistance with the ^{36}Cl measurements. Funding for this project was provided by Monash University and the National Centre for Groundwater Research and Training (NCGRT). NCGRT is an Australian Government initiative

supported by the Australian Research Council and the National Water Commission. In addition, two anonymous reviewers provided valuable and instructive feedback.

2.8. References

Allison, G.B. and M.W. Hughes, 1978. The use of environmental chloride and tritium to estimate total recharge to an unconfined aquifer. Australian Journal of Soil Research, Vol. 16, pp. 181-195.

Andrews, J.N., Fontes, J.-Ch., Mechelot, J.L. and D. Elmore, 1986. In-situ neutron flux, ^{36}Cl production and groundwater evolution in crystalline rocks at Stripa, Sweden. Earth and Planetary Science Letters, Vol. 77, pp. 49-58.

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Cendon, D.I., Unland, N.P. and H. Hoffman, 2014. Using ^{14}C and ^{3}H to understand groundwater flow and recharge in an aquifer window. Hydrol. Earth Syst. Sci., Vol. 18, pp. 4951-1964.

Bennetts, D.A., Webb, J.A., Stone, D.J.M. and D.M. Hill, 2006. Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. Journal of Hydrology, Vol. 323, pp. 178-192.

Bentley, H.W., Phillips, F.M., Davis, S.N., Gifford, S., Elmore, D., Tubbs, L.E. and H.E. Gove, 1982. Thermonuclear ^{36}Cl pulse in natural water. Nature, Vol. 300, pp. 737-740.

Bentley, H.W., Phillips, F.M., David, S.N., Habermehl, M.A., Airey, P.L., Calf, G.E., Elmore, D., Gove, H.E. and T. Torgersen, 1986a. Chlorine 36 dating of very old groundwater 1. The Great Artesian Basin, Australia. Water Resources Research, Vol. 22 (13), pp. 1991-2001.

Bentley, H.W., Phillips, F.M. and S.N. Davis, 1986b. Handbook of Environmental Isotope Geochemistry. The Terrestrial Environment (Amsterdam: Elsevier) vol. 2, p 427.

Bird, J.R., Calf, G.E., Davie, R.F., Fifield, L.K., Ophel, T.R., Evans, W.R., Kellet, J.R. and M.A. Habermehl, 1989. The role of ^{36}Cl and ^{14}C measurements in Australian groundwater studies. Radiocarbon, Vol. 31(3), pp. 877-883.

Blackburn, G. and S. McLeod, 1983. Salinity of Atmospheric Precipitation in the Murray-Darling Drainage Division, Australia. Australian Journal of Soil Research, Vol. 21, pp. 411-434.

Bureau of Meteorology (BOM), 2016. http://www.bom.gov.au, last access 21 January 2016.

Cartwright, I., Weaver, T.W., Fulton, S., Nichol, C., Reid, M. and X. Cheng, 2004. Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. Applied Geochemistry, Vol. 19, pp. 1233-1254.

Cartwright, I., Weaver, T.R., Simmons, C., Fifield, L.K., Lawrence, C.R., Chisari, R. and S. Varley, 2010. Physical hydrogeology and environmental isotopes to constrain the age, origins, and stability of a low-salinity groundwater lens formed by periodic river recharge: Murray Basin, Australia. Journal of Hydrology, Vol. 380, pp. 203-221.

Cartwright, I., Weaver, T.R., Cendon, D.I., Fifield, L.K., Tweed, S.O., Petrides, B. and I. Swane, 2012. Constraining groundwater flow, residence times, inter-aquifer mixing, and aquifer properties using environmental isotopes in the southeast Murray Basin, Australia. Applied Geochemistry, Vol. 27, pp. 1698-1709.

Cartwright, I., Fifield, L.K. and U. Morgenstern, 2013a. Using ^{3}H and ^{14}C to constrain the degree of closed-system dissolution of calcite in groundwater. Applied Geochemistry, Vol. 32, pp. 118-128.

Cartwright, I., Gilfedder, B. and H. Hoffman, 2013b. Chloride imbalance in a catchment undergoing hydrological change: Upper Barwon River, southeast Australia. Applied Geochemistry, Vol. 31, pp. 187-198.

Clark, I.D and P. Fritz, 1997. Environmental Isotopes in Hydrogeology. CRC Press/Lewis Publishers, Boca Raton.

Coplen, T.B., 1988. Normalisation of oxygen and hydrogen isotope data. Chemical Geology, Vol. 72, pp. 293-297.

Coram, J.E., 1996. Groundwater-surface water interactions around shallow lakes of the Western District Plains, Victoria. Master of Science, University of Melbourne.

Craig, H., 1961. Isotopic Variations in Meteoric Waters. Science, New Series, Vol. 133, No. 3465, pp. 1702-1703.

Crosbie, R.S., Morrow, D., Cresswell, R.G., Leaney F.W., Lamontagne, S. and M LeFournour, 2012. New insights to the chemical and isotopic composition of rainfall across Australia. CSIRO Water for a Healthy Country Flagship, Australia.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus, Vol. 16 (4), pp. 436-468.

DataSearch Victoria: Victoria Department of Sustainability and Environment Spatial Warehouse, http://services.land.vic.gov.au/SpatialDatamart/index.jsp, last access: 10 June 2015.

Davie, R.F., Kellett, J.R., Fifield, L.K., Evans, W.R., Calf, G.E., Bird, J.R., Topham, S. and T.R. Ophel, 1989. Chlorine-36 measurements in the Murray Basin: preliminary results from the Victorian and South Australian Mallee region. In: BMR Journal of Australian Geology and Geophysics, Vol. 11, pp. 261-272.

Davis, S.N., Whittemore, D.O. and J. Fabryka-Martin, 1998. Uses of chloride/bromide ratios in studies of potable water. Ground Water, Vol. 36(2), pp. 338-350.

Davis, S.N., Cecil, L.D., Zreda, M., and S. Moysey, 2001. Chlorine-36, bromide and the origin of spring water. Chemical Geology, Vol. 179, pp. 3-16.

Department of Environment, Land, Water and Planning, Water Measurement Information System (WMIS), http://data.water.vic.gov.au/monitoring.htm, last access: 10 June 2015.

Drever, J.I., 1997. The Geochemistry of Natural Water: Surface and Groundwater Environments. Prentice-Hall, New Jersey, USA. 436 p.

Edmunds, W.M., 2009. Geochemistry's vital contribution to solving water resource problems. Applied Geochemistry, Vol. 24, pp. 1058-1073.

Fifield, L.K., 1999. Accelerator mass spectrometry and its applications. Reports on Progress in Physics, Vol. 62, pp. 1223-1274.

Fifield, L.K., Tims, S.G., Stone, J.O., Argento, D.C. and M. De Cesare, 2013. Ultra-sensitive measurements of ^{36}Cl and ^{236}U at the Australian National University. Nuclear Instruments and Methods in Physics B, Vol. 294, pp. 126-131.

Finegan, J.M., 1996. Transport, attenuation, and degradation of organic chemicals in a basaltic aquifer system near Melbourne, Australia. PhD thesis. University of Melbourne. 295 p.

Fontes, J.C. and J.M. Garnier, 1979. Determination of the initial ^{14}C activity of the total dissolved carbon: age estimation of water in confined aquifer. In: Paquet, H. and Y. Tardy (Eds.), Proceedings of the Second International Symposium of Water-Rock Interaction, Vol. 1, pp. 363-376.

Gelhar, L.W., Welty, C. And K.R. Rehfeldt, 1992. A critical review of data on field-scale dispersion in aquifers. Water Resources Research, Vol. 28 (7), pp. 1955-1974.

Gill, B., 1989. Hydrogeological review of salinity problems in the Barwon/Corangamite region. Investigations Branch Report No. 1988/16. Rural Water Commission of Victoria. April 1989, 68 p.

Herczeg, A.I. and W.M. Edmunds, 2000. Inorganic ions as tracers. In: Cook, P., Herczeg, A. (Eds.), Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers, Boston, pp. 31-78.

Horton, T.W., Defliese, W.F., Tripati, A. and C. Oze, 2015. Evaporation induced ^{18}O and ^{13}C enrichment in lake systems: a global perspective on hydrologic balance effects. Quaternary Science Reviews, pp. 1-15.

Hughes, C.E. and J. Crawford, 2012. A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. Journal of Hydrology, Vol. 464-465, pp. 344-351.

Hutton, J.T. and T.I. Leslie, 1958. Accession of non-nitrogenous ions dissolved in rainwater to soils in Victoria. Australian Journal of Agricultural Research, Vol. 9, pp. 492-507.

Ingersol, E. and F.R. Pearson, Jr., 1964. Estimation of age and rate of motion of groundwater by the ^{14}C-method. Recent Researches in the Fields of Atmosphere, Hydrosphere, and Nuclear Geochemistry, Sugara Festival Volume, Eds. Y. Miyake and T Koyama, Maruzen, Tokyo.

Jurgens, B.C., Bohkle, J.K. and S.M. Eberts, 2012. TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data. US Geological Survey, Techniques and Methods Report 4-F3, US Geological Survey, Reston VA USA. 60 pp.

Keywood, M.D., Chivas, A.R., Fifield, L.K., Cresswell, R.G. and G.P. Ayers, 1997. The accession of chloride to the western half of the Australian continent. Aust. Journal of Soil Research, Vol. 35, pp. 1177-1180.

Keywood, M.D., Fifield, L.K., Chivas, A.R. and R.G. Cresswell, 1998. Fallout of chlorine 36 to the Earth's surface in the southern hemisphere. Journal of Geophysical Research, Vol. 103 (D7), pp. 8281-8286.

Kulongoski, J.T., Hilton, D.R., Cresswell, R.G., Hostetler, S. and G. Jacobson, 2008. Helium-4 characteristics of groundwaters from Central Australia: comparative chronology with chlorine-36 and carbon-14 dating techniques. Journal of Hydrology, Vol. 348, pp. 176-194.

Love, A.J., Herczeg, A.L, Leaney, F.W, Stadter M.F., Dighton, J.C. and D. Armstrong, 1994. Groundwater residence time and palaeohydrology in the Otway Basin, South Australia: ^{2}H, ^{18}O and ^{14}C data. Journal of Hydrology, Vol. 153, pp. 157-187.

Love, A.J., Herczeg, A.L., Sampson, L., Cresswell, R.G. and L.K. Fifield, 2000. Sources of chloride and implications for ^{36}Cl dating of old groundwater, southwestern Great Artesian Basin, Australia. Water Resources Research, Vol. 36(6), pp. 1561-1574.

McCaffrey, M.A., Lazar, B. and H.D. Holland, 1987. The evaporation path of seawater and coprecipitation of Br^- and K^+ with halite. Journal of Sedimentary Petrology, Vol. 57, pp. 928-937.

Milne, R., 2008. Leigh Catchment Action Plan: 2008 – 2013. Leigh Catchment Group, Buninyong, Victoria. 83 pp.

Morgenstern, U. and C.B. Taylor, 2009. Ultra low-level tritium measurement using electrolytic enrichment and LSC. Isotopes Environ. Health Stud., Vol. 45, pp. 96-117.

Parkhurst, D.L. and C.A.J. Appelo, 2013. Description of input and examples for PHREEQC Version 3 – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical reactions. U.S. Geological Survey Techniques and Methods, Book 6, Chapter A43, 497 p.

Petrides, B. and I. Cartwright, 2006. The hydrogeology and hydrogeochemistry of the Barwon Downs Graben aquifer, southwestern Victoria, Australia. Hydrogeology Journal, vol. 14, pp. 809-826.

Phillips, F.M., Smith, G.I., Bentley, H.W., Elmore, D. and H.E. Gove, 1983. Chlorine-36 dating of sediments: preliminary results from Searles Lake, California. Science, New Series, Vol. 222 (4626), pp. 925-927.

Phillips, P., Bentley, H.W., Davis, S.N., Elmore, D. and G.B. Swanick, 1986. Chlorine 36 dating of very old groundwater 2. Milk River Aquifer, Alberta, Canada. Water Resources Research, Vol. 22 (13), pp. 2003-2016.

Plummer, L.N., Eggleston, J.R., Andreasen, D.C., Raffensperger, J.P., Hunt, A.G. and G.C. Casile, 2012. Old groundwater in parts of the upper Patapsco aquifer, Atlantic Coastal Plain, Maryland, USA: evidence from radiocarbon, chlorine-36 and helium-4. Hydrogeology Journal, Vol. 20, pp. 1269-1294.

Quade, J., Chivas, A.R. and M.T. McCulloch, 1995. Strontium and carbon isotope tracers and the origins of soil carbonate in South Australia and Victoria. Palaeogeography, Palaeoclimatology, Palaeoecology, Vol. 113, pp. 103-117.

Quade, J. and T. Cerling, 2013. Carbonate stable isotopes; non-lacustrine terrestrial studies. In: Elias, S.A. and C.J. Mock (Eds.), Encyclopedia of Quaternary Science, pp. 322-332.

Raiber, M., Webb, J.A., Cendon, D.I., White, P.A. and G.E. Jacobsen, 2015. Environmental isotopes meet 3D geologic modelling: conceptualising recharge and structurally controlled aquifer connectivity in the basalt plain of southwestern Victoria, Australia. Journal of Hydrology, Vol. 527, pp. 262-280.

Roderick, P., 1988. Investigation of highly saline groundwater inflows between Winchelsea and Inverleigh. Investigations Branch Report No. 1988/7. Rural Water Commission of Victoria. August 1989, 27 p.

Scanlon, B.R., Keese, K.E., Flint, A.L., Flint, L.E., Gaye, C.B., Edmunds, W.M. and I. Simmers, 2006. Global synthesis of groundwater recharge in semiarid regions. Hydrologic Processes, Vol. 20, pp. 3335-3370.

Scheiber, L., Ayora, C., Vazquez-Sune, E., Cendon, D.I., Soler, A., Custodio, E. And J.C. Baquero, 2015. Recent and old groundwater in the Niebla-Posadas regional aquifer (southern Spain): Implications for its management. Journal of Hydrology, Vol. 523, pp. 624-635.

Stuiver, M. and H.A. Polach, 1977. Reporting of ^{14}C data. Radiocarbon, Vol. 19 (3), pp. 355-363.

Tamers, M.A., 1967. Validity of radiocarbon dates on groundwater. Geophysical Surveys, Vol. 2, pp. 217-239.

Tickell, S.J., Cummings, S., Leonard J.G. and J.A. Withers, 1991. Colac: 1:50 000 Map Geological Report. Geological Survey Report No. 89, Victoria Department of Manufacturing and Industry Development.

Tweed, S., Grace, M., Leblanc, M., Cartwright, I. and D. Smithyman, 2011. The individual response of saline lakes to a severe drought. Science of the Total Environment, Vol. 409, pp. 3919-3933.

Witebsky, S., Jayatilaka, C. and A. Shugg, 1995. Groundwater development options and environmental impacts, Barwon Downs Graben, southwestern Victoria. Victoria Department of Natural Resources and Environment Report.

Wood, W.W. and W.E. Sanford, 1995. Chemical and isotopic methods for quantifying ground-water recharge in a regional, semiarid environment. Ground Water, Vol. 33, pp. 459-468.

Zuber, A. and P. Maloszewski, 2001. Lumped Parameter Models. Environmental Isotopes in Hydrological Cycle, Vol. VI, Modelling. IAEA/UNESCO, Paris, Technical Document, pp. 5-36.

Chapter 3

Mean Transit Times in Headwater Catchments: Insights from the Otway Ranges, Australia

William Howcroft[1], Ian Cartwright[1, 2] and Uwe Morgenstern[3]

[1]School of Earth, Atmosphere and Environment, 9 Rainforest Walk, Monash University, Clayton, VIC 3800, Australia.

[2]National Centre for Groundwater Research and Training, [redacted] Flinders University, Adelaide, SA 5001, Australia.

[3]GNS Science, [redacted] New Zealand.

Correspondence to: [redacted]

Abstract

Understanding the timescales of water flow through catchments and the sources of stream water at different flow conditions is critical for understanding catchment behaviour and managing water resources. Here, tritium (^{3}H) activities, major ion geochemistry and streamflow data were used in conjunction with Lumped Parameter Models (LPMs) to investigate mean transit times (MTTs) and the stores of water in six headwater catchments in the Otway Ranges of southeast Australia. ^{3}H activities of stream water ranged from 0.20 to 2.14 TU, which are significantly lower than the annual average ^{3}H activity of modern local rainfall, which is between 2.4 and 3.2 TU. The ^{3}H activities of the stream water are lowest during low summer flows and increase with increasing stream streamflow. The concentrations of most major ions vary little with streamflow which, together with the low ^{3}H activities, imply that there is no significant direct input of recent rainfall at the streamflows sampled in this study. Instead, shallow younger water stores in the soils and regolith are most likely mobilised during the wetter months.

MTTs vary from approximately 7 to 230 years. Despite uncertainties of several years in the MTTs that arise from having to assume an appropriate LPM, aggregation errors, and uncertainties in the ^{3}H activities of rainfall, the conclusion that they are years to decades is robust. Additionally, the relative

differences in MTTs at different streamflows in the same catchment are estimated with more certainty. The MTTs in these and similar headwater catchments in southeast Australia are longer than in many catchments globally. These differences may reflect the relatively low rainfall and high evapotranspiration rates in southeast Australia compared with headwater catchments elsewhere.

The long MTTs imply that there is a long-lived store of water in these catchments that can sustain the streams over drought periods lasting several years. However, the catchments are likely to be vulnerable to decadal changes in landuse or climate. Additionally, there may be considerable delay in contaminants reaching the stream. An increase in nitrate and sulphate concentrations in several catchments at high streamflows may represent the input of contaminants through the shallow groundwater that contributes to streamflow during the wetter months. Poor correlations between ^{3}H activities and catchment area, drainage density, landuse, and average slope imply that the MTTs are not controlled by a single parameter but by variety of factors, including catchment geomorphology and the hydraulic properties of the soils and aquifers.

3.1 Introduction

Determining the timescales over which precipitation is transmitted from a recharge area through a catchment to where it discharges into rivers or streams (the transit time) is important to understanding catchment behaviour and is of inherent interest to resource managers. Streams with long MTTs are connected to relatively large stores of water in the underlying aquifers (Maloszewski and Zuber, 1982; Morgenstern et al., 2010) that may sustain streamflow during droughts that last up to a few years. However, longer-term changes, such as deforestation, agricultural development, climate change, and/or landscape change following bushfires is likely to affect both the quality and the quantity of river flows.

Headwater streams are important as they commonly support diverse ecosystems, provide recreational opportunities and, in many catchments, contribute a significant proportion of the total river flow (Freeman et al., 2007). Headwater streams also differ from lowland rivers in terms of their potential water inputs. Unlike lowland rivers, which typically receive groundwater inflows from regional aquifers or near-river floodplain sediments, the source(s) of water within headwater streams

are far less well understood. Headwater streams are commonly developed at elevations well above those of the regional water tables and/or occur on relatively impermeable bedrock. Yet such streams continue to flow even during prolonged dry periods. There are several potential water stores that could contribute to stream flow, including the soil zone, weathered or fractured basement rocks, and/or perched aquifers at the soil-bedrock interface (e.g. Sklash and Farvolden, 1979; Kennedy et al., 1986; Swistock et al., 1989; Bazemore et al., 1994; Fenicia et al., 2006; Jensco and McGlynn, 2011).

Estimates of MTTs in headwater catchments range from a few months to several decades (e.g. Soulsby et al., 2000; McGuire and McDonnell, 2006; Hrachowitz et al., 2009; McDonnell et al., 2010; Stewart and Fahey, 2010; Stewart et al., 2010; Mueller et al., 2013; Stockinger et al., 2014; Atkinson, 2014; Cartwright and Morgenstern, 2015, 2016a, 2016b; Duvert et al., 2016). However, in many regions globally, the range of MTTs in headwater catchments is not well known. Additionally, it is not always clear why MTTs vary between different areas. This lack of knowledge limits our abilities to protect and manage headwater catchments.

3.1.1 Estimating Mean Transit Times (MTTs)

Groundwater follows a myriad of flow paths between the recharge areas to where it discharges into streams or rivers. Consequently, groundwater does not have a discrete age but rather has a distribution of transit times. MTTs are commonly estimated using Lumped Parameter Models (LPMs) that describe the distribution of water with different ages or tracer concentrations in simplified aquifer geometries (Maloszewski and Zuber, 1982, 1996; Maloszewski et al., 1983; Cook and Bohlke, 2000; Maloszewski, 2000; Zuber et al., 2005). LPMs represent a viable and commonly-used alternative to estimating MTTs using numerical groundwater models that rely upon hydraulic parameters that are seldom known with certainty and which vary spatially. However, the LPMs are only approximations of actual flow systems and the MTTs may be broad estimates rather than specific values.

The LPMs may be utilised with stable (O, H) isotopes or major ions if the concentrations vary seasonally in rainfall (e.g., Soulsby et al., 2000; McGuire and McDonnell, 2006; Tetzlaff et al., 2007, 2009, Hrachowitz et al., 2009, 2010; Kirchner et al., 2010). Determining MTTs from stable isotope ratios or major ion concentrations relies on tracking the delay and dampening of the seasonal variations

between precipitation and discharge. However, use of these tracers typically requires sub-weekly sampling over time periods equal to or exceeding that of the transit times (Timbe et al., 2015). In addition, these tracers become ineffective when transit times exceed 4 to 5 years as the initial variations in rainfall are progressively dampened to below where they can be detected (Stewart et al., 2010).

Gaseous tracers (e.g. ^{3}He, chlorofluorocarbons, SF_6) are effective in determining residence times of groundwater (Cook and Bohlke, 2000) but are difficult to apply to surface water due to gas exchange. With a half-life of 12.32 years, tritium (^{3}H) has been used to estimate MTTs of up to 150 years (e.g. Morgenstern et al., 2010; Stewart et al., 2010). Unlike other radioactive tracers (e.g., ^{14}C), ^{3}H is part of the water molecule and its activities are affected only by radioactive decay and dispersion and not by geochemical or biogeochemical reactions in the soils or aquifers. Because ^{3}H activities are not affected by processes in the unsaturated zone, the MTTs reflect both recharge through the unsaturated zone and flow in the groundwater system.

Utilisation of ^{3}H as a tracer is facilitated by the fact that ^{3}H activities of rainfall have been measured globally for several decades (International Atomic Energy Agency, 2016). Due to atmospheric nuclear testing, ^{3}H activities in rainfall peaked during the 1950s and 1960s (the "bomb-pulse"). The bomb-pulse ^{3}H activities in the Southern Hemisphere were much lower than in the Northern Hemisphere (Tadros et al., 2014) and have now largely declined to below those of modern rainfall (Morgenstern et al., 2010). As a consequence, MTTs can generally be determined from single ^{3}H measurements (Morgenstern et al., 2010; Morgenstern and Daughney, 2012) in an analogous manner to how other radioactive isotopes (e.g., ^{14}C or ^{36}Cl) are used in regional groundwater systems. This also allows MTTs at different streamflows to be estimated (Morgenstern et al., 2010; Duvert et al., 2016; Cartwright and Morgenstern, 2015, 2016a, 2016b).

Using LPMs to estimate MTTs has a number of uncertainties. Due to the attenuation of the ^{3}H bomb-pulse in the Southern Hemisphere, the suitability of the LPM can no longer be evaluated by time-series ^{3}H measurements (Cartwright and Morgenstern, 2016a) as is still possible in the Northern Hemisphere (e.g. Blavoux et al., 2013). Hence, LPMs must be assigned based upon knowledge of the geometry of the flow system and/or information from previous time-series studies in similar catchments. While

not being able to assess the form of the LPM results in uncertainties in the calculated MTTs, the MTTs are less sensitive to the choice of LPM than is the case in the northern hemisphere (e.g. Blavoux et al., 2013).

Rivers can receive water from numerous stores, including groundwater, tributaries, soil water, and perched aquifers, each of which may have different MTTs. The mixing of water from different flow systems potentially produces water samples with a residence time distribution that does not correspond to those in the LPMs and calculated MTTs are lower than actual MTTs. This is known as the aggregation error (Kirchner, 2016; Stewart et al., 2017) and it increases as the difference between the transit times of the individual end-members increases. For transit times estimated from single ^{3}H activities, the aggregation error decreases with an increasing number of end-members as the mixing of numerous aliquots water with different transit times is similar to what is represented by the LPMs (Cartwright and Morgenstern, 2016a).

Despite the uncertainties in calculating MTTs, because the ^{3}H activities of the remnant bomb-pulse waters have largely decayed, Southern Hemisphere waters with low ^{3}H activities have longer MTTs than waters with high ^{3}H activities. This permits relative mean transit times to be readily assessed. Because ^{3}H is radioactive, there is no requirement for flow in the catchment to be time-invariant as long as the flow path geometry remains relatively constant.

3.1.2 Predicting Mean Transit Times

Fundamentally, MTTs are a function of the recharge rate, length of groundwater flow paths, and rates of groundwater flow and parameters that control these factors will control the MTTs. Large catchments may have some long groundwater flow paths and consequently have long MTTs (e.g. McGlynn et al., 2003; Hrachowitz et al., 2010). Catchments with higher drainage densities (i.e., higher total stream length per unit area) may contain numerous short groundwater flow paths and consequently have short MTTs (e.g. Hrachowitz et al., 2009). Large groundwater storage volumes will likely also result in long MTTs (e.g. Ma and Yamanaka, 2016). Groundwater flow is likely to be more rapid through steeper catchments due to the higher hydraulic gradients, resulting in shorter MTTs (e.g. McGuire et al., 2005). Forested catchments may have higher evapotranspiration and lower recharge

rates than cleared catchments (Allison et al., 1990), and the degree of forest cover exerts a control on MTTs (e.g., Tetzlaff et al., 2007). The hydraulic conductivities of the bedrock and soils are also important in controlling the timescales of water movement through catchments (e.g. Tetzlaff et al., 2009; Hale and McDonnell, 2016).

Identifying the controls on MTTs is important for understanding catchment functioning. It also potentially allows first order estimates of MTTs to be made in similar catchments for which detailed geochemical tracer data do not exist. In some catchments, correlations between ^{3}H activities and major ion geochemistry or the runoff coefficient (the proportion of rainfall exported from the catchment by the stream) also allow first order estimates of MTTs to be made (Morgenstern et al., 2010; Cartwright and Morgenstern, 2015, 2016a).

3.2 Objectives

This study evaluates the range of and controls on MTTs in headwater streams from the upper Gellibrand catchment of the Otway Ranges in southeast Australia. Specifically, we test the following hypotheses. Firstly that, in common with headwater catchments elsewhere in southeast Australia, the MTTs are several years to decades. Secondly, that the MTTs are most likely controlled by catchment attributes such as land cover, slope, or drainage density. Lastly, that shallower water stores within the catchment become progressively mobilised during higher rainfall periods contribute to streamflow at those times. We also use this study to assess whether there are geochemical proxies that could be used to make first order predictions of MTTs at times when no ^{3}H data is available. Documenting MTTs is critical to understanding and protecting headwater catchments and, while this study is based on a specific area, the results have relevance to catchments globally. There is not a complete understanding of the range of MTTs in headwater catchments, nor what controls these. Thus, these are important gaps in our understanding of headwater catchments.

3.3 Study Area

The Otway Ranges are located in southern Victoria, Australia, approximately 150 km southwest of Melbourne (Fig. 3-1). The region has a temperate climate, with average rainfall varying from approximately 1,000 mm yr^{-1} at Gellibrand and Forrest to approximately 1,600 mm yr^{-1} at Mount

Sabine (Department of Environment, Land, Water and Planning, 2017) (Fig. 3-1) with the majority of rainfall occurring during the austral winter (July to September). Average potential evapotranspiration is 1,000 to 1,100 mm yr^{-1} and exceeds precipitation during the summer months (Bureau of Meteorology, 2016). The Otway Ranges occur within the Great Otway National Park, and hold ecological, cultural, historical and recreational significance. Much of the area is dominated by eucalyptus forest but includes some commercial forestry, much of which is also eucalyptus.

The geology of the study area is described by Tickell et al. (1991). The basement comprises the Early Cretaceous Otway Group, which consists primarily of volcanogenic sandstone and mudstone with minor amounts of shale, siltstone, and coal. The Otway Group is considered to be a poor aquifer and crops out across most of the Lardners Creek and Gellibrand River Catchments, as well as within the higher elevation areas of the Yahoo Creek and Ten Mile Creek catchments (Fig. 3-1).

The Otway Group is uncomformably overlain by Tertiary sediments of the Eastern View Formation, Demons Bluff Formation, Clifton Formation and Gellibrand Marl. The Eastern View Formation is composed of three sand and gravel units that collectively form the Lower Tertiary Aquifer. These sediments crop out at various locations across the study area including at the Barongarook High (Fig. 3-1), which is the primary recharge area for the aquifer (Stanley, 1991; Petrides and Cartwright, 2006). The Eastern View Formation is overlain by the Demons Bluff Formation, which is a calcareous silt having negligible permeability. The formation crops out sparsely within the study area, mainly along Yahoo and Ten Mile Creeks. Overlying this unit is the Clifton Formation, which is a limonitic sand and gravel aquifer. This unit crops out along Porcupine, Ten Mile, Yahoo and Love Creeks. The Clifton Formation is overlain by the Gellibrand Marl, which consists of approximately 200 to 300 m of calcareous silt. The Gellibrand Marl crops out extensively within the Love Creek and Porcupine Creek catchments and acts as a regional aquitard. Along Love Creek and parts of the Gellibrand River, the Tertiary units have been intruded by the Yaugher Volcanics, which consist primarily of basalt, tuff and volcanic breccia. Deposits of alluvium are present along most of the stream courses, particularly Porcupine Creek and Love Creek.

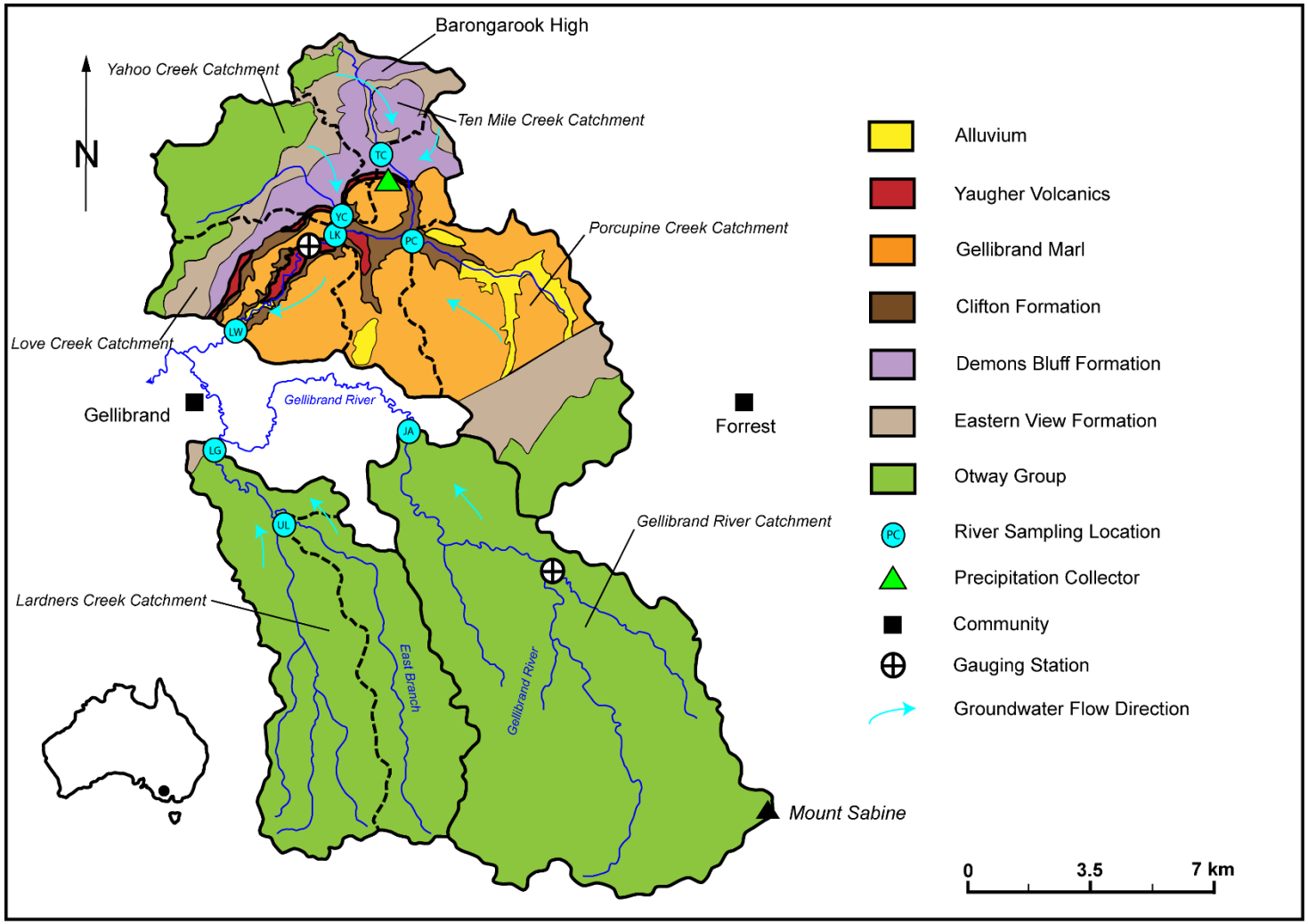

Figure 3-1: Map of study area showing catchments, sampling locations and bedrock geology. Inset map shows location of study area in Australia. Source: DataSearch Victoria (2015). LG = Lardners Gauge, UL = Upper Lardners, JA = Gellibrand River at James Access, PC = Porcupine Creek, TC = Ten Mile Creek, YC = Yahoo Creek, LK = Love Creek Kawarren, and LW = Love Creek Wonga. Current or discontinued gauging stations exist at all sites except for Upper Lardners.

Regional groundwater flows from the recharge area in the Barongarook High to the south and southwest (Leonard et al., 1981; Stanley, 1991; Atkinson et al., 2014). Additionally, localised recharge may occur elsewhere across the study area, particularly in those areas where the Eastern View Formation crops out. Regional groundwater discharges into the Gellibrand River, Love Creek, Porcupine Creek, Ten Mile Creek and Yahoo Creek (Hebblethwaite and James, 1990; Atkinson et al., 2013; Costelloe et al., 2015). In the higher elevations of the study area, including the upper reaches of Lardners Creek, the regional water table is likely to be below the base of the streambed (Costelloe et al., 2015). Based upon ^{14}C and ^{3}H activities, residence times of the regional groundwater are between 100 and 10,000 years (Petrides and Cartwright, 2012; Atkinson et al., 2014).

The Gellibrand River (Fig. 3-1) flows west-southwest for approximately 100 km from its highest point in the Otway Ranges before discharging into the Southern Ocean. This study focuses on six headwater catchments of the upper Gellibrand River: Lardners Creek, Love Creek, Porcupine Creek, Ten Mile Creek, Yahoo Creek and the Gellibrand River upstream of James Access (Fig. 3-1). The Lardners Creek catchment includes the whole catchment (Lardners Gauge) and a smaller upper sub-catchment (Upper Lardners) (Fig. 3-1). Similarly, Love Creek includes the whole catchment (Love Creek Wonga) and a smaller portion of the upper catchment (Love Creek Kawarren). Porcupine Creek, Ten Mile Creek and Yahoo Creek are also tributaries to Love Creek. Love Creek and Lardners Creek flow into the Gellibrand River near Gellibrand (Fig. 3-1). These headwater streams contribute a significant portion of flow to the Gellibrand River, which in turn provides water for several towns, supports important aquatic and terrestrial fauna, and provides water for agriculture. Current landuse in the upper Gellibrand catchment, including the cleared agricultural land which replaced the native eucalyptus forest, has been established for several decades. Despite their significance, the headwater catchments of the Otway Ranges face a number of threats, including urbanisation, further clearing of native vegetation, drought and bushfire, all of which have the potential to impact the quantity and quality of water within the streams.

The six catchments have areas ranging from 9.6 km^2 (Porcupine Creek) to 91.7 km^2 (Love Creek Wonga) (Table 3-1). Drainage densities are relatively similar and range from 8.7 x 10^{-4} m m^{-2} at Yahoo Creek to 10^{-3} m m^{-2} at Lardners Gauge and Upper Lardners (Table 3-1). Forest cover is lowest in the Love Creek

Wonga (78%) and Love Creek Kawarren (82%) catchments. Forest cover in the other catchments is 88% in the Porcupine Creek and Ten Mile Creek catchments, 91 to 92% in the Lardners Gauge and Upper Lardners catchments, and 95% in the Gellibrand River and Yahoo Creek catchments. Average slopes range from 5.7˚ (Ten Mile Creek) to 11.3˚ (James Access).

Catchment	Drainage Area (km^2)	Drainage Density ($m\ m^{-2}$)	Forest Cover (%)	Average Slope (°)	Runoff Coefficient (%)
Upper Lardners (UL)	20.0	1.0×10^{-3}	92	11.0	nc[1]
Lardners Gauge (LG)	51.6	1.1×10^{-3}	91	11.0	33.0
Gellibrand River (JA)	81.0	9.2×10^{-4}	95	11.3	39.0
Porcupine Creek (PC)	33.6	9.5×10^{-4}	88	5.9	11.4
Ten Mile Creek (TC)	9.6	8.8×10^{-4}	88	5.7	12.0
Yahoo Creek (YC)	16.6	8.7×10^{-4}	95	8.6	10.5
Love Creek Kawarren (LK)	74.4	9.3×10^{-4}	82	6.4	10.6
Love Creek Wonga (LW)	91.7	9.2×10^{-4}	78	6.7	8.6

Table 3-1: Summary of the attributes of the Gellibrand River catchments.

3.4 Methods

3.4.1 Sampling and Streamflow

River water samples were collected from eight locations in the catchments (Fig. 3-1). Lardners Creek was sampled at an active gauging station (Lardners Gauge) that is maintained by the Department of Environment, Land, Water and Planning (DELWP) (Site 235210) and from the Lardners Creek East Branch (Upper Lardners), approximately 3.5 km upstream from Lardners Gauge. Love Creek was sampled at Kawarren (Love Creek Kawarren), approximately 1 km upstream of DELWP gauging station 235234 and at the Wonga Road crossing (Love Creek Wonga), approximately 4.5 km downstream of Kawarren. River water samples were collected from the Gellibrand River, Porcupine Creek, Ten Mile Creek and Yahoo Creek at the sites of former DELWP gauging stations (Sites 235235, 235241, 235239 and 235240, respectively).

Streamflow at the time of sampling was determined for each of the eight locations with the exception of Upper Lardners, which is ungauged. Sub-daily streamflow is currently measured at Lardners Gauge

(Site 235210) and at Love Creek (Site 235234) (Department of Environment, Land, Water and Planning, 2017) (Fig. 3-1). Streamflow at James Access on the Gellibrand River was estimated using a correlation (R^2 = 0.97, p-value = 10^{-8}) between streamflow at the former gauging station at this location and that at the existing Upper Gellibrand River gauging station (Site 235202), approximately 7 km upstream (Fig. 3-1). Likewise, streamflow at the Porcupine Creek, Ten Mile Creek and Yahoo Creek sampling sites was estimated using correlations (R^2 = 0.95; 0.77, 0.84, respectfully with p-values <10^{-6}) between streamflow at the former gauging stations at these locations and the Love Creek gauging station.

River water samples were collected from each site in July 2014, September 2014, March 2015 and September 2015 (Supplement). An additional round of river water samples was collected from Lardners Gauge, Porcupine Creek, Ten Mile Creek and Love Creek Kawarren in November 2015. The water samples were collected from close to the centre of the streams using a polyethylene container fixed to an extendable pole. Additional data for James Access is from Atkinson (2014). A single precipitation sample was collected from Birnam in the Otway Ranges near Ten Mile Creek (Fig. 3-1) in September 2014 using a rainfall collector. The collector consisted of a polyethylene storage container equipped with a funnel positioned approximately 0.5 m above ground level. Prior to collection of the precipitation sample, the collector had been in the field for 78 days, during which time approximately 198 mm of rainfall was recorded at Forrest while 431 mm of rainfall was recorded at Mount Sabine (Department of Environment, Land, Water and Planning, 2017).

3.4.2 Geochemical Analyses

The electrical conductivity (EC) and pH of the river water and precipitation samples was measured in the field using a calibrated TPS® hand-held water quality meter and probes. The EC measurements have a precision of 1 µS/cm. Cation concentrations were measured at Monash University using a Thermo Fischer ICP-OES on samples that had been filtered through 0.45 µm cellulose nitrate filters and acidified to a pH <2 using double-distilled 16 M HNO_3. Anion concentrations were measured at Monash University on filtered, un-acidified samples using a Metrohm ion chromatograph. The precision of the cation and anion analyses, based upon replicate sample analysis, is ±2% while accuracy based on analysis of certified water standards is ±5%. HCO_3 concentrations were measured by colorimetric titration with H_2SO_4 using a Hach digital titrator and reagents and are precise to ±5%.

Total dissolved solids (TDS) concentrations were determined by summing the concentrations of cations and anions.

^{3}H analysis was conducted at the GNS Water Dating Laboratory in Lower Hutt, New Zealand. The samples were vacuum distilled and electrolytically enriched prior to analysis by liquid scintillation counting, as described by Morgenstern and Taylor (2009). Following further improvements, the sensitivity is now further increased to a lower detection limit of 0.02 TU via tritium enrichment by a factor of 95, and reproducibility of tritium enrichment of 1% is achieved via deuterium-calibration for every sample. ^{3}H activities are expressed as absolute values in tritium units (TU) where 1 TU represents a $^{3}H/^{1}H$ ratio of $1x10^{-18}$. The precision (1σ) is ~1.8% at 2 TU.

3.4.3 Catchment Attributes

Catchment attributes (Table 3-1) were determined using ArcGIS 10.2 (ESRI, 2013) and datasets from DataSearch Victoria (2015). The Hydrology Modelling tools in ArcGIS were used to generate the stream network from a 20 m digital elevation model. A threshold catchment area of 50 Ha reproduces the observed perennial stream network of the area. Catchment areas upstream of each sampling site and drainage densities were determined using the watershed tool. Mean slopes were calculated using the Spatial Analysis tools. Vector-based landuse datasets were converted to raster formats and reclassified. Landuse was assigned as forest (native vegetation and plantations) and cleared land, which includes urban and agricultural regions. Runoff coefficients were calculated using streamflow data for each of the catchments (except Upper Lardners) for March 1986 to July 1990 (Department of Environment, Land, Water, and Planning, 2017), the only interval for which contiguous streamflow data are available for each catchment. The runoff coefficient calculations assumed a uniform average annual rainfall of 1.3 m for each catchment (Bureau of Meteorology, 2017). Correlations between catchment attributes and other parameters are considered to be reasonably strong where $R^2 \geq 0.7$.

3.4.4 Calculating Mean Transit Times

The lumped parameter models implemented in the TracerLPM Excel workbook (Jurgens et al., 2012) were used to estimate MTTs. The ^{3}H activity of water sampled from a stream at time t ($C_0(t)$) is related to the input (C_i) of ^{3}H via the convolution integral:

$$C_0(t) = \int_0^\infty C_i(t - \mathrm{T}) g(\mathrm{T}) e^{-\lambda \mathrm{T}} d\mathrm{T} \qquad (3\text{-}1)$$

where T is the transit time, t – T is the time that the groundwater entered the flow system, λ is the decay constant (0.0563 yr^{-1} for ^{3}H) and g(T) is the exit age distribution function, for which closed form analytical solutions have been derived (e.g. Maloszewski and Zuber, 1982; Maloszewski and Zuber, 1996; Kinzelbach et al., 2002). MTTs were estimated by matching the predicted ^{3}H activities from the LPMs to the observed ^{3}H activities of the samples.

The ^{3}H input is based on the annual Melbourne rainfall record (International Atomic Energy Agency, 2016; Tadros et al., 2014). Modern rainfall in the study area has a slightly lower predicted ^{3}H activity (~2.8 TU) than that in Melbourne, which is approximately 150 km from the study area and has a ^{3}H activity ~3.0 TU (Tadros et al., 2014). A ^{3}H activity of 2.8 TU was used for modern (2010 to 2016) rainfall as well as for the years prior to the atmospheric nuclear tests (pre-1951). The ^{3}H activities for rainfall between 1950 and 2009 are those of Melbourne rainfall decreased by 6.7% to account for the expected difference in ^{3}H activities in the rainfall between the Otway Ranges and Melbourne.

As discussed earlier, the use of single ^{3}H activities to estimate MTTs requires that an LPM be assigned. Here two LPMs were utilised: the Exponential Piston-Flow model (EPM) and the Dispersion model (DM), which are among the most commonly used LPMs (McGuire and McDonnell, 2006; Stewart et al., 2010). The EPM describes flow in aquifers with both exponential and piston-flow portions. This model may be applied to unconfined aquifers where recharge through the unsaturated zone resembles piston flow and flow within the aquifer resembles exponential flow (Morgenstern et al., 2010). TracerLPM defines an EPM ratio, which represents the relative contribution of exponential and piston flow (Jurgens et al., 2012). The EPM ratio is $1/f$ - 1, where f is the proportion of aquifer volume exhibiting exponential flow.

The Dispersion Model (DM) is based on the one-dimensional advection-dispersion equation for a semi-infinite medium (Jurgens et al., 2012). While the DM can be applied to a wide variety of aquifer configurations, conceptually it is probably less realistic than other LPMs. Nonetheless, it has been successfully used to predict tracer concentrations over time in a number of flow systems (e.g. Maloszewski, 2000). Utilisation of this model requires defining a dispersion parameter, D_p, which represents the ratio of dispersion to advection.

The average annual ^3H activities of modern rainfall in central and southeast Australia are predicted to vary between 2.4 and 3.2 (Tadros et al., 2014). ^3H activities of 9 to 17 month rainfall samples from elsewhere in Victoria are between 2.72 and 2.99 TU (Atkinson, 2014; Cartwright and Morgenstern, 2015; Cartwright et al., 2018) and fall within the range of predicted ^3H activities for their locations. Interpolating the data from that study suggests that modern rainfall in the Otway Ranges has an annual average ^3H activity of ~2.8 TU (which is slightly lower than the ~3.0 TU recorded at Melbourne ~150 km to the east of the study area). A value of 2.8 TU was used as the average annual ^3H activity of modern (2010 to 2016) rainfall as well as for the years prior to the atmospheric nuclear tests (pre-1951). The ^3H input in the intervening years is based on the ^3H activities of rainfall in Melbourne (International Atomic Energy Agency, 2016; Tadros et al., 2014). These were decreased by 6.7% to account for the expected difference in ^3H activities in the rainfall between the Otway Ranges and Melbourne.

There are several uncertainties in the MTT calculations. The analytical uncertainty ranges between 0.02 and 0.04 TU (Supplement). To assess the effect of uncertainties in rainfall ^3H activities, MTTs were recalculated assuming that modern and pre-1950 rainfall had an average ^3H activity of either 2.4 TU or 3.2 TU with the ^3H activities of the intervening years adjusted proportionally. As this range encompasses the estimated annual ^3H activities of rainfall over most of central and southeast Australia, it allows a conservative estimate of uncertainties to be made.

The aggregation or macroscopic mixing of waters also introduces uncertainties (Kirchner, 2016; Stewart et al., 2017). Consider a stream fed by several tributaries. The expected MTT (MTT_e) can be calculated using the streamflow data, ^3H activities, and MTTs of each tributary via:

$$MTT_e = aMTT_1 + bMTT_2 + cMTT_3 + \ldots. \quad (3\text{-}2)$$

(Stewart et al., 2017). In Eq. (3-2), a, b, and c represent the fraction of total flow contributed by tributaries 1, 2, 3. If the aggregation is minimal, MTT_e will be similar to that estimated from the measured ^3H activity via the LPM. The successful application of Eq. (3-2) relies on the MTTs of the different tributaries being definable from their ^3H activities (which in itself may not be straightforward due to aggregation within those sub-catchments). Nevertheless, it provides a broad estimate of the error due to macroscopic mixing that is otherwise difficult to assess.

3.4.5 Groundwater Volume

The volume (V) of groundwater stored within an aquifer that interacts with the stream annually (sometimes referred to as the turnover volume) is related to the MTT by:

$$V = Q * MTT \quad (3\text{-}3),$$

where Q is streamflow (Maloszewski and Zuber, 1982; Morgenstern et al., 2010).

3.5 Results

3.5.1 Streamflow

Streamflow was highest during July 2014 (Supplement), ranging from $8.6x10^3$ m^3 day^{-1} at Ten Mile Creek to $255x10^3$ m^3 day^{-1} at James Access. Streamflow was lowest during March and November 2015, ranging from $0.1x10^3$ m^3 day^{-1} at Ten Mile Creek to $8.8x10^3$ m^3 day^{-1} at James Access. Figure 3-2 illustrates the streamflows for the sampling rounds relative to the flow duration curves for the catchments. Samples were generally collected between the 10th and 100th percentiles of streamflow, which encompasses a wide range of flow conditions. Samples were collected during the recession periods after high flow events that follow rainfall or during baseflow conditions (Fig. 3-3). Overland flow was not observed during any of the sampling events and small ephemeral tributaries in the catchments were dry.

Runoff coefficients range from 33% and 39% at Lardners Gauge and James Access, respectively, to between 9% and 12% at Porcupine Creek, Ten Mile Creek, Yahoo Creek Wonga and Love Creek Kawarren (Table 3-1). The higher runoff coefficients at Lardners Gauge and James Access relative to

the other catchments may be due to the fact that these rivers drain steeper catchments and are underlain almost entirely by low hydraulic conductivity Otway Group basement rocks.

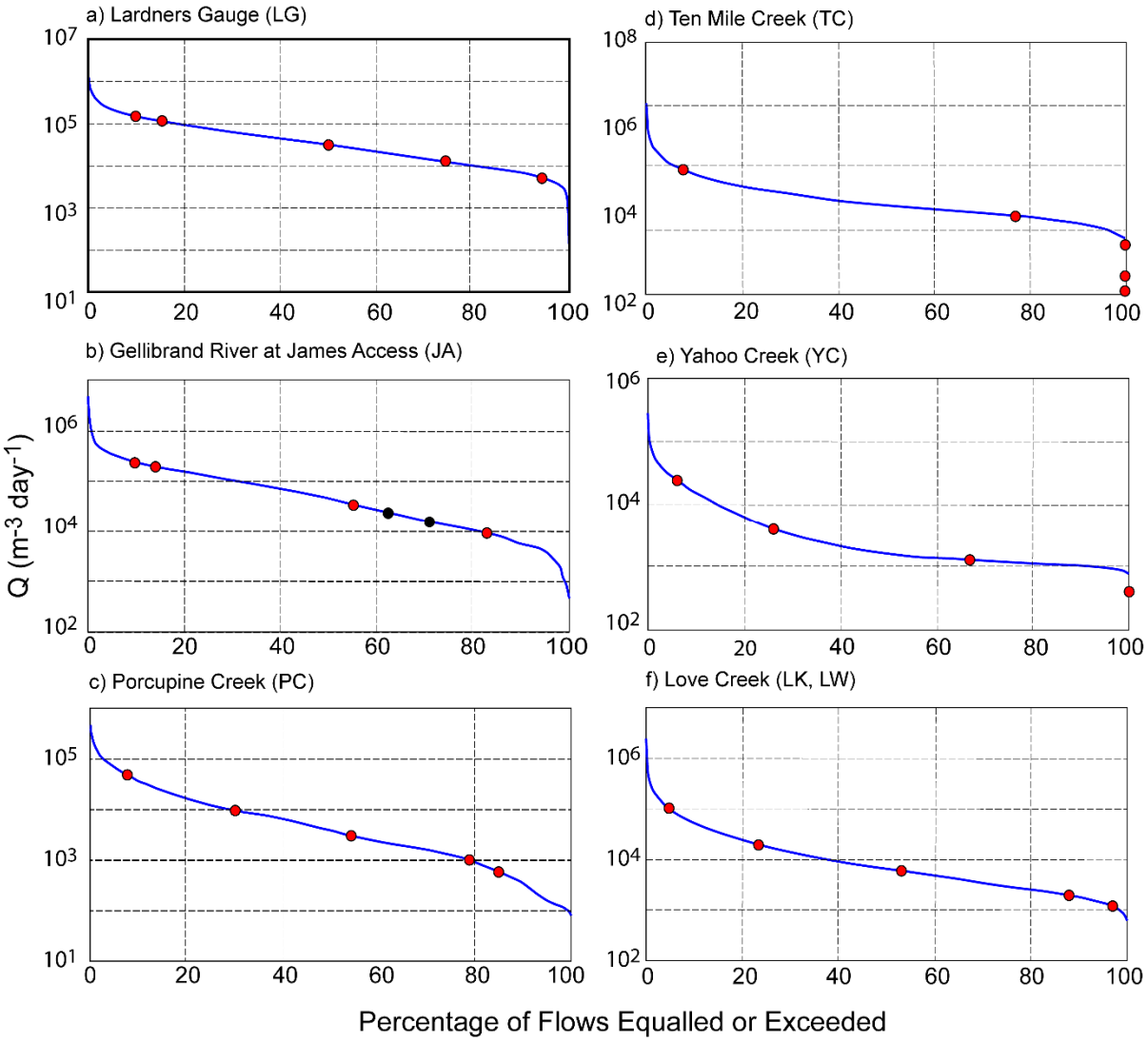

Figure 3-2: Streamflows at which samples were collected relative to flow duration curves for Lardners Gauge (a), Gellibrand River at James Access (b) – additional data (black circles) from Atkinson (2014), Porcupine Creek (c), Ten Mile Creek (d), Yahoo Creek (e), and Love Creek (f). Streamflow data from Department of Environment, Land, Water and Planning (2017).

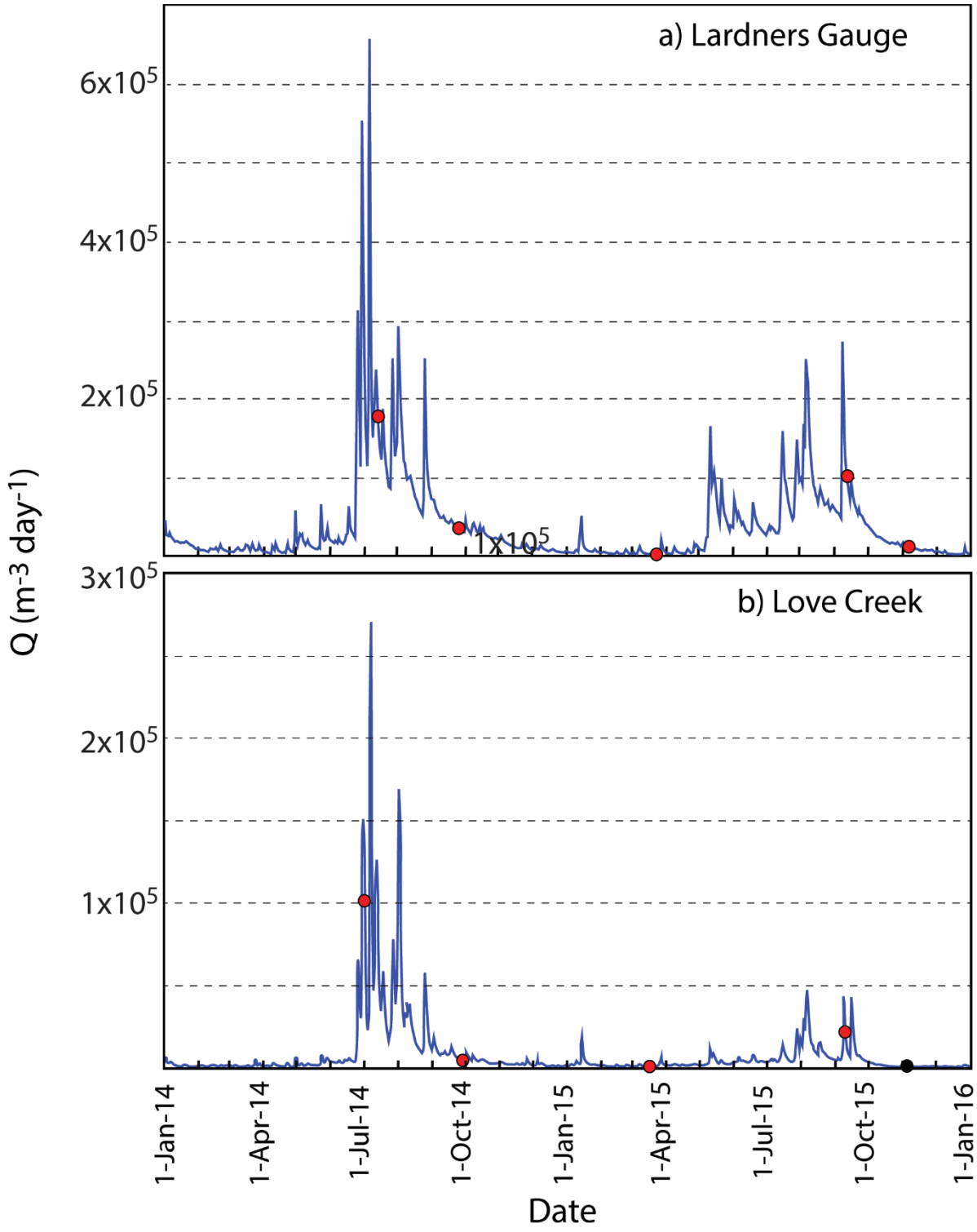

Figure 3-3: Hydrographs for Lardners Gauge (a) and Love Creek (b) together with the timing of sample collection. Data from Department of Environment, Land, Water and Planning (2017).

3.5.2 Tritium Activities

As discussed above, the annual average ^{3}H activities of modern rainfall in much of central and southeast Australia are between 2.4 and 3.2 TU (Tadros et al., 2014). The 78 day precipitation sample collected from near Ten Mile Creek in September 2014 had a tritium activity of 2.45 TU. This is lower than both the expected ^{3}H activities for the Otway Ranges (~2.8 TU: Tadros et al., 2014) and those of 9 to 12 month rainfall samples elsewhere in Victoria (2.72 and 2.99: Atkinson, 2014; Cartwright and Morgenstern, 2015; 2016a; Cartwright et al., 2018). However, the Ten Mile Creek sample reflects rainfall over only part of the year and may not be representative.

Tritium activities of the rivers are <2.14 TU, which are lower than the average annual ^{3}H activities of modern rainfall and indeed the Ten Mile Creek rainfall sample. The ^{3}H activities vary from 0.20 TU at Porcupine Creek in March 2015 to 2.14 TU at Yahoo Creek in July 2014 (Fig. 3-4). The higher ^{3}H activities in the rivers are within the range of ^{3}H activities of 1.80 to 2.25 TU for soil pipe water in higher elevations in the Gellibrand Catchment (Atkinson, 2014) (Fig. 3-4). In general, ^{3}H activities were highest at high stream streamflow (July 2014) and lowest at low streamflow (March and November 2015).

The ^{3}H activities of Love Creek at the upstream (Love Creek Kawarren) and downstream (Love Creek Wonga) locations in individual events varied by <0.1 TU. The ^{3}H activities in Lardners Creek between Upper Lardners and Lardners Gauge were slightly more variable (up to 0.17 TU). The range of ^{3}H activities between the events was most variable at Porcupine Creek (0.20 to 1.97 TU), followed by Yahoo Creek (0.43 to 2.14 TU), Love Creek Kawarren (0.48 to 1.91 TU), Love Creek Wonga (0.55 to 1.88 TU), Ten Mile Creek (0.44 to 1.74 TU), Upper Lardners (1.54 to 1.99 TU), James Access (1.73 to 2.08 TU) and Lardners Gauge (1.64 to 1.97 TU) (Fig. 3-4). Overall, the highest ^{3}H activities were similar across all catchments but the lower values varied considerably. The ^{3}H activities increase with increasing streamflow up to approximately 10^{4} m^{3} day^{-1}, above which ^{3}H activities do not increase appreciably (Fig. 3-4). Despite differences in catchment size, slope, geology, and landuse, there is a strong correlation between ^{3}H activities and streamflow across the catchments ($^{3}H = 0.2613 \ln(Q) + 0.8973$; $R^{2} = 0.75$, p-value = 0.15).

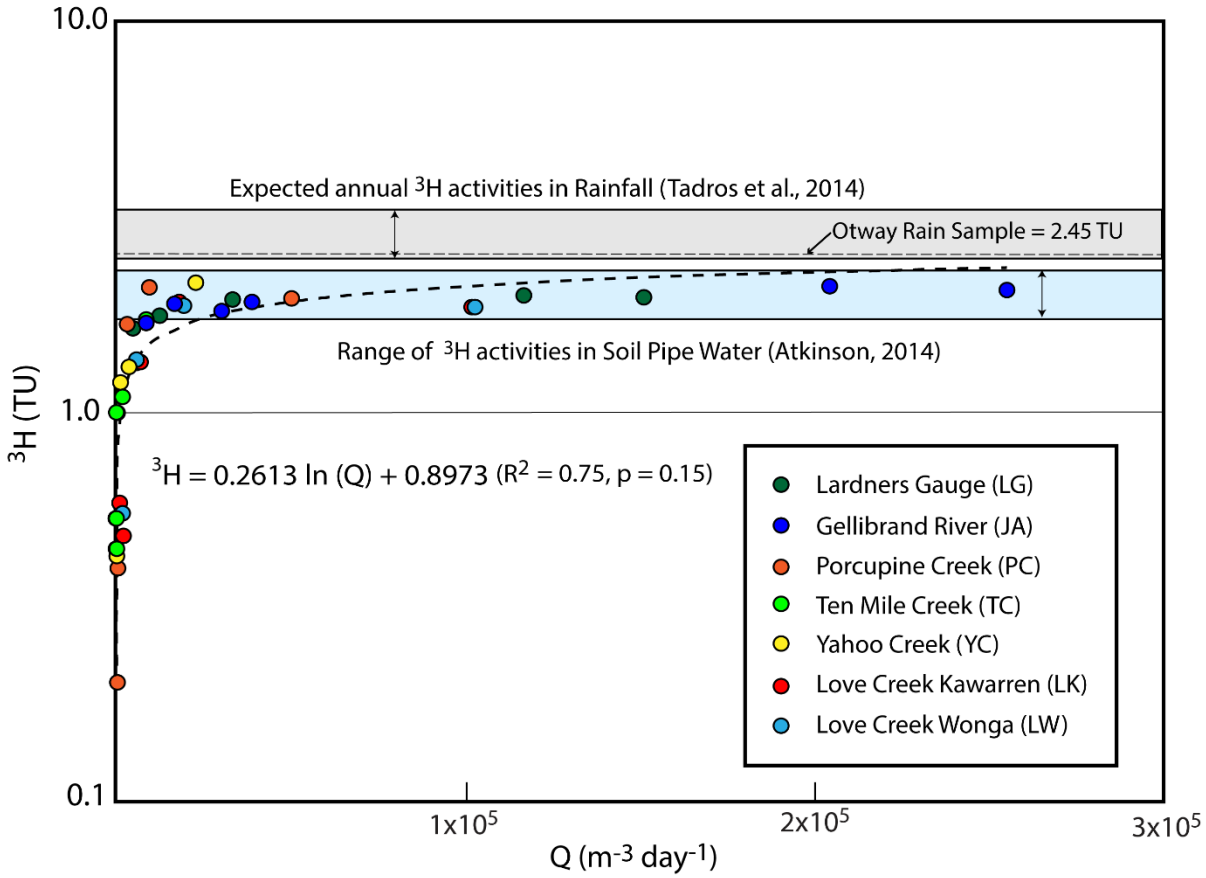

Figure 3-4: ^{3}H activity of stream water as a function of streamflow for all catchments except Upper Lardners, which is ungauged. ^{3}H data from Supplement, streamflow data from Department of Environment, Land, Water and Planning (2017) or calculated as discussed in the text. Shaded boxes show the expected annual average of rainfall ^{3}H activities from Tadros et al. (2014) and soil waters from Atkinson (2014).

3.5.3 Major Ion Geochemistry

River water geochemistry is similar across all catchments and is dominated by Na, Cl and HCO_3 (Supplement). TDS concentrations are generally less than 100 mg/L at Lardners Gauge, Upper Lardners and James Access but typically exceed 200 mg/L in Love Creek Wonga, Love Creek Kawarren, Porcupine Creek, Ten Mile Creek and Yahoo Creek. TDS concentrations increase downstream in Lardners and Love Creeks and are inversely correlated with streamflow in all catchments.

At Love Creek, Ten Mile Creek, Yahoo Creek and Upper Lardners, there is no correlation between ^{3}H activities and EC, TDS or major ion concentrations (Fig. 3-5). However, at Porcupine Creek, there is a strong correlation (R^2 > 0.95, p-values < 0.01) between ^{3}H activities and EC, TDS, and all major ion concentrations with the exception of chloride, nitrate and sulphate. In addition, there is a strong correlation (R^2 = 0.84, p-value = 0.002) between ^{3}H activities and TDS at Lardners Gauge (Fig. 3-5).

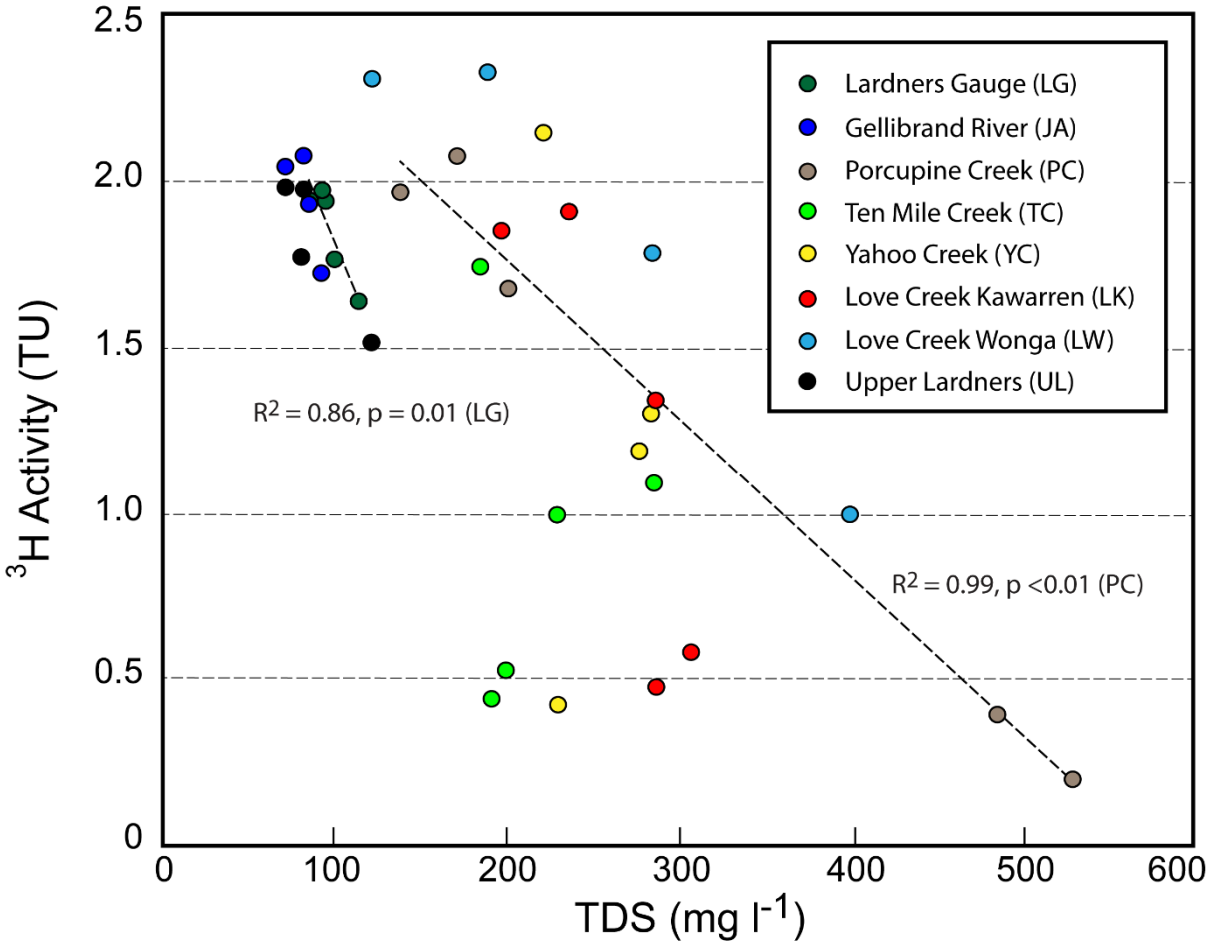

Figure 3-5: ^{3}H activities as a function of TDS for all catchments (data from Supplement). Strong inverse correlations between ^{3}H activities and TDS exist for Lardners Gauge and Porcupine Creek.

At Upper Lardners, James Access and Ten Mile Creek, there is a strong correlation (R^2 > 0.8, p-values < 0.11) between nitrate concentration and ^{3}H activities (Fig. 3-6a). The range of nitrate concentrations (0.08 to 2.0 mg/L) were relatively similar during each sampling event across all catchments except for in July 2014, when nitrate concentrations exceeded 3 mg/L at Love Creek Kawarren and Love Creek Wonga. A similar correlation exists between sulphate concentrations and ^{3}H activities at James Access and at Upper Lardners, but not at Ten Mile Creek (Fig. 3-6b). However, sulphate concentrations at these locations are lower than they are in the other catchments.

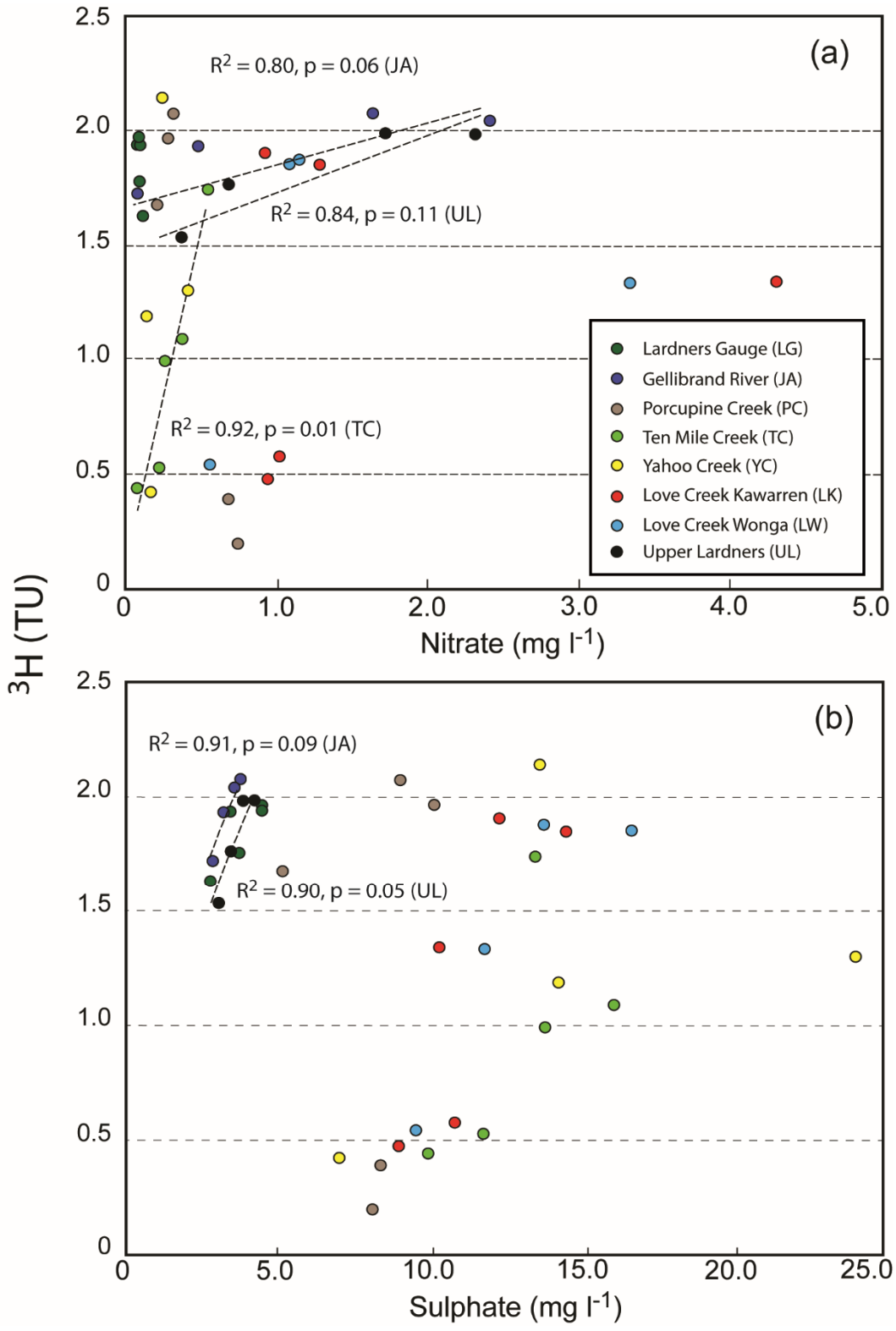

Figure 3-6: ^{3}H activities as function of a) Nitrate concentrations and b) Sulphate concentrations. Data from Supplement. Strong ($R^2 > 0.7$) correlations indicated.

3.6 Discussion

The combination of stream streamflow, ^{3}H activities, major ion geochemistry, and catchment attributes allow aspects of the behaviour of the upper Gellibrand catchments to be understood. This section addresses the changing stores of water in the catchments, the range and uncertainties of MTTs, and whether MTTs can be predicted from catchment attributes or geochemical data.

3.6.1 Sources of River Inflows

It is important to determine how the water stores that contribute to streamflow change between high and low flows. Groundwater inflows are most probably the dominant source of water during the summer months. However, at times of higher streamflow there may be mobilisation of younger shallower water stores (e.g., water from the soils or the regolith) as the catchment wets up (c.f. Hrachowitz et al., 2013; Cartwright and Morgenstern, 2015, 2016a) or mixing between baseflow and recent rainfall (c.f., Morgenstern et al., 2010). The river water samples were collected during baseflow conditions or during recession periods after high streamflows that follow rainfall (Fig. 3-3) when recent rainfall is less likely to directly contribute to streamflows. That the major ion geochemistry varies little with streamflow also suggests that there is not significant dilution of groundwater inflows with recent rainfall during the sampling periods (c.f. Sklash and Farvolden, 1979; Kennedy et al., 1986; Jensco and McGlynn, 2011; Cartwright and Morgenstern, 2015).

Together, these observations suggest that there is no significant direct input of recent rainfall during the sampling periods. The flow system may is concluded to be a continuum that is dominated by older groundwater inflows at low flows while progressively shallower and younger stores of water (such as soil water or perched groundwater) are mobilised during wetter periods. The observations that nitrate and sulphate concentrations in several of the catchments are higher at high streamflows (Fig. 3-6) may reflect the input of contaminants from recent agricultural activities to the streams. This observation agrees with the conceptualisation that shallower stores of water in the catchment, which are more likely to be impacted by contamination, are mobilised during the wetter periods of the year.

3.6.2 Mean Transit Times

If the conceptualisation of the flow system is correct, MTTs may be calculated using a single LPM. If there were some dilution by recent rainfall, using a single LPM yields the minimum MTT of the baseflow component. (Morgenstern et al., 2010). MTTs in the headwaters catchments were estimated using the EPM and the DM. For the EPM, EPM ratios of 0.33 (75% exponential flow), 1.0 (50% exponential flow) and 3.0 (25% exponential flow) were adopted. The EPM model accords with the expected geometry of flow in the catchment (vertical recharge through the unsaturated zone followed by flow along flow paths of varying length), and EPM models with these EPM ratios have reproduced the ^{3}H time series in headwater catchments with similar geometries elsewhere (Maloszewski and Zuber, 1982; Morgenstern and Daughney, 2012; Blavoux et al., 2013; Morgenstern et al. 2010). For the DM, Dp values of 0.05 and 0.5 were adopted, which are appropriate for kilometre-scale flow systems (Zuber and Maloszewski, 2001; Gelhar et al., 1992). Utilisation of a variety of LPMs allows the impact of the assumed model on the MTTs to be assessed.

Calculated MTTs ranged from approximately 7 years at Yahoo Creek in July 2014 to 230 years at Porcupine Creek in March 2015 (Table 3-2). In general, the lowest MTTs were estimated from the EPM with an EPM ratio = 3.0 while the highest MTTs were estimated using the DM with $D_p = 0.5$. Because of the remnant bomb pulse ^{3}H, a few samples with ^{3}H activities between 1.2 to 1.7 TU yield MTTs that are non-unique for models with high piston flow components (i.e., the EPM with EPM ratio = 3.0 and the DM with $D_p = 0.05$; Table 3-2, Fig. 3-7). MTTs estimated from all LPMs were similar for ^{3}H activities greater than 1 TU (Fig. 3-7). However, as ^{3}H activities decrease, the relative difference between the estimates increases. At the lowest ^{3}H activity of 0.20 TU, the relative difference across the range of transit times is approximately 164 years.

MTTs for Lardners Gauge, Upper Lardners and James Access were similar, and are between 7 and 26 years. In contrast, MTTs for Porcupine Creek ranged from approximately 7 to 234 years, while those for Ten Mile Creek, Yahoo Creek, Love Creek Wonga, and Love Creek Kawarren ranged from approximately 13 to 150, 7 to 155, and 10 to 140 years, respectively. In all catchments, the longest MTTs are recorded at the lowest streamflows (March 2015) while the shortest MTTs occur at the highest streamflows (July 2014 and September 2015) (Fig. 3-8). At Lardners Gauge, James Access,

Porcupine Creek and Love Creek, the samples collected at the highest flow rates have MTTs that are slightly longer than that of the samples collected at the second highest streamflow (Fig. 3-8). Whether this reflects changes to the flow system or is due to uncertainties in the MTT estimates is not certain.

The volume of water in the aquifers that contributes to the streamflow may be estimated from Eq. (3-3). Both the Lardners Gauge and the Love Creek Wonga catchments have active streamflow monitoring, and the calculations are carried out for these catchments. Using the relationship between MTT and streamflow (Fig. 3-8) and streamflow data for 2014 and 2015 (Department of Environment, Land, Water and Planning, 2017), the average MTT for the two catchments is estimated at 29.7 years (Love Creek Wonga) and 10.8 years (Lardners Gauge). For the average annual streamflow over these two years, the turnover volumes are 2.6×10^5 m^3 (Love Creek Wonga) and 4.5×10^5 m^3 (Lardners Gauge). These volumes are small relative to the likely volumes of water stored in the catchments. For the catchment areas (Table 3-1) and a porosity of 0.1 to 0.3, which is appropriate for most soils and aquifers, this volume of water could be stored in a layer that is 0.01 to 0.1 m thick.

3.6.3 Uncertainties in MTT Estimates

The uncertainties in the MTTs arising from the analytical uncertainties (Supplement) range from ±0.9 years for the sample with the highest ^{3}H activity to ±10 years for the sample with the lowest ^{3}H activity. These equate to relative uncertainties of ~±10%. Having to assume an LPM reflects a major uncertainty for calculating the MTTs, especially for waters with ^{3}H activities <1 TU (Fig. 3-7). For a water with a ^{3}H activity of 2 TU, the uncertainty in MTTs is ±1.2 years (±13%), while for waters with ^{3}H activities of 1 TU and 0.5 TU they are ±5 years (±8%) and ±31 years (±30%), respectively. The EPM with an EPM ratio of 3.0 and the DM with a D_p value of 0.05 have a large component of piston flow and are possibly less realistic representations of the flow systems; however, the differences between the MTTs estimated using the other LPMs are still considerable.

Location	Date	Q 10^3 m^3 day^{-1}	^3H (TU)	MTT (years)				
				EPM			DM	
				0.33	1.0	3.0	0.05	0.5
Upper Lardners (UL)	10/07/2014	-	1.99	9.9	9.6	8.8	9.0	11.2
	28/09/2014	-	1.77	15.7	12.9	11.8	12.2	17.6
	20/03/2015	-	1.54	24.2	18.5	(16.2, 41.4)	16.3	26.2
	10/09/2015	-	1.99	8.8	8.2	8.6	8.3	9.9
Lardners Gauge (LG)	10/07/2014	151.3	1.94	10.8	10.2	9.3	9.6	12.3
	28/09/2014	32.8	1.94	10.6	10.1	9.2	9.5	12.1
	20/03/2015	5.0	1.64	19.8	15.4	(14.1, 45.7)	14.2	21.6
	10/09/2015	116.6	1.97	9.1	8.5	8.7	8.6	10.2
	4/11/2015	12.7	1.77	13.8	12.4	11.2	11.6	15.8
Gellibrand River (JA)	13/03/2012	18.5	1.90	15.5	12.3	11.8	11.7	17.7
	26/04/2012	30.4	1.80	19.2	14.8	13.1	13.4	21.4
	10/07/2014	255.2	2.04	8.7	8.7	8.1	8.2	9.7
	28/09/2014	39.1	1.93	10.8	10.2	9.4	9.7	12.4
	20/03/2015	8.8	1.73	16.2	13.5	12.2	12.6	18.2
	10/09/2015	204.4	2.08	7.3	6.8	7.7	7.0	8.1
Porcupine Creek (PC)	10/07/2014	50.4	1.97	10.3	9.8	9.0	9.2	11.7
	27/09/2014	3.3	1.68	19.3	14.9	(13.9, 44.7)	13.8	21.0
	20/03/2015	1.0	0.20	179.1	100.0	69.5	89.6	233.5
	10/09/2015	9.7	2.08	7.3	6.8	7.7	7.0	8.1
	4/11/2015	0.6	0.40	136.6	94.8	68.4	78.7	161.5
Ten Mile Creek (TC)	10/07/2014	8.6	1.74	17.1	13.6	12.5	12.7	18.8
	27/09/2014	0.6	1.00	58.3	68.5	62.5	60.1	66.3
	20/03/2015	0.2	0.44	128.4	92.5	67.2	76.4	149.2
	10/09/2015	1.7	1.09	48.3	55.5	62.0	57.0	53.5
	4/11/2015	0.1	0.53	109.4	90.3	67.2	73.3	130.2
Yahoo Creek (YC)	11/07/2014	23.0	2.14	6.9	6.8	7.2	7.0	7.6
	28/09/2014	1.2	1.19	44.7	52.0	(60.6, 27.4)	(55.3, 24.8)	49.2
	20/03/2015	0.4	0.43	132.1	93.1	67.4	77.2	153.7
	10/09/2015	3.9	1.30	34.8	31.3	(34.3, 60.0)	(27.6, 50.7)	37.9
Love Creek Kawarren (LK)	10/07/2014	102.9	1.85	13.3	11.5	10.5	10.9	15.0
	27/09/2014	6.7	1.34	35.3	33.5	(32.3, 59.2)	(24.8, 51.2)	38.4
	20/03/2015	2.0	0.48	121.4	91.2	67.0	75.1	141.1
	10/09/2015	18.6	1.91	10.4	9.8	9.5	9.5	11.9
	4/11/2015	1.2	0.58	100.3	88.6	66.8	71.5	120.4
Love Creek Wonga (LW)	10/07/2014	103.5	1.86	13.1	11.4	10.4	10.8	14.8
	28/09/2014	6.0	1.34	35.7	34.2	(32.1, 59.3)	(24.8, 51.4)	38.8
	20/03/2015	2.0	0.55	109.1	89.4	66.4	72.6	127.0
	10/09/2015	19.6	1.88	11.0	10.4	9.8	9.9	12.6

Table 3-2: Summary of calculated mean transit times (MTTs) for the upper Gellibrand River catchments.

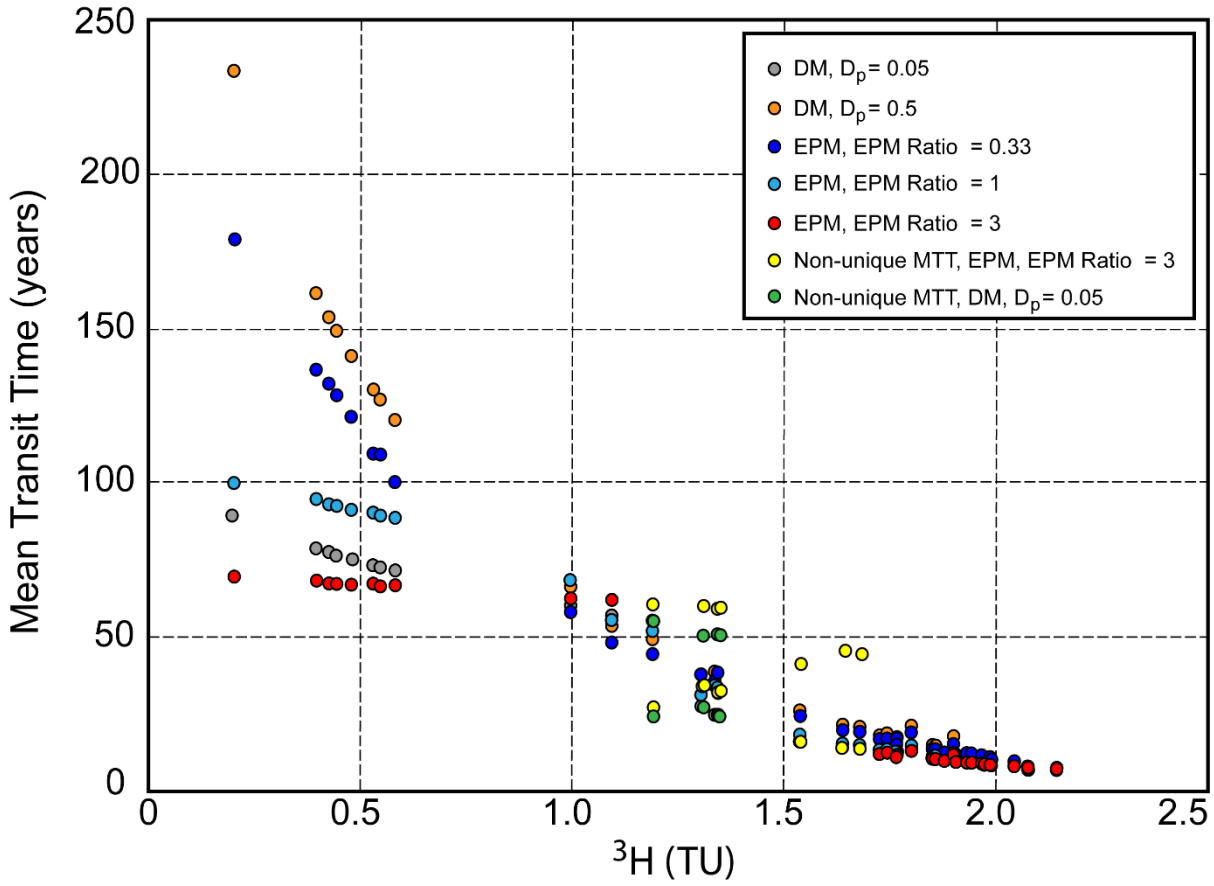

Figure 3-7: Variation in MTTs for ^{3}H activities in the river water samples ranging from 0.20 to 2.14 TU using the Exponential Piston Flow Model (EPM) with EPM ratios of 0.33, 1.0 and 3.0, and the Dispersion Model (DM) with D_p values of 0.05 and 0.5.

The influence of uncertainties in the ^{3}H input was assessed by varying the modern and pre bomb pulse ^{3}H activities between 2.4 and 3.2 TU and adjusting the ^{3}H activities in the intervening years accordingly. As discussed above, this encompasses the predicted range of average annual ^{3}H activities in most of central and southeast Australia. These calculations used the EPM with an EPM ratio of 1.0 but the effect is similar in the other models. The relative difference between MTTs is generally highest when ^{3}H activities exceed 1 TU (Fig. 3-9). For ^{3}H activities of 2 TU, the uncertainty in MTTs is ±5 years (±54%), while for waters with ^{3}H activities of 1 TU and 0.5 TU they are ±10 years (±15%) and ±5 years (±5%), respectively.

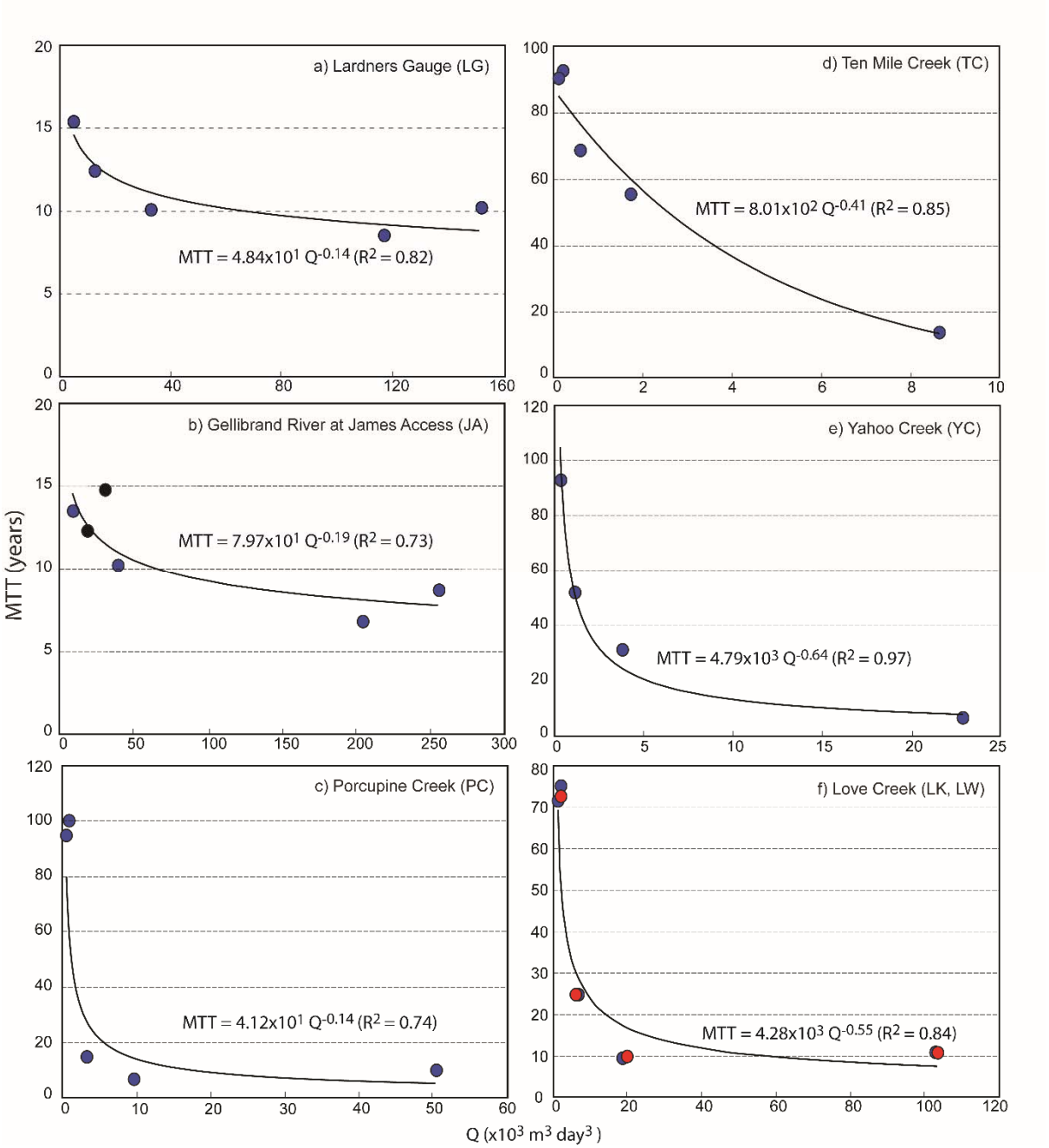

Figure 3-8: MTTs calculated using the EPM model with an EPM ratio of 1.0 (Table 3-3) as a function of streamflow (Q) for Lardners Gauge (a), Gellibrand River at James Access (b) - black circles are data by Atkinson (2014), Porcupine Creek (c), Ten Mile Creek (d), Yahoo Creek (e), and Love Creek (f) - blue circles are Love Creek Kawarren and red circles Love Creek Wonga. Streamflow data from Department of Environment, Land, Water and Planning (2017) or calculated as discussed in text.

^{3}H activities in rainfall can vary seasonally. Catchments with MTTs in excess of a few years do not preserve seasonal variations in stable isotope ratios or major ion concentrations (Stewart et al., 2010). In a similar way, the seasonal variation in rainfall ^{3}H activities are unlikely to be preserved in the catchment waters (Morgenstern et al., 2010). Thus, using annual ^{3}H activities as the input is

appropriate. However, if recharge has a strong seasonality, its ^{3}H activities may be different from those of annual rainfall. Rainfall in the Otway Ranges is distributed throughout the year and it is likely that some recharge occurs throughout the year. However, as is the case elsewhere in the Southern Hemisphere (Morgenstern et al., 2010), the ^{3}H activities in summer rainfall are closely similar to the average annual ^{3}H activities (Tadros et al., 2014; International Atomic Energy Agency, 2017). The observation that the ^{3}H activities of summer (December to February) rainfall at Mount Buffalo in northeast Victoria were similar (2.86 TU) to those of two annual rainfall samples (2.99 and 2.85 TU) support this assertion (Cartwright and Morgenstern, 2015). With such a seasonal distribution of ^{3}H activities, the uncertainties in MTTs resulting from using the average annual ^{3}H activities are less than those that arise from the general uncertainty in the ^{3}H input function.

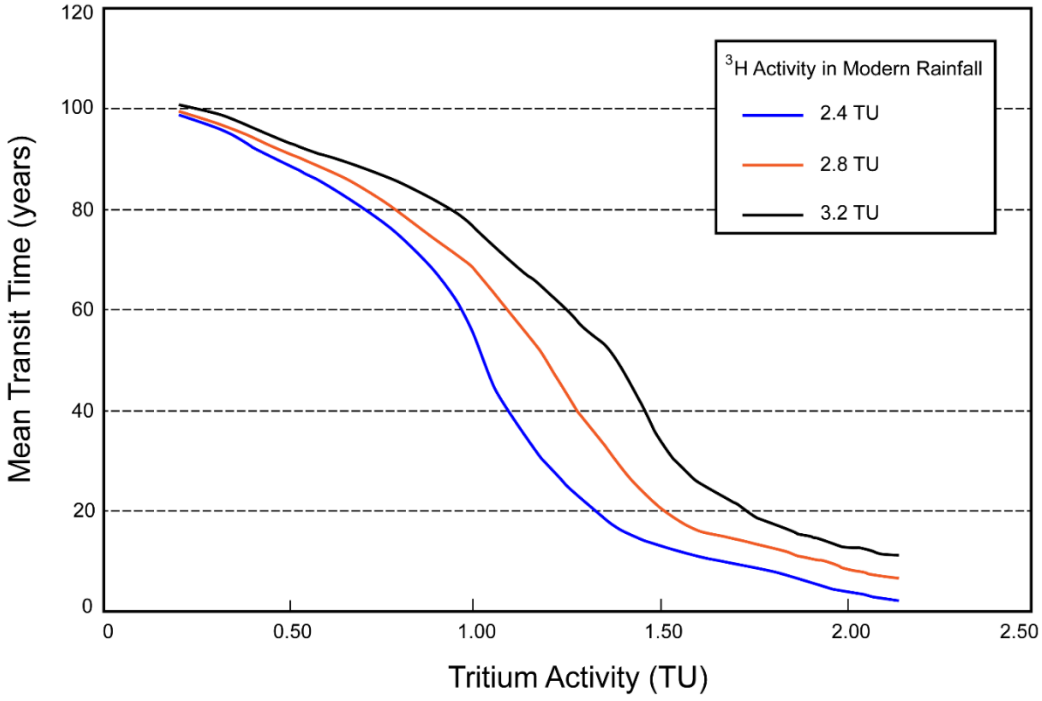

Figure 3-9: Impact of varying rainfall ^{3}H inputs on MTTs calculated using the EPM model with an EPM ratio of 1.0. The three rainfall inputs modern and pre bomb-pulse ^{3}H activities of 2.4, 2.8 and 3.2 TU and the ^{3}H activity of the bomb-pulse rainfall was varied by a similar proportion as discussed in the text.

The impact of macroscopic mixing was estimated using Eq. (3-2) and the streamflow data and MTTs for Porcupine, Ten Mile and Yahoo Creeks that flow into Love Creek upstream of Love Creek Kawarren (Fig. 3-1). The analysis used the EPM with an EPM ratio of 1.0 (Table 3-2) but, again, similar results were obtained with the other LPMs. Based on the streamflow data, these three streams contribute 77

to 82% of total stream flow at Love Creek Kawarren (Table 3-2). The remaining portion of flow in Love Creek is assumed to be contributed by undefined inputs such as groundwater inflow and inputs from smaller tributaries. It was assumed that there was one unidentified input, the ^{3}H activity of which was estimated by the difference between the weighted ^{3}H activities of Porcupine, Ten Mile and Yahoo Creeks and the ^{3}H activity at Love Creek Kawarren. The MTT of this input was determined from the ^{3}H activity using the EPM.

Sample Date	MTT, Love Creek Kawarren (years)	
10/07/2014	True MTT	15.4
	Sample MTT	11.5
	Difference (years)	3.9
	Difference (%)	25.5
27/09/2014	True MTT	40.9
	Sample MTT	33.5
	Difference (years)	7.4
	Difference (%)	18.1
20/03/2015	True MTT	87.4
	Sample MTT	91.2
	Difference (years)	3.8
	Difference (%)	4.4
10/09/2015	True MTT	15.5
	Sample MTT (years)	9.8
	Difference (years)	5.7
	Difference (%)	36.7

Table 3-3: Estimates of the difference between calculated mean transit times (MTTs) and that estimated from the mixing of waters from different tributaries at Love Creek Kawarren.

In March 2015, the estimated MTT calculated using the LPM at Love Creek Kawarren was higher than MTT_e calculated using Eq. (3-2) by 3.7 years or 4% (Table 3-3). At other times, the differences were 3.9 to 7.4 years (18 to 37%). These calculations may not truly address aggregation as there may be more than one unidentified additional store of water and there may be aggregation within the individual sub-catchments (which impacts their estimated MTTs). Nevertheless, they do indicate that the potential uncertainties in MTTs due to aggregation are potentially several years (as discussed by Stewart et al., 2017). For waters with similar ^{3}H activities, Cartwright and Morgenstern (2016a) estimated that the aggregation error may be up to 20% where two waters with MTTs of 10 and 50

years or 1 and 5 years mixed but noted that this error became progressively lower if more stores of water with a similar range of MTTs mixed.

If the uncertainties are uncorrelated, an overall uncertainty is given by the square root of the sum of the squares of the individual uncertainties. Assuming that uncertainties due to analytical uncertainties and aggregation are uniformly 10% and 20%, respectively, and the uncertainties from the range of LPMs and the ^{3}H input of rainfall are as discussed above. For a water with a ^{3}H activity of 2 TU, the overall uncertainty in MTTs are approximately ±60% (±5.4 years), whereas for waters with ^{3}H activities of 1 TU and 0.5 TU they are ±28% (±17 years) and ±38% (±35 years), respectively.

While these uncertainties are considerable, the observation that the ^{3}H activities of the streams are locally 10% of those of modern rainfall (and far less than the rainfall ^{3}H activities at the peak of the bomb-pulse) necessitates that the MTTs must be several decades. Because the aggregation error, which is probably the most difficult to assess, results in MTTs being underestimated (Kirchner et al., 2016; Stewart et al., 2017) some MTTs may be longer than calculated. Relative differences in MTTs between and within catchments may be estimated with more certainty. Because the catchments are located in a relatively small area, the ^{3}H inputs are likely to be closely similar. Thus, uncertainties in the ^{3}H input are less likely to impact the comparison of MTTs between catchments. Additionally, as the geometry of the flow system in each catchment is unlikely to vary substantially at different streamflows, not being able to assess the suitability of the LPM has less impact on the relative differences in MTTs at different streamflows in the same catchment.

3.6.4 Predicting Mean Transit Times

There are weak ($R^2 \leq 0.7$) or no correlations between ^{3}H activities and catchment area, drainage density or forest cover (Table 3-32). There is a strong correlation between ^{3}H activities and average slope ($R^2 = 0.87$, p-value 0.01) during March 2015, when streamflow was lowest but not at other times. The variability of MTTs from James Access, Lardners Gauge, and Upper Lardners (which occur on the Otway Group (Fig. 3-1) and from Porcupine Creek, Yahoo Creek, Love Creek, and Ten Mile Creek (which have similar lithologies in their catchments: Fig. 3-1) indicates the MTTs are not simply related to the geology. A combination of the catchment properties together with the hydraulic conductivities of the soils and aquifers or evapotranspiration rates likely control the MTTs. The hydraulic properties and

evapotranspiration rates are probably spatially variable and are difficult to estimate, which makes it difficult to assess their influence. The observation that the relationship between ^{3}H activities and streamflow in all the catchments are similar (Fig. 3-4) suggests that the MTTs at high flows reflect the inflow of water from the shallower water stores, which will largely be independent of the catchment attributes.

There is a strong positive correlation between ^{3}H activities and the runoff coefficient (R^2 = 0.94, p-value = 0.27) (Fig. 3-10). This may be due to both the runoff coefficient and MTTs being controlled by the rates of recharge and groundwater flow. The Lardners Gauge and James Access sites have much higher runoff coefficients than the other catchments, and the correlation with ^{3}H activities may reflect the difference between the two groups of catchments. If this is the case, the runoff coefficient may be useful in determining gross rather than subtle differences in MTTs.

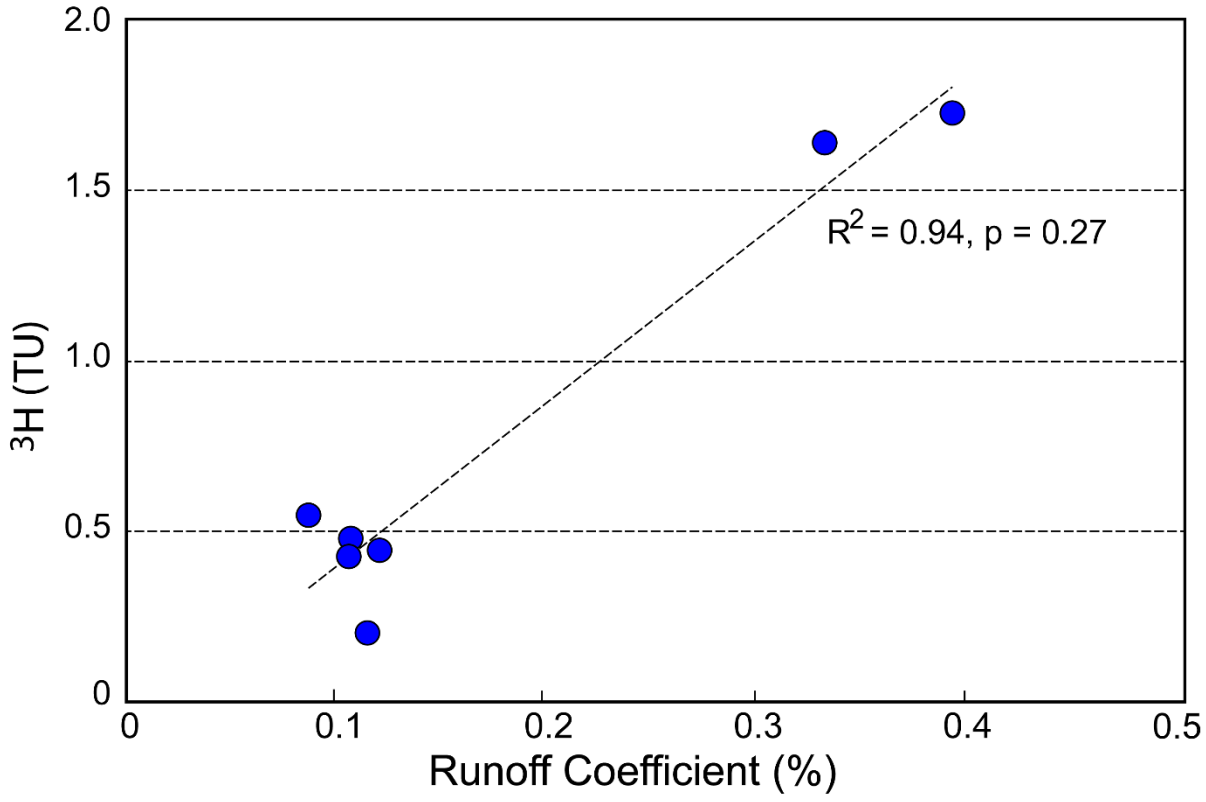

Figure 3-10: ^{3}H activities vs. runoff coefficients for the March 2015 samples (data from Table 3-1 and Supplement). Although a strong correlation (R^2 = 0.94) exists, it may be a result of the grouping of the samples.

EC and streamflow were measured on a monthly basis at the gauging station on Porcupine Creek (Site 235241) between January 1990 and January 1994 (Department of Environment, Land, Water and Planning, 2017). A strong correlation between MTTs and EC at this location (MTT = $1.362e^{0.0061*EC}$: R^2 = 0.96, p-value = 10^{-8}) allows MTTs at this site to be estimated over this four year period (Fig. 3-11). The estimated MTTs range from 3 to 50 years with the longest MTTs corresponding to low summer flows and the shortest MTTs during high winter flows. Although based upon a limited number of samples, these results demonstrate the high variability of transit times within the catchment and the value of finding proxies for ^3H.

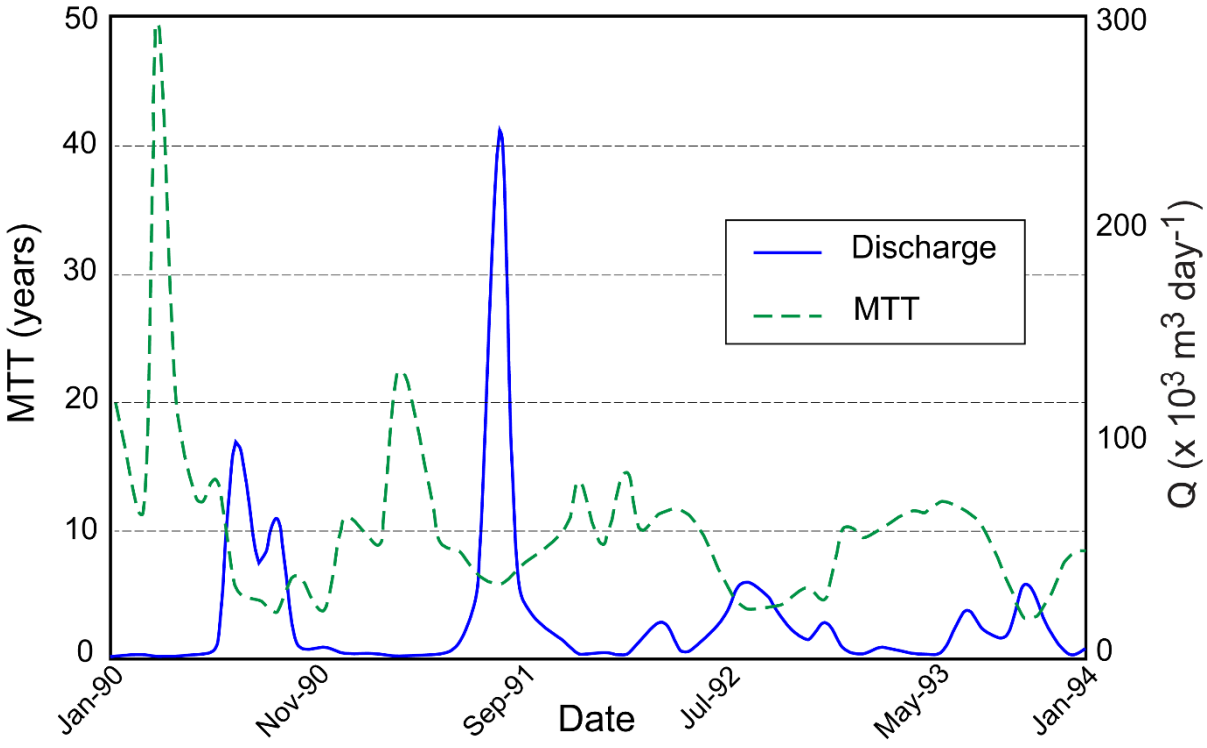

Figure 3-11: Variation in MTT as a function of streamflow at Porcupine Creek for January 1990 to January 1994 calculated using the relationship between EC and ^3H activity (Supplement) and monthly EC data from the Department of Environment, Land, Water and Planning (2017). Streamflow data also from the Department of Environment, Land, Water and Planning (2017).

3.7 Summary and Conclusions

The calculated MTTs in the six headwater catchments in the Upper Gellibrand catchment of Otway Ranges vary from approximately 7 to 230 years, verifying one of the hypotheses. While there are significant uncertainties in the MTT estimates, the conclusion that they range from years to several decades and are longer at low streamflows is robust. Similar MTTs are recorded in other catchments

in southeast Australia (e.g., Cartwright and Morgenstern, 2015, 2016a, 2016b). Especially at low streamflow, the MTTs are far longer than in most headwater catchments worldwide (e.g., Stewart et al., 2010) and are some of the longest yet recorded. The average MTT of 15±22 years calculated by Stewart et al. (2010) was for MTTs based on ^{3}H activities, which makes it directly comparable with MTTs from the South Australian catchments.

Understanding the reasons for the difference in MTTs between catchments is important for understanding catchment behaviour. The catchments in southeast Australia have similar dimensions, slopes, and stream densities to those elsewhere making it unlikely that the differences in MTTs result from catchment geomorphology. The Gellibrand catchments have only thin near-river alluvial sediments thus diminishing the likelihood of bank storage and return flows of young waters during the recession from the high streamflows. However, many headwater catchments globally lack extensive alluvial sediments. The hydraulic properties of the soils and aquifers may also result in slow recharge rates and long MTTs. These are very poorly known and it is difficult to assess their influence.

Due to the high transpiration rates of eucalyptus forests, recharge rates in Australian catchments are generally lower than elsewhere globally (Allison et al., 1990). However, the observation that there is no correlation between the percentage of forest cover and MTTs in the upper Gellibrand catchments where land clearing occurred several decades ago is problematic for proposing this as a simple control. Despite being in the more temperate region of southeast Australia, the average rainfall in the Otway Ranges of 1,000 to 1,600 mm yr^{-1} is modest compared with upland areas in many parts of the world and the average evapotranspiration rate of 1,000 to 1,100 mm yr^{-1} includes a sizeable component of evaporation (which is more prevalent on the cleared land) (Bureau of Meteorology, 2016). The long MTTs in the catchments from southeast Australia may, therefore, reflect the low rainfall and high evaporation and/or transpiration rates that limit recharge.

The long MTTs are significant for understanding and managing the catchments. Firstly, there are likely to be long-lived stores of water in these catchments that can sustain the streams during droughts that last up to a few years, although longer-term changes (such as land use change or climate change) may eventually affect the streamflows. The long MTTs also imply that any contaminants in groundwater are likely to be released into the streams over years to decades (c.f. Morgenstern and Daughney, 2012).

The locally higher nitrate and sulphate concentrations at high streamflows may reflect the input of contaminants from recent agricultural activities to the streams via the younger groundwater that is mobilised at those times.

Even at baseflow conditions, it was not possible to simply predict the MTTs across the catchments from catchment attributes or the geochemistry, although local correlations exist (this refutes one of the hypotheses). The MTTs are most likely controlled by a combination of catchment attributes and also soil properties, hydraulic conductivities, and evapotranspiration rates. This is in keeping with the observation that previous studies have identified correlations between a range of parameters and MTTs (i.e. no single attribute appears to provide the dominant control on MTTs across different regions). Characterising hydraulic properties and evapotranspiration rates on a catchment-wide scale is difficult, which limits the ability to predict MTTs. The runoff coefficient that is a reasonable indicator of MTTs elsewhere in southeast Australia (Cartwright and Morgenstern, 2015) was the best predictor of MTTs. This may reflect the fact that both the runoff coefficient and MTTs are controlled by recharge and groundwater flow rates.

This study illustrates that, while broad ranges of MTTs may be estimated from ^{3}H, precise determination of MTTs is difficult. Additionally, it highlights the challenge in understanding the reasons for the long MTTs in the Australian catchments compared with headwater catchments elsewhere. The potential controls on MTTs in catchments are numerous and more studies in catchments with different climate, landuse, geomorphology, and geology are needed if the desire to be able to predict catchment behaviour regionally or globally is to be realised.

3.8 Data Availability

All geochemistry data utilised in this study are contained in the Supplement. Streamflow data and historic EC data for Porcupine Creek are publicly available from the Victorian State Government, Department of Environment, Land, Water & Planning (DELWP), Water Measurement Information System (http://data.water.vic.gov.au/monitoring.htm).

3.9 Author Contributions

William Howcroft undertook the sampling program and oversaw the analysis of the geochemical parameters and the MTT calculations. Uwe Morgenstern was responsible for the ^{3}H analysis. The manuscript was prepared by William Howcroft, Ian Cartwright and Uwe Morgenstern.

3.10 Acknowledgements

Field work and laboratory analyses were conducted with the help of Massimo Raveggi, Rachelle Pearson, Wang Dong, Kwadwo Osei-Bonsu and Lei Chu. Funding for this project was provided by Monash University and the National Centre for Groundwater Research and Training (NCGRT). NCGRT is an Australian Government initiative supported by the Australian Research Council and the National Water Commission via Special Research Initiative SR0800001. We also thank two anonymous reviewers and HESS editor Markus Hrachowitz for their perceptive and helpful comments.

3.11 References

Allison, G.B., Cook, P.G., Barnett, S.R., Walker, G.R., Jolly, I.D., and Hughes, M.W.: Land clearance and river salinisation in the western Murray Basin, Australia, J. Hydrol., 119, 1-20, doi: 10.1016/0022-1694(90)90030-2, 1990.

Atkinson, A.P.: Surface water – groundwater interactions in an upland catchment (Gellibrand River, Otway Ranges, Victoria, Australia), Ph.D. Thesis, Monash University, Australia, 2014.

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Hoffman, H., Unland, N.P., Cendon, D.I., and Chisari, R.: A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry, Hydrol. Process., 24, 1-12, doi: 10.1002/hyp.10122., 2013.

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Cendon, D.I., Unland, N.P., and Hoffman, H.: Using ^{14}C and ^{3}H to understand groundwater flow and recharge in an aquifer window, Hydrol. Earth Syst. Sci., 18, 4951-1964, doi: 10.5194/hess-18-4951-2014, 2014.

Bazemore, D.E., Eshleman, K.N., and Hollenbeck, K.J.: The role of soil water in storm flow generation in a forested headwater catchment: Synthesis of natural tracer and hydrometric evidence, J. Hydrol., 162, 47-75, doi: 10.1016/0022-1694(94)90004-3, 1994.

Blavoux, B., Lachassagne, P., Henriot, A., Ladouche, B., Marc, V., Beley, J.-J., Nicoud, G., Olive, P.: A fifty-year chronicle of tritium data for characterising the functioning of the Evian and Thonon (France) glacial aquifers, J. Hydrol., 494, 116-133, doi: 10.1016/j.jhydrol.2013.04.029, 2013.

Bureau of Meteorology: Comonwealth of Australia, Bureau of Meteorology, http://www.bom.gov.au, last access: 21 January 2016.

Cartwright, I., and Morgenstern, U.: Transit times from rainfall to baseflow in headwater catchments estimated using tritium: the Ovens River, Australia, Hydrol. Earth Syst. Sci., 19, 3771-3785, doi: 10.5194/hess-19-3771-2015, 2015.

Cartwright, I., and Morgenstern, U.: Contrasting transit times of water from peatlands and eucalypt forests in the Australian Alps determined by tritium: implications for vulnerability and the source of water in upland catchments, Hydrol. Earth Syst. Sci., 20, 4757-4773, doi: 10.5194/hess-20-4757-2016, 2016a.

Cartwright, I., and U. Morgenstern, U.: Using tritium to document the mean transit time and source of water contributing to a chain-of-ponds river system: Implications for resource protection, Appl. Geochem., 75, 9-19, doi: 10.1016/j.apgeochem.2016.10.007, 2016b.

Cartwright, I., Weaver, T.R., Stone, D. and Reid, M.: Constraining modern and historical recharge from bore hydrographs, ^{3}H, ^{14}C, and chloride concentrations: Applications to dual-porosity aquifers in dryland salinity, Murray Basin, Australia. J. Hydrol., 332, 69-92, doi: 10.1016/j.jhydrol.2006.06.034, 2007.

Cook, P.G., and Bohlke, J.K.: Determining timescales for groundwater flow and solute transport, in: Environmental Tracers in Subsurface Hydrology, Kluwer, Boston, USA, 1-30, 2000.

Cook, P.G., Jolly, I.D., Leaney, F.W., Walker, G.R., Allan, G.L, Fifield, L.K., and Allison, G.B.: Unsaturated zone tritium and chlorine 36 profiles from southern Australia: Their use as tracers of soil water movement. Water Resour. Res., 30, 1709-1719, doi: 10.1029/94WR00161, 1994.

Costelloe, J.F., Peterson, T.J., Halbert, K., Western, A.W., and McDonnell, J.J.: Groundwater surface mapping informs sources of catchment baseflow, Hydrol. Earth Syst. Sci., 19, 1599-1613, doi: 10.5195/hess-19-1599-2015, 2015.

DataSearch Victoria: Victoria Department of Sustainability and Environment Spatial Warehouse: http://services.land.vic.gov.au/SpatialDatamart/index.jsp, last access: 10 June 2015.

Department of Environment, Land, Water and Planning: Water Measurement Information System (WMIS): http://data.water.vic.gov.au/monitoring.htm, last access: 10 February 2017.

Duvert, C., Stewart, M.K., Cendon, D.I., and Raiber, M.: Time series of tritium, stable isotopes and chloride reveal short-term variation in groundwater contribution to a stream, Hydrol. Earth Syst. Sci., 20, 257-277, doi: 10.5194/hess-20-257-2016, 2016.

ESRI. ArcGis Desktop: Release 10.2. Redlands, CA: Environmental Systems Research Institute, 2013.

Fenicia, F., Savenije, H.H.G., Matgen, P., and Pfister, L.: Is the groundwater reservoir linear? Learning from data in hydrologic modelling, Hydrol. Earth Syst. Sci., 10, 139-150, doi: 10.5194/hess-10-139-2006, 2006.

Freeman, M.C., Pringle C.M., and Jackson, C.R.: Hydrologic connectivity and the contribution of stream headwaters to ecologic integrity at regional scales, J. Am. Water Resour. Ass., 43(1), 5-14, doi: 10.1111/j.1752-1688.2007.00002.x, 2007.

Gelhar, L.W., Welty, C., and Rehfeldt, K.R.: A critical review of data on field-scale dispersion in aquifers, Water Resour. Res., 28, 1955-1974, doi: 10.1029/92WR00607, 1992.

Hale, V.C., and McDonnell, J.J.: Effect of bedrock permeability on stream base flow mean transit time scaling relationships: 1. A multiscale catchment intercomparison, Water Resour. Res., 52, 1358-1374, doi: 10.1002/2014WR016124, 2016.

Hebblethwaite, D., and James, B.: Review of surface water data, Kawarren, Hydrology & Surface Water Resources Section, Investigations Branch, Technical Services Division, Rural Water Commission of Victoria, Investigations Report No. 1990/45, 1990.

Hrachowitz, M., Savenije, H., Bogaard, T.A., Tetzlaff, D., and Soulsby, C.: What can flux tracking teach us about water age distribution patterns and their temporal dynamics? Hydrol. Earth System Sci., 17, 533-564. doi: 10.5194/hess-17-533-2013, 2013.

Hrachowitz, M., Soulsby, C., Tetzlaff, D., Dawson, J.J.C., and Malcom, I.A.: Regionalization of transit time estimates in montane catchments by integrating landscape controls. Water Resour. Res., 45, WR05421, doi: 10.1029/2008WR007496, 2009.

Hrachowitz, M., Soulsby, C., Tetzlaff, D., and Speed, M.: Catchment transit times and landscape controls – does scale matter? Hydrol. Process., 24, 117-125, doi: 10.1002/hyp.7510, 2010.

International Atomic Energy Agency: Global Network of Isotopes in Precipitation, available at: http://www.iaea.org/water, last access: March, 2016.

Jensco, K.G., and McGlynn, B.: Hierarchical controls on runoff generation: Topographically driven hydrologic connectivity, geology and vegetation. Water Resour. Res., 47, W11527, doi: 10.1029/2011WR010666, 2011.

Jurgens, B.C., Bohkle, J.K., and Eberts, S.M.: TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data, US Geol. Surv., Techniques and Methods Report 4-F3, US Geological Survey, Reston, USA. 60 pp., 2012.

Kennedy, V.C., Kendall, C., Zellweger, G.W., Wyerman, T.A., and Avanzino, R.J.: Determination of the components of storm flow using water chemistry and environmental isotopes, Mattole River Basin, California, J. Hydrol., 84, 107-140, doi: 10.1016/0022-1694(86)90047-8, 1986.

Kinzelbach, W., Aeschbach, W., Alberich, C., Goni, I.B., Beyerle, U., Brunner, P., Chiang, W. H., Rueedi, J., and Zoellmann, K.: A survey of methods for groundwater recharge in arid and semi-arid regions: early warning and assessment report series: Nairobi, Kenya, Division of Early Warning and Assessment, United Nations Environment Programme, 101 pp., 2002.

Kirchner, J.W., Tetzlaff, D., and Soulsby, C.: Comparing chloride and water isotopes as hydrologic tracers in two Scottish catchments, Hydrol. Process., 24, 1631-1645, doi: 10.1002./hyp.7676, 2010.

Kirchner, J.W. Aggregation in environmental systems – Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments, Hydrol. Earth Syst. Sci., 20, 279-297, doi: 10.5194/hess-20-279-2016, 2016.

Leonard, J., Lakey, R., and Cumming, S.: 1981. Gellibrand groundwater investigation interim report, December 1981, Geological Survey of Victoria, Department of Minerals and Energy, Unpublished Report 1981/132, 1981.

Ma, W., and Yamanaka, T.: Factors controlling inter-catchment variation of mean transit time with consideration of temporal variability, J. Hydrol., 534, 193-204, doi: 10.1016/j.jhydrol.2015.12.061, 2016.

Maloszewski, P.: Lumped-parameter models as a tool for determining the hydrologic parameters of some groundwater systems based on isotope data, IAHS-AISH Publication 262, Vienna, Austria, pp. 271-276, 2000.

Maloszewski, P., and Zuber, A.: Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability, J. Hydrol., 57, 207-231, doi: 10.1016/0022-1694(82)90147-0, 1982.

Maloszewski, P., and Zuber, A.: On the calibration and validation of mathematical models for the interpretation of tracer experiments in groundwater, Adv. Water Resour., 15, 47-62, doi: 10.1016/0309-1708(92)90031-V, 1992.

Maloszewski, P., and Zuber, A.: Lumped parameter models for the interpretation of environmental tracer data, in: International Atomic Energy Agency, Manual on mathematical models in isotope hydrogeology, TECDOC-910: Vienna, Austria, International Atomic Energy Agency Publishing Section, 9-58, 1996.

Maloszewski, P., Rauert, W., Stichler, W., and Herrmann, A.: Application of flow models in an alpine catchment area using tritium and deuterium data, J. Hydrol., 66, 319-330, doi: 10.1016/0022-1694(83)90193-2, 1983.

McDonnell, J.J., McGuire, K., Aggarwal, P., Beven, J., Biondi, D., Destouni, G., Dunn, S., James, A., Kirchner, J., Kraft, P., Lyon, S., Maloszewski, P., Newman, B., Pfister, L., Rinaldo, A., Rodhe, A., Sayama, T., Seibert, J., Solomon, K., Soulsby, C., Stewart, M., Tetzlaff, D., Tobin, C., Troch, P., Weiler, M., Western, A., Worman, A., and Wrede, S.: How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis, Hydrol. Process., 24, 1745-1754, doi: 10.1002/hyp.7796, 2010.

McGlynn, B., McDonnell, J., Stewart, M., and Seibert, J.: On the relationship between catchment scale and streamwater residence time, Hydrol. Process., 17, 175-181, doi: 10.1002/hyp.5085, 2003.

McGuire, K.J., and McDonnell, J.J.: A review and evaluation of catchment transit time modelling, J. Hydrol., 330, 543-563, doi: 10.106/j.jhydrol.2006.04.020, 2006.

McGuire, K.J., McDonnell, J.J., Weiler, M., Kendall, C., McGlynn, B.L., Welker, J.M. and J. Seibert, 2005. The role of topography on catchment-scale water residence time. Water Resources. Research, Vol. 41, W05002, doi: 10.1029/2004WR003657, 2005.

Morgenstern, U., and Daughney, C.J.: Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand, J. Hydrol., 456-457, 79-93, doi: 10.1016/j.jhydrol.2012.06.010, 2012.

Morgenstern, U., and Taylor, C.B.: Ultra low-level tritium measurement using electrolytic enrichment and LSC, Isot. Environ. Health Stud., 45, 96-117, doi: 10.1080/10256010902931194, 2009.

Morgenstern, U., Stewart, M.K., and Stenger, R.: Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit times with streamflow, Hydrol. Earth Syst. Sci., 14, 2289-2301, doi: 10.5194/hess-14-2289-2010, 2010.

Mueller, M.H., Weingartner, R., and Alewell, C.: Importance of vegetation, topography and flow paths for water transit times of baseflow in alpine headwater catchments, Hydrol. Earth Syst. Sci., 17, 1661-1679, doi: 10.5194/hess-17-1661-2013, 2013.

Petrides, B., and Cartwright, I.: The hydrogeology and hydrogeochemistry of the Barwon Downs Graben aquifer, southwestern Victoria, Australia, Hydrogeol. J., 14, 809-826, doi: 10.1007/s10040-005-0018-8, 2006.

Sklash, M.G., and Farvolden, R.N.: The role of groundwater in storm runoff, J. Hydrol., 43, 45-65, doi: 10.1016/0022-1694(79)90164-1, 1979.

Soulsby, C., Malcolm, R., Helliwell, R., Ferrier, R.C., and Jenkins, A.: Isotope hydrology of the Allt a' Mharcaidh catchment, Cairngorms, Scotland: implications for hydrologic pathways and residence time, Hydrol. Process., 14, 747-762, doi: 10.1002 / (SICI) 1099-1085(200003)14, 2000.

Stanley, D.R.: Resource evaluation of the Kawarren Sub-Region on the Barwon Downs Graben, RWC Investigations Branch Unpublished Report 1991/36, Rural Water Commission of Victoria, 1991.

Stewart, M.K., and Fahey, B.D.: Runoff generating processes in adjacent tussock grassland and pine plantation catchments as indicated by mean transit time estimation using tritium, Hydrol. Earth Syst. Sci., 14, 1021-1032, doi: 10.5194/hess-14-1021-2010, 2010.

Stewart, M.K., Morgenstern, U., and McDonnell, J.J.: Truncation of stream residence times: how the use of stable isotopes has skewed our concept of streamwater age and origin, Hydrol. Process., 24, 1646-1659, doi: 10.1002/hyp.7576, 2010.

Stewart, M.K., Morgenstern, U., Gusyev, M.A., and Maloszewski, P.: Aggregation effects on tritium-based mean transit times and young water fractions in spatially heterogeneous catchments and groundwater systems, and implications for past and future applications of tritium, Hydrol. Earth Syst. Sci., 21, 4615-4627, doi: 10.5194/hess-21-4615-2017, 2017.

Stockinger, M.P., Bogena, H.R., Lucke, A., Diekkruger, B., Weiler, M., and Vereecken, V.: Seasonal soil moisture patterns: Controlling transit time distributions in a forested headwater catchment, Water Resour. Res., 50, 5270-5289, doi: 10.1002/2013WR014815, 2014.

Swistock, B.R., DeWalle, D.R., and Sharp, W.E.: Sources of acidic storm flow in an Appalachian headwater stream, Water Resour. Res., 25, 2139-2147, doi: 10.1029/WR025i010p02139, 1989.

Tadros, C.V., Hughes, C.E., Crawford, J., Hollins, S.E., and Chisari, R.: Tritium in Australian precipitation: a 50 year record, J. Hydrol., 513, 262-273, doi: 10.1016/j.jhydrol.2014.03.031, 2014.

Teng, M.L.: Modelling the seasonal variation of groundwater yield and recharge of the Barwon Downs Aquifer, South-Western Victoria, MS Thesis, University of Melbourne, Australia, 1996.

Tetzlaff, D., Malcolm, I.A., and Soulsby, C.: Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments, J. Hydrol., 346, 93-111, doi: 10.1016/j.jhydrol.2007.08.016, 2007.

Tetzlaff, D., Seibert, J., and Soulsby, C.: Inter-catchment comparison to assess the influence of topography and soils on catchment transit times in a geomorphic province; the Cairngorm mountains, Scotland, Hydrol. Process., 23, 1874, doi: 10.1002/hyp.7318, 2009.

Tickell, S.J., Cummings, S., Leonard, J.G., and Withers, J.A.: Colac: 1:50 000 Map Geological Report, Geological Survey Report No. 89, Victoria Department of Manufacturing and Industry Development, 1991.

Timbe, E., Windhorst, D., Celleri, R., Timbe, L., Crespo, P., Frede, H.-G., Feyen, J., and Breuer, L.: Sampling frequency trade-offs in the assessment of mean transit times of tropical montane catchment waters under semi-steady-state conditions. Hydrol. Earth Syst. Sci., 19, 1153-1168, doi: 10.5194/hess-19-1153-2015, 2015.

Witebsky, S., Jayatilaka, C., and Shugg, A.: Groundwater development options and environmental impacts – Barwon Downs Graben South-western Victoria, Department of Water Resources, Victoria, Draft Report, 1992.

Yang, Q., Xiao, H., Zhao, L., Yang, Y., Li, C., Zhao, L., and Yin, L.: Hydrological and isotopic characterization of river water, groundwater and groundwater recharge in the Heihe River basin, northwest China, Hydrol. Process., 25, 1271-1283, doi: 10.1002/hyp.7896, 2011.

Zuber, A., and Maloszewski, P.: Lumped Parameter Models, Environmental Isotopes in Hydrological Cycle, Vol. VI, Modelling, IAEA/UNESCO, Paris, Technical Document, 2001.

Zuber, A., Witczak, S., Rozanski, K., Sliwka, I., Opoka, M., Mochalski, P., Kuc, T., Karlikowska, J., Kania, J., Jackowicz-Korczynski, M., and Dulinski, M.: Groundwater dating with ^{3}H and SF_6 in relation to mixing patterns, transport modelling and hydrochemistry, Hydrol. Process., 19, 2247-2275, doi: 10.1002/hyp.5669, 2005.

Supplement. Geochemistry of the upper Gellibrand catchment streams

Location[a]	Date	Q	EC	pH	TDS	HCO_3	F	Cl	Br	NO_3	SO_4	Si	Na	Mg	K	Ca	^3H
		10^3 m^3 day^{-1}	µS/cm	S.U.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	TU
Upper Lardners (UL)	10/07/2014	nm[c]	142	6.26	74	7.8	0.02	30.5	0.06	2.31	3.9	5.5	18.2	2.7	0.7	2.1	1.99±0.04[b]
	28/09/2014	nm	168	6.03	83	15.1	0.03	30.1	0.07	0.68	3.4	6.7	18.8	3.4	1.3	3.1	1.77±0.04
	20/03/2015	nm	192	7.11	118	41.8	0.03	31.5	0.07	0.37	3.1	7.2	21.1	5.1	1.9	5.7	1.54±0.04
	10/09/2015	nm	154	6.48	81	11.3	0.03	33.0	0.08	1.72	4.2	6.1	18.7	2.8	1.1	2.4	1.99±0.03
Lardners Gauge (LG)	10/07/2014	151.3	164	6.19	85	9.5	0.02	35.8	0.08	3.03	4.5	5.3	19.9	3.1	1.6	2.4	1.94±0.04
	28/09/2014	32.8	182	6.45	94	18.3	0.02	34.0	0.09	1.21	3.3	6.2	22.6	3.8	1.3	3.4	1.94±0.04
	20/03/2015	5.0	197	6.71	114	35.0	0.03	35.3	0.10	0.29	2.7	6.6	21.7	4.9	1.9	5.0	1.64±0.04
	10/09/2015	116.6	179	5.87	92	12.3	0.03	38.9	0.09	2.23	4.5	5.9	21.0	3.3	1.4	2.8	1.97±0.03
	4/11/2015	12.7	172	6.68	100	22.2	0.03	36.4	0.09	1.78	3.5	6.4	20.6	3.7	1.7	3.4	1.77±0.04
Gellibrand River @ James' Access (JA)	13/03/2012[d]	18.5	160	nm	93	39.0	0.07	26.0	0.05	0.05	3.3	nm	14.7	3.0	1.5	5.0	1.90±0.09
	26/04/2012[d]	30.4	161	nm	85	27.0	0.07	27.2	0.07	0.40	2.8	nm	16.6	3.8	1.4	6.0	1.80±0.08
	10/07/2014	255.2	151	6.70	74	10.0	0.03	27.6	0.06	2.41	3.6	6.2	17.6	2.6	1.0	2.6	2.04±0.04
	28/09/2014	39.1	164	6.66	87	21.4	0.05	28.0	0.08	0.48	3.2	6.7	19.0	3.3	1.1	3.8	1.93±0.04
	20/03/2015	8.8	162	6.71	94	28.5	0.03	28.0	0.07	0.08	2.9	6.3	18.6	3.6	1.5	4.4	1.73±0.04
	10/09/2015	204.4	146	6.68	84	17.8	0.04	29.7	0.08	1.64	3.7	6.6	17.5	2.7	1.0	3.0	2.08±0.03
Porcupine Creek (PC)	10/07/2014	50.4	281	6.33	138	11.5	0.05	61.1	0.08	0.28	10.2	6.5	34.9	5.1	1.7	6.4	1.97±0.04
	27/09/2014	3.3	380	6.76	200	51.2	0.04	68.4	0.17	0.21	5.1	7.2	44.6	7.2	2.2	14.0	1.68±0.04
	20/03/2015	1.0	723	7.30	528	271.8	0.12	90.1	0.26	0.74	8.1	13.4	61.9	15.8	7.6	58.4	0.20±0.02
	10/09/2015	9.7	319	6.51	171	15.0	0.04	83.1	0.15	0.31	9.1	7.2	41.3	6.1	1.7	6.8	2.08±0.04
	4/11/2015	0.6	661	6.95	485	235.7	0.13	99.1	0.31	0.68	8.3	11.7	60.1	14.2	6.7	47.7	0.40±0.02
Ten Mile Creek (TC)	10/07/2014	8.6	397	6.43	184	7.8	0.05	90.4	0.22	0.54	13.5	4.6	54.3	7.1	1.8	3.5	1.74±0.04
	27/09/2014	0.6	463	6.48	229	29.3	0.02	101.6	0.31	0.26	13.8	4.8	65.8	8.1	1.2	3.6	1.00±0.03
	20/03/2015	0.2	406	6.47	191	4.6	0.02	102.8	0.33	0.08	10.0	4.8	59.1	5.8	0.9	2.3	0.44±0.02
	10/09/2015	1.7	562	6.45	285	12.8	0.06	156.1	0.43	0.37	16.1	5.7	77.2	9.8	1.4	4.9	1.09±0.02
	4/11/2015	0.1	392	6.49	199	7.6	0.03	107.8	0.34	0.22	11.8	4.6	57.6	5.8	1.0	2.5	0.53±0.02

Location[a]	Date	Q	EC	pH	TDS	HCO_3	F	Cl	Br	NO_3	SO_4	Si	Na	Mg	K	Ca	^3H
		10^3 m^3 day^{-1}	µS/cm	S.U.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	TU
Yahoo Creek (YC)	11/07/2014	23.0	368	5.73	221	37.8	0.03	94.1	0.20	0.24	13.7	5.7	53.3	7.9	2.1	6.1	2.14±0.04
	28/09/2014	1.2	505	6.09	276	69.5	0.03	103.8	0.33	0.14	14.2	3.0	66.9	9.2	1.8	7.3	1.19±0.03
	20/03/2015	0.4	471	6.52	229	26.8	0.03	112.3	0.37	0.17	7.0	4.0	65.1	7.3	0.9	5.3	0.43±0.02
	10/09/2015	3.9	569	6.22	283	5.6	0.04	153.0	0.37	0.41	24.1	5.2	72.8	10.9	2.0	8.7	1.30±0.03
Love Creek Kawarren (LK)	10/07/2014	102.9	402	6.66	197	21.7	0.13	83.8	0.18	1.28	14.5	5.0	47.2	7.6	5.2	10.2	1.85±0.03
	27/09/2014	6.7	570	6.75	286	59.8	0.05	105.9	0.33	4.30	10.3	4.9	66.5	11.0	6.7	16.1	1.34±0.03
	20/03/2015	2.0	527	6.99	286	62.0	0.04	114.3	0.34	0.94	9.1	6.1	66.2	8.9	3.4	15.2	0.48±0.02
	10/09/2015	18.6	456	6.71	236	25.9	0.06	112.0	0.24	0.92	12.3	6.5	55.8	8.5	2.9	10.8	1.91±0.03
	4/11/2015	1.2	522	6.23	307	68.8	0.07	124.0	0.37	1.02	10.9	5.8	65.6	9.6	2.7	17.9	0.58±0.02
Love Creek Wonga (LW)	10/07/2014	103.5	411	6.58	204	22.3	0.08	86.2	0.19	1.08	16.7	6.0	48.3	9.0	3.5	10.5	1.86±0.04
	28/09/2014	6.0	721	6.93	367	84.2	0.10	135.9	0.42	3.33	11.8	6.4	76.7	17.8	6.4	23.5	1.34±0.03
	20/03/2015	2.0	857	7.27	481	128.7	0.06	178.8	0.57	0.56	9.6	9.8	86.2	23.0	8.1	35.9	0.55±0.02
	10/09/2015	19.6	514	6.82	271	37.3	0.07	125.2	0.26	1.15	13.8	7.0	57.7	11.1	3.5	14.1	1.88±0.03
Birnam Rainfall	27/09/2014	-	80	6.49	25	5.7	0.00	8.5	0.02	0.23	1.5	0.0	5.1	0.7	2.6	0.8	2.45±0.04

Notes:

a) Locations on Fig. 3-1
b) Uncertainty
c) Not measured
d) Data from Atkinson (2014)

Chapter 4

Bank Storage and Return Flow: Residence Times and Influence on River Water Chemistry in the upper Barwon River, Australia

In preparation for submission to Applied Geochemistry

Abstract

The residence times of bank storage and return flow and its influence on river water chemistry in the upper Barwon River of southeast Australia were investigated using stable (^{18}O, ^{2}H, and ^{13}C) and radioactive (^{3}H and ^{36}Cl) isotopes, major ion geochemistry, river discharge data, and electrical conductivity (EC)-discharge hysteresis loops. Downstream increases in ^{3}H activities following high winter river flows indicate that bank storage and return flow contributes to river discharge for periods of at least several months. However, EC-discharge hysteresis patterns indicate that individual storm events make additional contributions to bank storage and return flow throughout the year, with residence times on the order of a few weeks. The upper Barwon River has ^{3}H activities >1.75 TU throughout the year, suggesting that the contribution of older regional groundwater, which has below-detection ^{3}H activities (~0.04 TU), is minor in comparison to bank return flows. However, downstream increases in total dissolved solids (TDS) concentrations, $\delta^{13}C$ values and $R^{36}Cl$ values demonstrate that regional groundwater inputs are nevertheless instrumental in delivering solutes to the river. Elevated $R^{36}Cl$ values in river water in the uppermost portion of the catchment are likely due to plant uptake and recycling of bomb-pulse ^{36}Cl, which suggests Cl residence times of up to ~60 years. The results of this study clearly demonstrate that river water is comprised of both young and old water. Thus, managing rivers and near-river environments should include careful consideration of both inputs.

4.1. Introduction

Determining the residence times of water and solutes in river catchments is important for protecting water quality, riparian vegetation and groundwater dependent ecosystems. Likewise, understanding residence times is also important in terms of interpreting bio- and hydrogeochemical reactions within the river and the near-river environments, understanding the fate and transport of nutrients and solutes, and predicting when changes that occur within a catchment, such as urbanisation or land use, might affect the river. The temporal variation of stable isotope ratios in river water suggests that, globally, about one-third of total river flow is derived from precipitation that fell within the past two to three months (Jasechko et al., 2016). However, ^{3}H activities imply that river water in many catchments commonly has residence times of years or even decades (Soulsby et al., 2000; McGuire and McDonnell, 2006; Stewart et al., 2010; Cartwright and Morgenstern, 2015; Duvert et al., 2016). Together, these statements suggest that river water is a mixture of both young and old water. Less clear, however, is from what stores that water is derived, the relative importance of these stores in supporting river flow, and their residence times.

4.1.1. The Importance of Bank Storage and Return Flow

There are numerous stores that potentially contribute water to rivers. These include groundwater, bank storage and return flow, perched aquifers, water held in the unsaturated zone, and interflow (McCallum et al., 2010; Hrachowitz et al., 2011; Cartwright et al., 2014). The relative importance of these inputs in determining total river flow can vary throughout the year, i.e. both seasonally and following storm events. For example, Squillace (1996) demonstrated that bank storage and return flow can act as an important source of water during low-flow conditions. Conversely, McCallum et al. (2010) demonstrated that bank storage and return flow can be important contributors to river flow during storm events.

Bank storage occurs when the river level is higher than that of the groundwater in the adjacent aquifers. This results in the infiltration of river water into the near-river sediments, where it mixes with groundwater. The mixed water has a chemical composition and

residence time intermediate between that of the river and of groundwater. Bank infiltration can occur both seasonally (i.e. during high winter flows) and during individual storm events that may occur throughout the year. When river levels recede as a result of a decline in seasonal rainfall, or following flood events, the water flows back into the river as bank return flow. While the mechanisms of bank storage and return flow are reasonably well understood, its residence time is not. Numerical modelling suggests that bank return flow can occur over periods ranging from weeks to years or even decades (e.g. Squillace, 1996; Whiting and Pomeranets, 1997; McCallum et al., 2010, Doble et al., 2011; McCallum and Shanafield, 2016). However, to the author's knowledge, there have been no field-based estimates to evaluate the residence times of water in the river banks.

4.1.2. Hysteresis

Hysteresis patterns, which are defined as a non-linear relationship between river discharge and the concentration of a solute, can provide insight into river catchment functioning. Traditionally used to examine nutrient concentrations (e.g. Bowes et al., 2015) or turbidity/sediment transport (e.g. House and Warwick, 1998) as function of discharge, hysteresis patterns can also provide information on the source(s) of water feeding a river. Hysteresis patterns can take two forms, clockwise and anti-clockwise. With clockwise patterns, solute concentrations decrease in magnitude with a corresponding increase in discharge, before increasing again as discharge decreases. Conversely, with anti-clockwise patterns, the opposite holds true. Clockwise patterns suggest a water source close to the sampling location, whereas anti-clockwise patterns suggest a water source far from the sampling location (Williams, 1989). In this study, hysteresis patters in electrical conductivity (EC) are utilised to evaluate the importance and timing of bank storage and return flow in contributing to river discharge during individual storm events.

4.1.3. Evaluating the Residence Times of Water

The residence or transit times of groundwater and surface water can be evaluated using radioactive tracers such as ^{3}H, ^{14}C and ^{36}Cl (e.g. Bentley et al., 1986; Torgersen et al., 1991; McCallum et al., 2014; Kwicklis and Farnham, 2014). In many respects, ^{3}H is an ideal tracer as it is part of the water molecule, does not undergo significant fractionation as result of evaporation, and behaves conservatively in the environment. With a half-life of 12.32 years, ^{3}H can be used to determine residence times of up to about 150 years. ^{14}C, with a half-life of 5,730 years, can be used to evaluate residence times of up to approximately 30 ka (Clarke and Fritz, 1997) from dissolved inorganic carbon (DIC). However, the interpretation of ^{14}C activities in surface water is complicated by biogeochemical reactions such as mineralisation of particulate and dissolved organic carbon (DOC), exchange with the atmosphere, and dissolution of particulate inorganic carbon (Broecker and Walton, 1959; Taylor, 1997; Bourke et al., 2014). ^{36}Cl has a half-life of 301,000 years and can be used to estimate solute residence times of up to ~1 Ma. Similar to ^{3}H, ^{36}Cl is expected to behave conservatively. In this study, ^{3}H and ^{36}Cl are employed to evaluate water and solute residence times in the upper Barwon River of southeast Australia.

4.1.4. Objectives

The main objective of this study is to examine the residence times of bank storage and return flow in the upper Barwon River of southeast Australia. This is primarily conducted through the use of stable and radioactive isotopes in combination with major ion geochemistry of the river water and river discharge data to understand processes on an annual timescale. Additionally, solute-discharge hysteresis patterns are used to examine bank storage and return flows on shorter timescales due to storm events. Relative to other rivers in the region, the upper Barwon River is highly saline (Roderick, 1988; Gill, 1989; Coram, 1996) and this study also investigates the role of bank storage and return flow in determining river water chemistry. While this research is based upon a specific region, the questions addressed are important for similar river systems in semi-arid regions globally.

4.2. Setting

The Barwon River Catchment is located in southwestern Victoria, Australia approximately 100 km west of Melbourne. Comprising an area of approximately 3,900 km^2 (DataSearch Victoria, 2015), the catchment is utilised primarily for grazing, cropping and forestry. Towns within the catchment include Geelong and Ballarat, as well as numerous rural communities, including Forrest, Winchelsea and Inverleigh (Fig. 4-1).

The Barwon River Catchment includes the Barwon, Leigh and Moorabool Rivers. However, this investigation focuses only on the upper Barwon River upstream of Inverleigh (Fig. 4-1). The headwaters of the upper Barwon River drain the northern and western slopes of the Otway Ranges, which reach a maximum elevation of approximately 650 m AHD (Australia Height Datum). The Otway Ranges are largely forested with native eucalyptus and plantation hardwoods; the remainder of the catchment consists mainly of grassland that is utilised extensively for grazing and cropping.

The Upper Barwon catchment has a temperate climate, with average annual rainfall ranging from approximately 450 mm at Inverleigh to approximately 1,600 mm at Mount Sabine in the Otway Ranges (Department of Environment, Land, Water and Planning, 2017). The majority of rainfall occurs during the austral winter months (July to September). During the summer months, potential evaporation exceeds precipitation (Bureau of Meteorology, 2017). There are a number of permanent and semi-permanent brackish to hypersaline lakes within the study area, the largest of which is Lake Murdeduke (Fig. 4-1).

The main tributaries to the upper Barwon River are Boundary Creek, Birregurra Creek, the West Barwon River and the Barwon River East Branch. The Barwon River is perennial, unregulated and, based upon downstream increases in discharge, EC and major ion concentrations, is considered to be gaining (Cartwright et al., 2013a; Cartwright et al., 2014). River flows are strongly seasonal, with approximately 60% of annual discharge occurring between the months of July and September and approximately 5% occurring between

January and March (DWR, 1989). Average annual discharge at Inverleigh during the period from 2000 to 2015 was approximately 1.4 x 10^5 m^3 $year^{-1}$.

The geology of the study area is described by Tickell et al. (1991). The basement comprises the early Cretaceous Otway Group, which consists primarily of volcanogenic sandstone and mudstone. The Otway Group crops out extensively in the Otway Ranges (Fig. 4-1) and is considered to be a poor aquifer. The Otway Group is overlain by Tertiary sediments comprising the Eastern View Formation, the Demons Bluff Formation, the Gellibrand Marl and the Moorabool Viaduct Sand. These Tertiary units are in turn overlain by the Quaternary Newer Volcanics and unconsolidated sediments comprising alluvium, lunettes and swamp and lake deposits.

The Eastern View Formation is comprised of a thick sequence of sand and gravel units that collectively form the Lower Tertiary Aquifer. The Eastern View Formation crops out extensively in the southeast of the study area and in the Barongarook High (Fig. 4-1), which is the primary recharge area for the Lower Tertiary Aquifer. The Demons Bluff formation is a low hydraulic conductivity calcareous silt that crops out only sparsely in the catchment. This formation is overlain by the Gellibrand Marl, which consists of approximately 200 to 300 m of calcareous silt and clays. The Gellibrand Marl crops out extensively in the south-central portion of the study area (Fig. 4-1) and is a regional confining layer to the underlying Lower Tertiary Aquifer. Due to the presence of the Gellibrand Marl, there is likely to be very little hydraulic connectivity between the Lower Tertiary Aquifer and the overlying shallow, unconfined aquifers (Petrides and Cartwright, 2006).

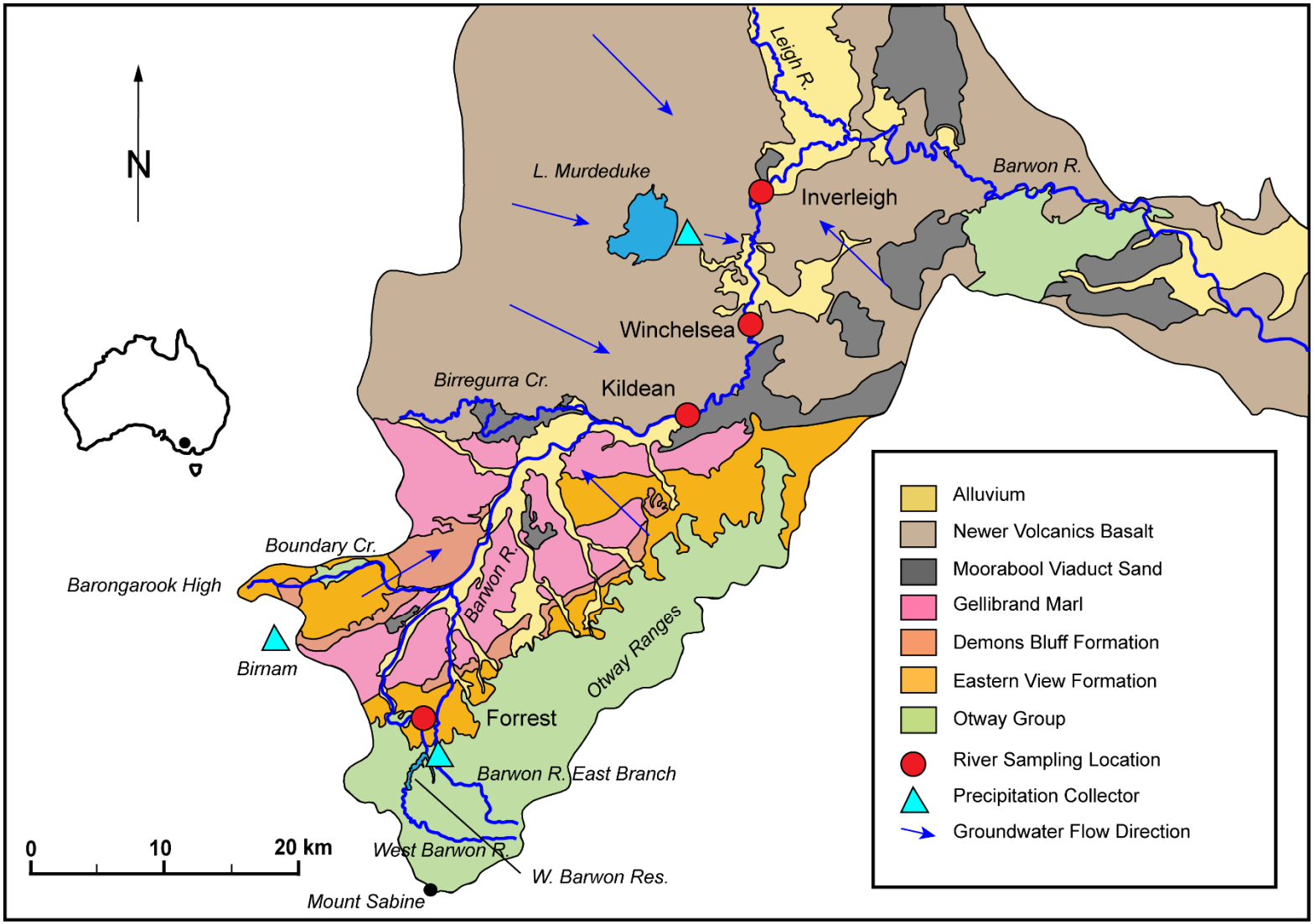

Figure 4-1: Map of the study area showing generalised geology (DataSearch Victoria, 2015), river sampling locations, precipitation collector locations and groundwater flow direction.

The Moorabool Viaduct Sand is a thin, discontinuous unit of clayey sand that crops out at various locations across the catchment, including near Kildean Lane, Winchelsea and Inverleigh (Fig. 4-1). Coram (1996) estimated that the hydraulic conductivity of this unit is approximately 4.3 m day^{-1}. The Quaternary Newer Volcanics, which crop out over most of the northern and central portions of the study area (Fig. 4-1), are broadly grouped into older- and younger-phase deposits. The older-phase Newer Volcanics, which are comprised mainly of weathered olivine basalt, are considered a poor aquifer, with groundwater generally only occurring within joints, vesicles, and poorly connected interflow layers. The younger-phase Newer Volcanics consist of basalt, scoria, undifferentiated pyroclastics, pyroclastic surge deposits and pyroclastic fall deposits. They are less weathered, have a higher degree of fracturing than the older-phase volcanics and, for these reasons, are more permeable. Collectively, the older- and younger-phase Newer Volcanics have an average thickness of approximately 30 m in the study area. On a regional scale, the Newer Volcanics have a hydraulic conductivity of approximately 10^{-2} m day^{-1} (Howcroft et al., 2017) but, locally, can be as high as 8.6 m day^{-1} (Coram, 1996).

Along the Barwon River and most of its tributaries are Quaternary alluvial deposits comprised of clay, silt, sand, and gravel that have a thickness of up to 10 m (Tickell et al., 1991). Near Winchelsea, Inverleigh and Kildean Lane, these deposits extend several kilometres from the river. At Forrest, the alluvium has a maximum horizontal extent of approximately 600 m. Based upon slug tests, Coram (1996) estimated that the hydraulic conductivity of these deposits ranges from approximately $4x10^{-1}$ to $3x10^{2}$ m day^{-1}. Together with the Moorabool Viaduct Sand, the alluvium represents a significant store for bank infiltration, which likely contributes a significant portion of flow following periods of high discharge (Cartwright et al., 2014). Numerous groundwater observation bores are present within the catchment. However, only a few have been installed within the alluvial deposits or within the Moorabool Viaduct Sand; these are monitored only periodically.

Groundwater flow direction within the Quaternary units is influenced by local topography. Recharge to the shallow aquifers occurs across the basin and groundwater discharges into

the Barwon River (Cartwright et al., 2013a; Howcroft et al., 2017). Based on ^{14}C activities, residence times of the shallow groundwater system are up to 20,000 years (Howcroft et al., 2017). Groundwater in the headwaters of the catchment has generally low total dissolved solids (TDS) concentrations (<500 mg/L) but towards the centre of the catchment, particularly near Lake Murdeduke, TDS concentrations are locally in excess of 10,000 mg/L (Coram, 1996; Howcroft et al., 2017). This high salinity groundwater probably originates by evaporation in the saline lakes such as Lake Murdeduke (Howcroft et al., 2017).

4.3. Methodology

4.3.1. River Water and Precipitation Sampling

River discharge, electrical conductivity (EC) and temperature are measured sub-daily in the upper Barwon River at Inverleigh (Site 233218), Winchelsea (Site 233201) and Kildean Lane (Site 233247) (Department of Environment, Land, Water and Planning, 2017). River water samples were collected from the upper Barwon River at Forrest, Kildean, Winchelsea and Inverleigh (Fig. 4-1) in October 2013, December 2013, February 2014, July 2014 and September 2014. During this period, average annual rainfall (measured at Winchelsea) was approximately 90% of the long term (1989-2017) average (Department of Environment, Land, Water and Planning, 2017). Additional river water samples were collected at Forrest in March 2015 and September 2015. The water samples were collected from ~20 cm below the surface of the river using a polyethylene container connected to an extendable pole. Samples were collected during recession periods after high discharge events or during baseflow conditions (Fig. 4-2). Overland flow was not observed during any of the sampling events. Additional geochemistry data for the Barwon River, its tributaries and groundwater were sourced from Cartwright et al. (2013a) and Howcroft et al. (2017).

Precipitation samples were collected using rainfall collectors on the east shore of Lake Murdeduke, the east side of the West Barwon Reservoir, and at Birnam in the Otway Ranges (Fig. 4-1). The rainfall collectors consisted of polyethylene storage containers equipped with funnels positioned approximately 0.5 m above ground level. Water within the containers

was periodically sampled, the containers rinsed and then replaced. The precipitation samples were collected over variable lengths of time between September 2014 to May 2015 with a total of six samples from Birnam, two from the West Barwon Reservoir and one from Lake Murdeduke.

4.3.2. Analytical Techniques

The EC and pH of the water samples were measured in the field at the time of sampling using a calibrated TPS® hand-held water quality meter and probes. The EC and pH measurements have precisions of ±1 µS/cm and ±0.02 pH standard units (SU), respectively. HCO_3 concentrations, with a precision of ±5%, were measured in the field using a Hach® digital titrator and reagents. All river water samples were analysed for cations, anions, $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$ and ^{3}H. The river water samples collected between October 2013 and July 2014 (four sampling events) were also analysed for ^{36}Cl. The precipitation samples were analysed for cations, anions, $\delta^{18}O$, $\delta^{2}H$, ^{3}H (one sample only) and ^{36}Cl (four samples).

Cation concentrations were determined at Monash University using a ThermoFinnigan ICP-OES on samples that had been filtered through 0.45 µm cellulose nitrate filters and acidified to pH <2 using double-distilled 16 M HNO_3. Anion concentrations were measured at Monash University on filtered, un-acidified samples through use of a Metrohm ion chromatograph (IC). The precision of the cation and anion analyses, based upon replicate sample analysis, is ±2% while the accuracy, based on the analysis of certified water standards, is ±5%. Charge balance errors were ≤5% for the river water samples while those of the precipitation samples were ≤8%. Total dissolved solids (TDS) concentrations were derived by summing the cation and anion concentrations.

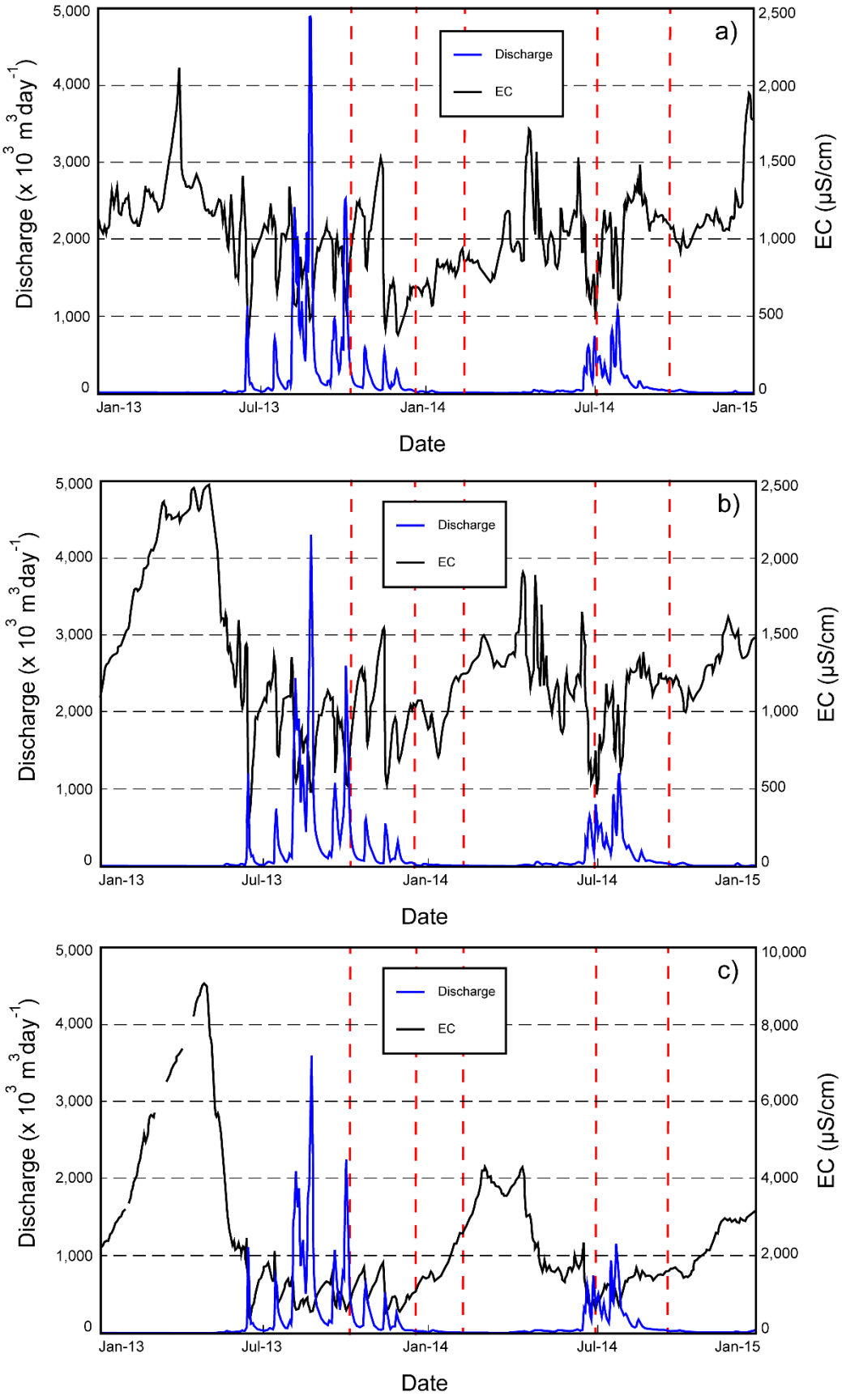

Figure 4-2: Discharge and EC at a) Kildean, b) Winchelsea and c) Inverleigh in 2013 and 2014 (Department of Environment, Land, Water and Planning (2017). Dashed vertical red lines indicate dates at which samples were collected.

$\delta^{18}O$ and $\delta^{2}H$ values were measured at Monash University using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}O$ values were determined through equilibration with He-CO_2 at 32 °C for 24 to 48 hours in a ThermoFinnigan Gas Bench. $\delta^{2}H$ was measured via reaction with Cr at 850 °C using an automated Finnigan MAT H/Device. $\delta^{18}O$ and $\delta^{2}H$ were measured relative to internal standards calibrated using IAEA, SMOW, GISP and SLAP. Data were normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW. The precision (1σ), based on replicate analysis, is ± 0.1% for $\delta^{18}O$ and ± 1% for $\delta^{2}H$. $\delta^{13}C$ was measured on CO_2 from DIC, which was liberated by acidification using H_3PO_4 in a Helium atmosphere in a ThermoFinnigan Gas Bench. $\delta^{13}C$ values are expressed relative to V-PDB and the precision, based on replicate samples, is ± 0.2%.

^{36}Cl activities were determined at the Australian National University (ANU) using accelerator mass spectrometry (AMS) and analytical techniques described by Fifield (1999) and Fifield et al. (2013). ^{36}Cl activities are expressed as $R^{36}Cl$ whereby $R^{36}Cl = {}^{36}Cl/Cl \times 10^{-15}$. Uncertainties in the $R^{36}Cl$ values derived from the counting statistics of the number of ^{36}Cl counts combined in quadrature with a 3% reproducibility range between 5 and 6%.

^{3}H activities were measured at either ANSTO or at the GNS Water Dating Laboratory in Lower Hutt, New Zealand. The samples were first distilled and then electrolytically enriched prior to analysis by liquid scintillation counting, as described in Morgenstern and Taylor (2009) and Tadros et al. (2014). ^{3}H activities are expressed in tritium units (TU) with a relative uncertainty of ± 5% for the samples analysed at ANSTO and ±2% by those analysed at GNS Science.

4.4. Results

4.4.1. River Discharge

Discharge was highest during the July 2014 sampling event, ranging from 526×10^3 m^3 day^{-1} at Kildean to 755×10^3 m^3 day^{-1} at Inverleigh (Table 4-1). Discharge was lowest during the February 2014 sampling event and ranged from 1.5×10^3 m^3 day^{-1} at Winchelsea to 3.1×10^3

m^3 day^{-1} at Inverleigh. River discharge increased downstream during the October 2013, July 2014 and September 2014 sampling events but was largely unchanged in December 2013 and in February 2014. Overall, mean annual discharge within the Barwon River was approximately two to three times higher in 2013 than it was in 2014 (Department of Environment, Land, Water and Planning, 2017).

4.4.2. Major Ion Geochemistry

River water geochemistry is similar at each sampling location. Although the TDS concentrations of the river water are much lower than groundwater, the relative concentrations of the major ions are similar to groundwater (Table 4-1, Fig. 4-3). TDS concentrations were generally less than 100 mg/L at Forrest but typically exceeded 300 mg/L at Kildean, Winchelsea and Inverleigh. In comparison, groundwater TDS concentrations range from approximately 1,600 mg/L to 44,000 mg/L (Howcroft et al., 2017). TDS and major ion concentrations in river water increase downstream (Fig. 4-4a) and were highest (up to 1,514 mg/L) during low, summer flows (July 2014) and lowest during high, winter flows (July 2014). Cl and HCO_3 account for approximately 75% and 18% on a molar basis, respectively, of the anions in the river water. Na, Mg and Ca comprise 63%, 21% and 14% on a molar basis, respectively, of the cations in the river water. With increasing TDS (i.e., downstream from Forrest), the relative proportion of HCO_3 and Ca decreases while that of Cl and Na increases. River pH ranged from 5.87 to 7.59 and increased downstream during each sampling event (Table 4-1).

Cl concentrations in rainfall ranged from 8.5 to 15.7 mg/L (Table 4-1), which are higher than the mean concentration reported by Blackburn and McLeod (1983) for Kybybolite (6.6 mg/L) in eastern South Australia and 5.36 mg/L reported by Crosbie et al. (2012) for Melbourne. The higher Cl concentrations in the upper Barwon region may be due to regional differences in rainfall chemistry, evaporation within the collectors, and wind-blown salt from Lake Murdeduke, fallout of salts from overlying vegetation, and/or temporal variability of rainfall chemistry.

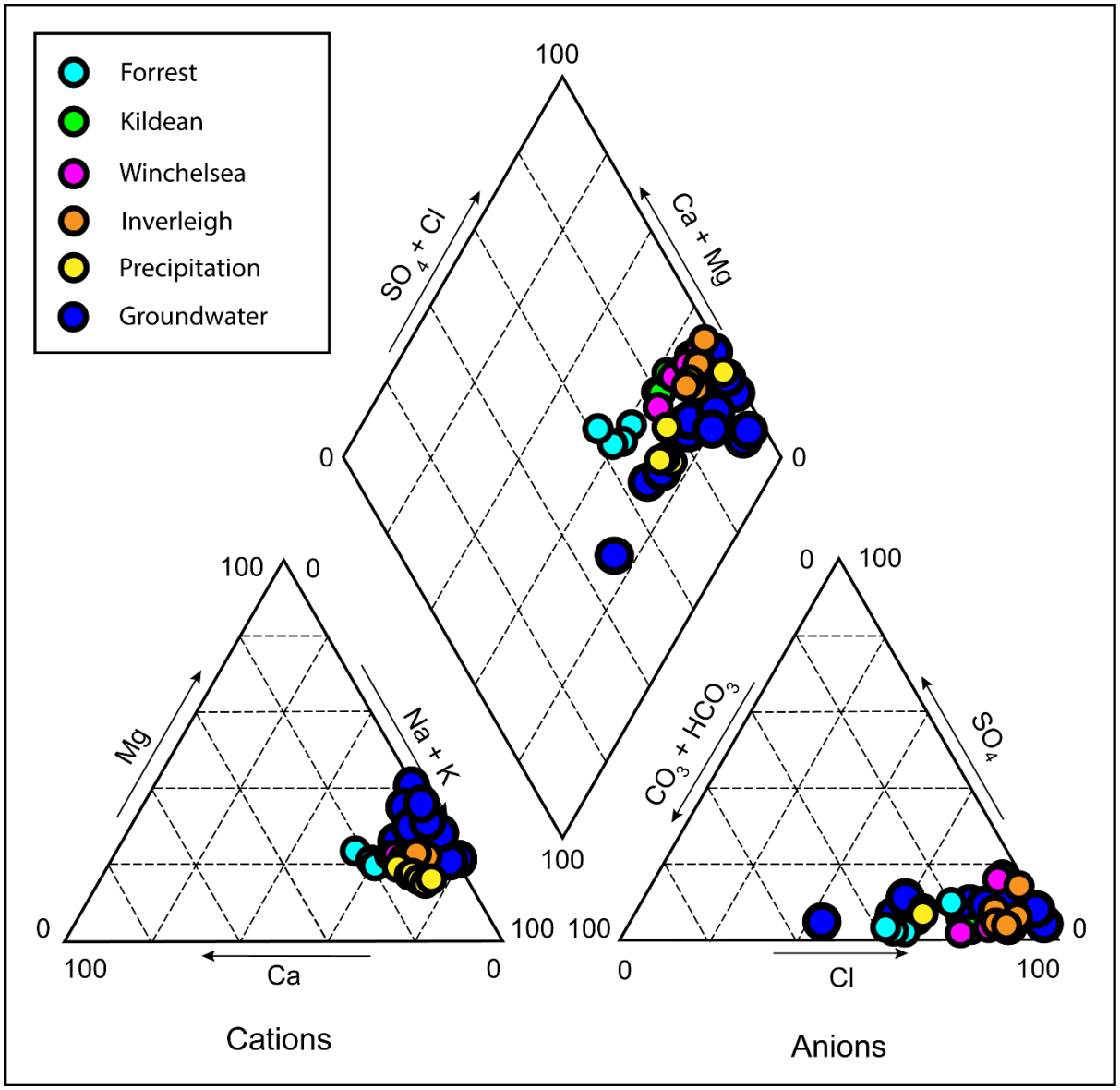

Figure 4-3: Piper diagram of river water, precipitation and groundwater. Groundwater data from Howcroft et al., 2017.

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

δ^2H and $\delta^{18}O$ values of Barwon River water, its tributaries, groundwater and precipitation (Table 4-1) are illustrated in Fig. 4-5 along with the Melbourne Meteoric Water Line (MMWL), which is defined as $\delta^2H = 7.43 * \delta^{18}O + 8.6$ (Hughes and Crawford, 2012). Most of the river water and precipitation samples plot on or close to the MMWL and are distributed around the δ^2H and $\delta^{18}O$ values for modern Melbourne rainfall (δ^2H = -28.4‰, $\delta^{18}O$ = -4.98‰; Hughes and Crawford, 2012). Waters plotting to the right of the MMWL have probably undergone evaporation (Clark and Fritz, 1997). This is especially apparent in the

groundwater samples, which define an array with a slope of 3.9. There is no correlation between stable isotope values of the river water and discharge, EC or major ion concentrations (Table 4-1). Except for July 2014, $\delta^{18}O$ and $\delta^{2}H$ values of the river water generally increase downstream (Fig. 4-4b, 4-4c), which is likely due to evaporation and, to a lesser extent, altitude effects (Clarke and Fritz, 1997).

$\delta^{13}C$ values of DIC in river water are most variable at Forrest, where they range from -21.4‰ to -10.1‰, but are less variable at Kildean, Winchelsea and Inverleigh, where they range from -12.9 to -16.6‰ with an average value of -15‰ (Table 4-1, Fig. 4-4d). There are no significant correlations between $\delta^{13}C$ values and discharge, EC, TDS, major ion concentrations, $\delta^{18}O$ or $\delta^{2}H$ values (Table 4-1).

4.4.4. Radioisotopes (^{3}H, ^{36}Cl)

The ^{3}H activities of the river water samples ranged from 1.76 TU at Kildean in February 2014 to 2.66 TU at Inverleigh in October 2013 (Table 4-1). ^{3}H activities were highest (2.35 TU to 2.66 TU) in October 2013 and increased downstream (Fig. 4-4e). In December 2013, ^{3}H activities decreased between Forrest and Kildean, but then increased again at Winchelsea and Inverleigh. A similar trend is apparent in February 2014. In July and September 2014, ^{3}H activities were similar to within 5% at each sampling location. There is no correlation between ^{3}H activities and discharge, EC, TDS, major ion concentrations or stable isotope values.

Location	Date	Distance from Forrest	Q	EC	pH	TDS	HCO_3	Cl	NO_3	SO_4	Na	Mg	K	Ca	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$	^{3}H	$R^{36}Cl$
		km	10^3 m^3 day^{-1}	µS/cm	S.U.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(‰)	(‰)	(‰)	TU	(x 10^{-15})
Forrest	9/10/2013	-	-	180	6.32	91	25.4	31.6	0.03	3.6	18.7	3.4	0.9	5.1	-4.89	-27.40	-10.1	2.35	42.1
	16/12/2013		-	175	5.87	91	30.5	29.2	0.07	1.8	19.9	3.8	0.8	5.8	-4.89	-27.29	-17.9	2.11	46.1
	10/02/2014		-	190	5.88	83	28.5	30.7	0.12	1.5	19.0	3.3	0.4	5.2	-5.00	-27.21	-13.9	2.21	42.1
	9/07/2014		-	191	5.91	95	17.1	35.0	0.41	6.8	21.0	3.8	1.5	5.1	-4.61	-26.64	-21.4	1.96	37.7
	27/09/2014		-	184	6.21	89	30.9	27.9	0.08	2.2	15.6	3.7	1.1	5.7	-4.29	-23.96	-14.8	2.12	-
	20/03/2015		-	220	6.14	110	37.3	32.3	0.09	0.7	20.7	4.3	1.9	7.0	-3.05	-20.54	-14.6	2.05	-
	10/09/2015		-	201	5.92	102	28.7	34.1	0.14	5.5	21.0	3.8	1.6	5.3	-3.88	-24.94	-15.9	2.07	-
Kildean	9/10/2013	43	263	927	6.76	523	55.6	254.3	0.95	33.6	132.6	21.5	3.2	17.2	-2.67	-13.70	-13.0	2.59	21.1
	16/12/2013		46.5	568	6.54	333	51.2	158.7	1.42	10.2	75.5	14.6	1.4	15.9	-3.74	-22.26	-16.5	1.95	22.1
	10/02/2014		2.9	980	6.62	507	95.2	228.5	1.18	11.7	127.8	23.9	2.3	23.8	-1.62	-13.19	-14.7	1.76	31.2
	9/07/2014		526	456	6.43	227	9.3	95.4	2.15	28.4	59.6	9.6	3.4	10.8	-5.10	-27.96	-15.7	2.05	25.3
	27/09/2014		32.6	1,132	6.64	515	43.9	301.5	0.53	30.6	144.8	24.8	2.3	25.0	-3.87	-21.77	-14.6	2.02	-
Winchelsea	9/10/2013	57	301	904	6.76	562	54.3	225.9	0.30	30.8	127.9	20.9	3.0	16.0	-2.87	-13.94	-12.9	2.64	21.3
	16/12/2013		44.7	801	6.92	402	54.9	182.6	1.65	12.4	102.4	18.8	1.7	18.8	-4.06	-21.74	-16.3	2.09	24.5
	10/02/2014		1.5	1,245	7.09	704	146.4	302.6	0.77	10.6	169.5	30.3	2.9	28.3	-1.29	-13.58	-15.5	1.77	22.0
	9/07/2014		700	598	6.75	312	15.1	106.4	3.89	30.1	80.3	12.9	4.0	14.6	-5.15	-28.15	-16.6	1.97	21.7
	27/09/2014		39.3	1,199	6.66	568	59.8	324.3	0.28	30.7	157.9	27.0	2.8	26.3	-3.77	-21.72	-14.5	2.09	-
Inverleigh	9/10/2013	72	327	921	6.88	551	54.7	228.8	0.32	30.9	130.5	21.9	3.2	16.6	-2.80	-13.51	-16.6	2.66	24.0
	16/12/2013		45.7	1,005	6.81	504	62.2	244.4	0.78	18.5	131.2	23.2	3.7	15.4	-3.55	-22.17	-16.3	2.12	22.7
	10/02/2014		3.1	2,801	7.59	1,514	159.8	764.2	1.55	52.3	424.5	71.4	5.6	32.8	-1.32	-13.09	-14.3	1.83	19.7
	9/07/2014		755	805	6.95	390	8.5	186.1	1.99	43.9	102.6	17.7	4.2	16.4	-4.92	-27.22	-14.9	2.00	20.7
	27/09/2014		40.5	1,540	6.79	723	56.1	421.1	0.65	41.5	212.5	35.4	3.3	27.4	-3.59	-21.94	-13.6	1.96	-
Birnam Rain	27/09/2014	-	-	80	6.49	25	5.7	8.5	0.23	1.5	5.1	0.7	2.6	0.8	-4.4	-22	-	2.45	13.7
	20/12/2014		-	-	-	-	-	-	-	-	-	-	-	-	-0.8	-10	-	-	20.1
	9/05/2015		-	95	5.67	43	11.3	15.7	0.07	2.1	6.5	1.1	5.2	1.3	-4.5	-24	-	-	-
	18/05/2015		-	74	6.48	30	0.6	15.6	0.05	2.1	7.7	1.0	1.9	0.8	-5.4	-30	-	-	-

Location	Date	Distance from Forrest	Q	EC	pH	TDS	HCO_3	Cl	NO_3	SO_4	Na	Mg	K	Ca	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$	^{3}H	$R^{36}Cl$
		km	10^3 m^3 day^{-1}	µS/cm	S.U.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(‰)	(‰)	(‰)	TU	(x 10^{-15})
Birnam Rain	18/07/2015	-	-	65	5.44	29	5.7	10.6	0.08	1.4	4.3	0.9	4.3	1.1	-5.8	-33	-	-	-
	5/11/2015		-	67	5.88	29	7.3	10.2	0.20	1.8	5.4	0.8	2.8	0.9	-3.4	-16	-	-	-
W Barwon Res. Rain	18/07/2015	-	-	62	4.34	25	BDL	14.1	0.31	1.6	5.0	0.8	1.8	0.9	-5.6	-30	-	-	19.1
	5/11/2015		-	69	4.62	28	2.4	13.5	0.05	1.5	6.3	1.0	2.4	0.9	-3.5	-17	-	-	-
L. Murdeduke Rain	18/05/2015	-	-	77	5.76	29	0.2	15.4	0.14	1.4	8.2	1.3	0.4	1.6	-3.7	-26	-	-	20.2

Table 4-1: Geochemistry of the upper Barwon River and rainfall.

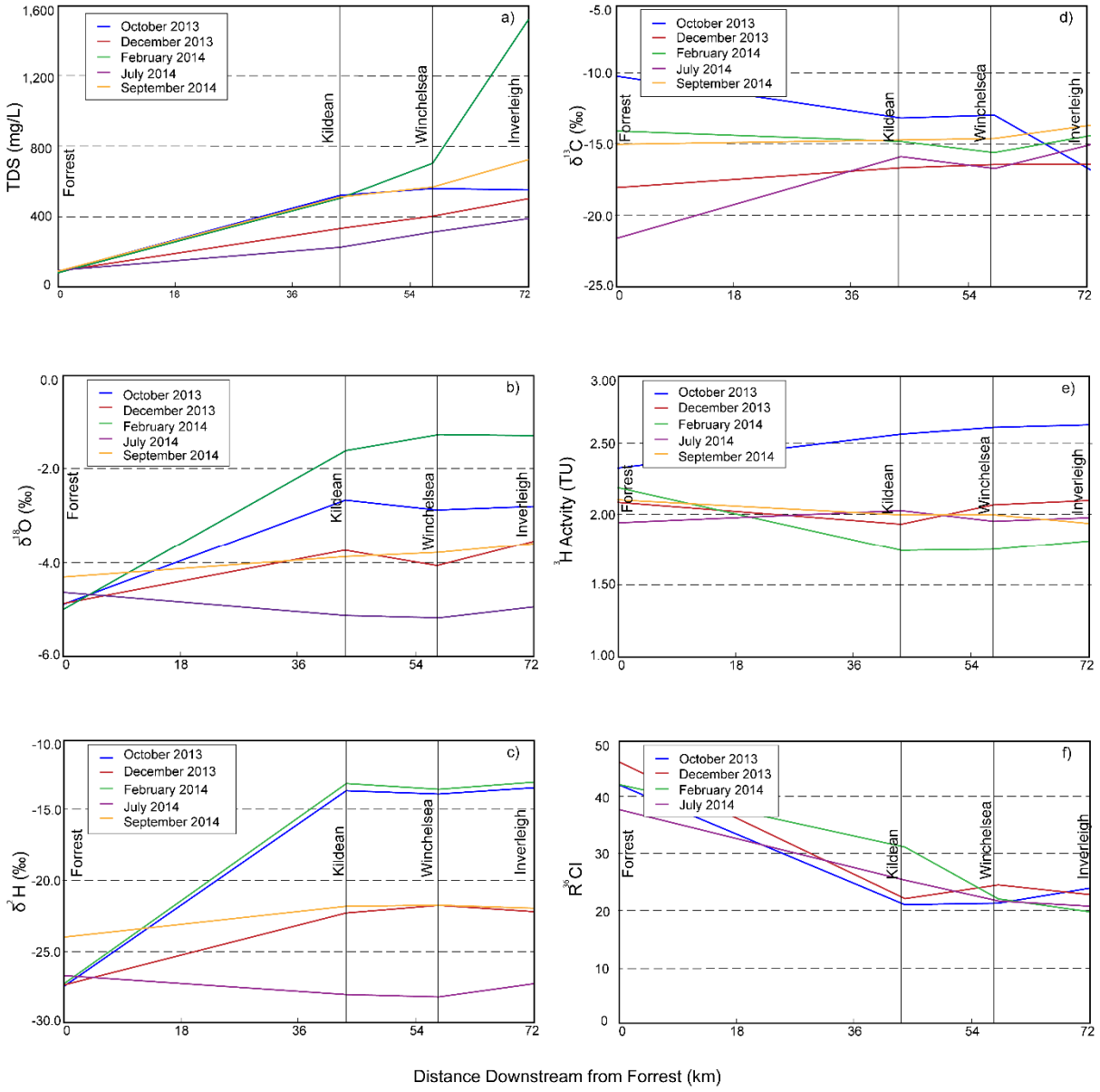

Figure 4-4: Downstream variation in: a) TDS concentrations, b) $\delta^{18}O$ values, c) $\delta^{2}H$ values, d) $\delta^{13}C$ values, e) ^{3}H activities, and f) $R^{36}Cl$ values. Data from Table 4-1.

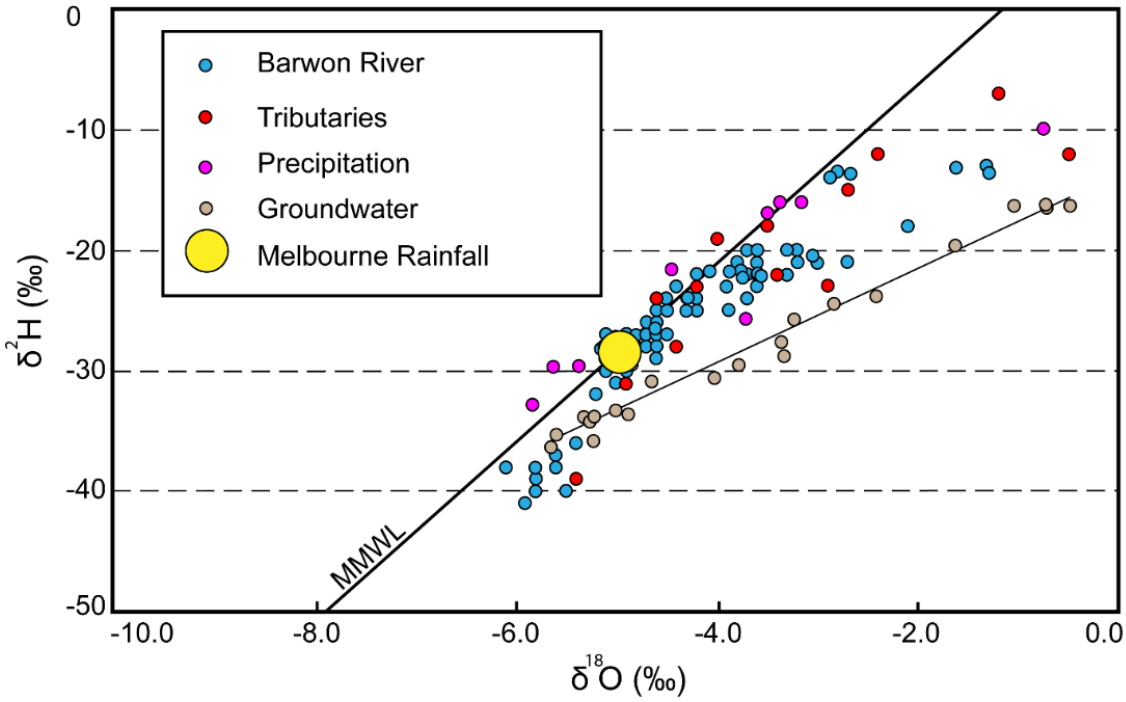

Figure 4-5: Stable isotope ratios for the main Barwon River, tributaries, groundwater and precipitation relative to the Melbourne Meteoric Water Line (MMWL) and modern Melbourne rainfall (Hughes and Crawford, 2012). Also illustrated is the best fit line to the groundwater data (R^2 = 0.98) from Howcroft et al. (2017). Tributary and additional Barwon River water data from Cartwright et al. (2013a).

The ^{3}H activity of the precipitation sample collected at Birnam in the Otway Ranges in September 2014 was 2.45 TU (Howcroft et al., 2017), which is below the expected average annual ^{3}H activity of modern rainfall in this area of 2.8 TU (interpolated from the data of Tadros et al. (2014)). This rainfall ^{3}H activity is also below the values of 2.72 and 2.99 TU from 9 to 12 month samples of rainfall collected elsewhere in Victoria (Atkinson, 2014; Cartwright and Morgenstern, 2015, 2016; Cartwright et al., 2018). However, the rainfall sample collected from Birnam reflects rainfall over only part of the year and may, therefore, not be representative.

$R^{36}Cl$ values of river water ranged from 19.7 at Inverleigh in July 2014 to 46.1 at Forrest in December 2013 (Table 4-1). During each sampling event, $R^{36}Cl$ values were highest at Forrest (37.7 to 46.1) and decreased downstream (Fig. 4-4f). $R^{36}Cl$ values in precipitation (four samples) ranged from 13.7 to 20.2. Three of the four samples have $R^{36}Cl$ values of ~20, which is similar to the predicted $R^{36}Cl$ value of rainfall for the region (~20: Davie et al.,

1989). There is no correlation between $R^{36}Cl$ values and discharge, most major ion concentrations or stable isotope values. However, there is a broad inverse relationship (R^2 = 0.77) between $R^{36}Cl$ values and chloride concentrations in river water (Fig. 4-6).

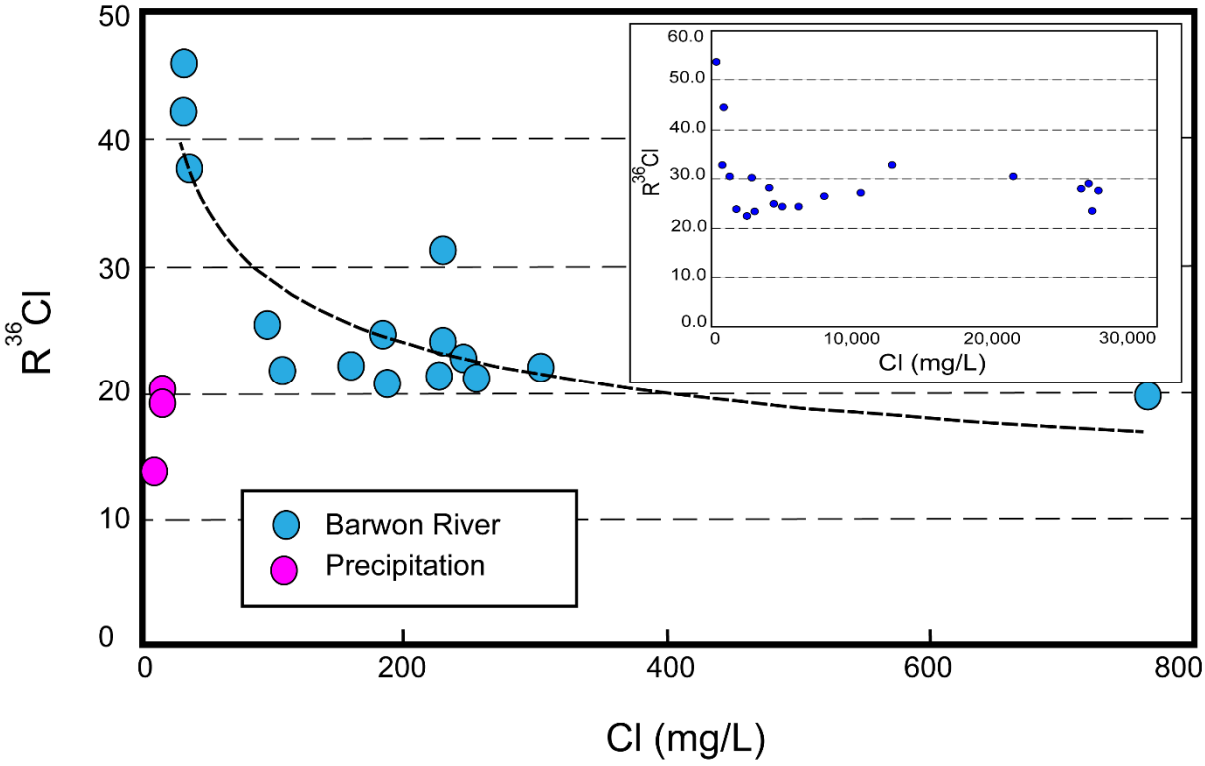

Figure 4-6: $R^{36}Cl$ as a function of chloride concentration in river water, precipitation and groundwater (inset). Data from Table 4-1 and Howcroft et al. (2017). Dashed line represents best fit correlation between river $R^{36}Cl$ and Cl in river water, where $R^{36}Cl = 96.8 \times Cl^{-0.26}$ (R^2 = 0.77).

4.5. Discussion

The stable and radioisotope results in combination with the major ion geochemistry, river discharge and groundwater geochemistry (Howcroft et al., 2017) allow the role of bank storage and return flow in maintaining river flow and chemistry to be assessed. In addition, the residence times of water and solutes within the river can be evaluated.

4.5.1. Seasonal Variations in Bank Storage and Return Flow

The downstream increases in ^3H activities, which are most marked in October 2013 but which are also apparent in December 2013 and February 2014 imply that, during these times, progressively younger water was entering the river. As no overland flow was

observed at the time of sampling, and because there are no significant tributaries between Kildean and Inverleigh, the increase in ^{3}H activities is interpreted to be the result of relatively young bank return flow. While soil water and draining of pools on the floodplain could potentially be contributing to river flow, these potential inputs likely to be insignificant during the dry summer months.

The increase in ^{3}H activities is most apparent in October 2013, which was the first sampling event after high winter flows when most bank storage is expected to occur. Consequently, a relatively high proportion of total river flow at this time was likely derived from bank return flow. The lower ^{3}H activities between October 2013 and February 2014 (Fig. 4-4e) imply that bank return flows made a progressively lower contribution to total river flow (with regional groundwater (having below-detection ^{3}H activities) making an increasingly higher contribution). The downstream increase in ^{3}H may be due to higher volumes of bank storage and return flow contributing to river flow in the central part of the catchment (near Winchelsea and Inverleigh), which may be facilitated by the larger extent of alluvial sediments at these locations compared to that at Forrest or Kildean (Fig. 4-1). This would result in the mixed water (recent bank storage water and older groundwater) at these locations having higher ^{3}H activities than in the upper part of the catchment.

If bank infiltration occurs primarily during the winter months (July to September), when river flows are highest (Fig. 4-2), the downstream increases in ^{3}H activities in October 2013, December 2014 and February 2014 suggest that the bank storage and return flow has a residence time of at least several months. However, since no samples were collected between February 2014 and the following high winter river discharge period, it is possible the residence time is greater. A downstream increase in ^{3}H activities is not apparent in the September 2014 data. However, average annual flows in 2014 were two to three times lower than in 2013 (Fig. 4-2). It is therefore likely that less river water was stored within the near-river sediments and subsequently released as bank return flow.

4.5.2. Short Duration Bank Storage and Return Flow

In addition to the seasonal pattern of bank storage and return flow that occurs after high winter flows, bank storage and return flow can also occur during individual, high-flow events. This is evident in the form of clockwise EC-discharge hysteresis loops during the rainfall-induced high flow events that occurred in October 2013, December 2013 and August 2014 (Fig. 4-7). In Fig. 4-7, EC is normalised relative to the initial EC at the beginning of the rainfall event. In each event, river EC decreased as river discharge increased, which reflects the input of comparatively fresh event water into the river. As river discharge falls, there is a corresponding increase in EC. However, the EC on the receding limb of the hydrograph is lower than that at the same discharge on the rising limb.

As noted earlier, clockwise hysteresis in solute concentrations (in this case EC) suggests a source close to the monitoring point (Lloyd et al., 2016), and these observations are interpreted to be the result of bank return flow re-entering the river following the high flow events. The period of time required for EC to return to its original value (the return period) is thus a measure of the residence time of bank storage and return flow. At Kildean, the return period was approximately 6 days for the October 2013 flow event, 20.5 days for the December 2013 flow event, and nearly 8 days for the August 2014 flow event. At Winchelsea, the return periods for the same high flow events were approximately 6 days (October 2013), 12 days (December 2013), and 8 days (August 2014) while those at Inverleigh were 7 days, 14 days and 8.5 days respectively. These results suggest that, in additional to the seasonal bank storage and return flows with residence times of several months, there are short duration bank storage and return flow events that have residence times of a few weeks.

4.5.3. Residence Times at Forrest

Mean transit times (MTTs) at Forrest were estimated from the ^{3}H activities of the river water using the lumped parameter models (LPMs) contained in the programmable Excel spreadsheet TracerLPM (Jurgens et al., 2012). The assumptions and methodology are as

discussed in Howcroft et al. (2018). Two LPMs were utilised: the Exponential Piston-Flow Mode (EPM) with EPM ratios of 0.33, 1.0 and 3.0, and the Dispersion Model (DM) with Dispersion Parameters (D_p) of 0.05 and 0.25. These are commonly used LPMs and in catchments elsewhere, they have been shown to reproduce the time series of ^3H activities (e.g. Stewart and Thomas, 2008; Morgenstern et al., 2010). A modified ^3H record for Melbourne rainfall (IAEA, 2017) was utilised as the ^3H input. Modern rainfall in Melbourne (located approximately 100 km from the study area) has a ^3H activity of approximately 3.0 TU, while modern rainfall in the study area has a predicted ^3H activity of approximately 2.8 TU (Tadros et al., 2014). Thus, a ^3H value of 2.8 TU was utilised for modern (2010 to 2016) rainfall, as well as for years prior to atmospheric nuclear testing (pre-1951). ^3H activities for rainfall in intervening years were decreased by 6.7% to account for the expected difference in ^3H activities in the study area relative to Melbourne.

Calculated MTTs ranged from approximately 4 years in October 2013 to 10 years in July 2014 (Table 4-2). Overall, MTTs calculated using the different LPMs are similar. Uncertainties in the historic ^3H activities of rainfall produce small (generally less than 10%) uncertainties in MTTs when ^3H activities are greater than ~1 TU (Howcroft et al., 2018). Uncertainties in the ^3H activity of modern rainfall and macroscopic mixing (aggregation) result in variations in estimated MTTs that are commonly around 10 to 15% (Cartwright and Morgenstern, 2015, 2016; Howcroft et al., 2018). While these uncertainties hinder the calculation of precise MTTs, the conclusion that they are a few years is robust.

These MTTs are less than the global average MTT of 15 years for headwater catchments and 10 years for macroscale catchments (Stewart et al., 2010). They are also considerably less than those of headwater streams in the adjacent Gellibrand River Catchment, where MTTs are typically decades to centuries (Howcroft et al., 2018).

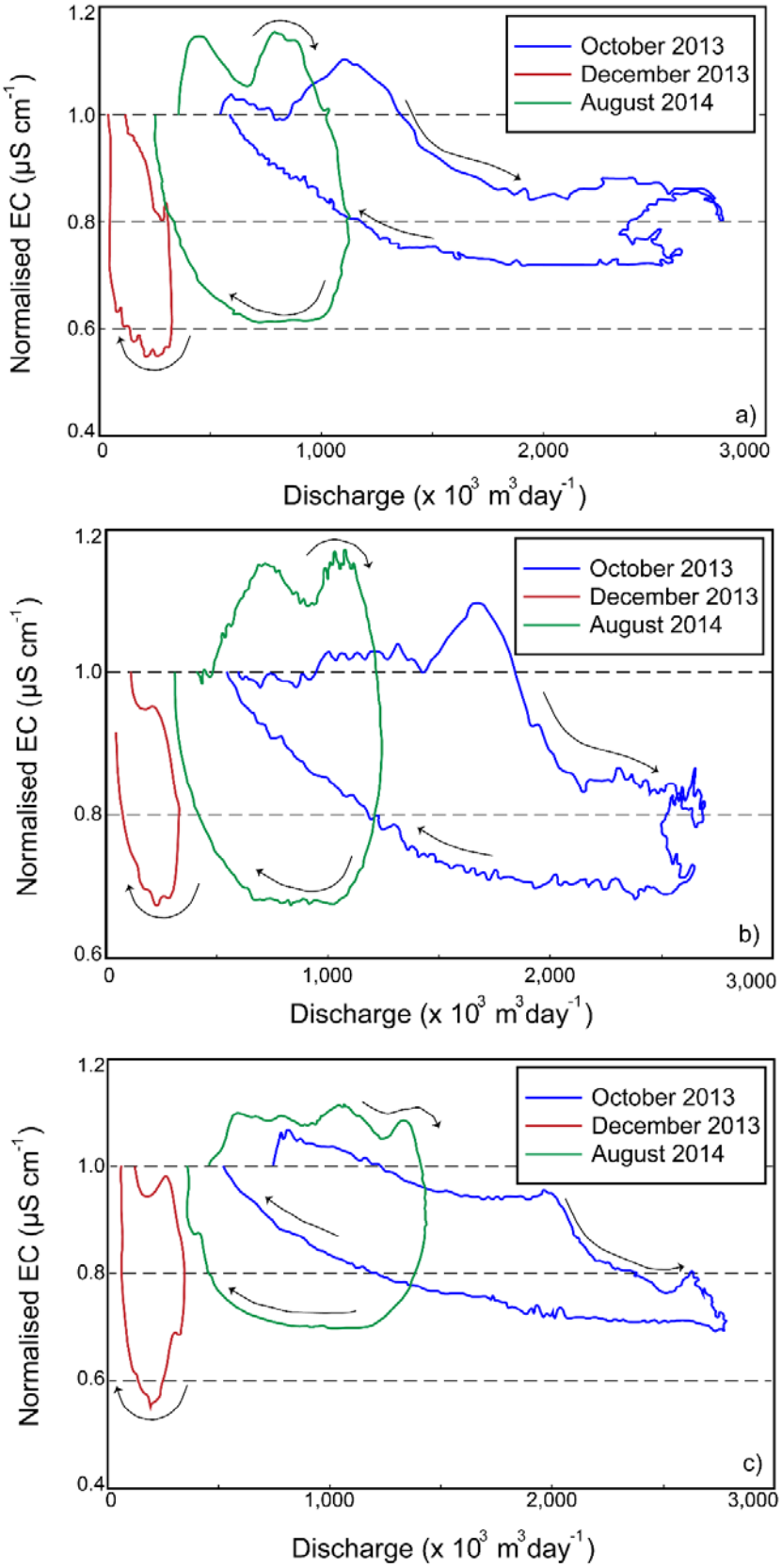

Figure 4-7: Normalised EC-discharge hysteresis loops for storm events in October 2013, December 2013, and August 2014 at a) Kildean, b) Winchelsea and c) Inverleigh. Data from Department of Environment, Land, Water and Planning (2017).

Date	EPM			DM	
	0.33	1.0	3.0	0.05	0.25
9/10/2013	4.4	4.2	5.4	4.8	4.4
16/12/2013	8.0	8.1	7.5	7.6	8.0
10/02/2014	6.2	6.2	6.6	6.4	6.2
9/07/2014	10.3	9.9	9.0	9.3	10.2
27/09/2014	7.1	6.9	7.3	7.1	7.2
20/03/2015	8.0	7.7	8.0	7.8	8.0
10/09/2015	7.5	7.0	7.8	7.2	7.4

Table 4-2: MTTs (years) at Forrest Using the Exponential Piston Flow Model (EPM) with EPM ratios of 0.33, 1.0 and 3.0, and the Dispersion Model (DM) with Dispersion Parameters (Dp) of 0.05 and 0.25.

A similar analysis of MTTs was not conducted on the ^{3}H data for Kildean, Winchelsea or Inverleigh as the river water at these locations is probably a mixture of groundwater and bank return flow, which cannot be modelled using single LPMs. Near-river alluvial deposits are also present at Forrest, although their extent is less than that near Kildean, Winchelsea and Inverleigh (Fig. 4-1). Nonetheless, it is possible that bank return flow contributes some portion of total river discharge at Forrest, in which case the derived MTTs may underestimate the actual values. Over the course of seven sampling events, however, the ^{3}H activities at Forrest were relatively similar, which suggests that a single store of water may be feeding the river at this location.

4.5.4. Residence Times of Solutes

At Forrest, $R^{36}Cl$ values of river water vary from 37.7 to 46.1, which are higher than that of both the precipitation samples (13.7 to 20.2, Table 4-1) and the predicted $R^{36}Cl$ value (~20) for regional rainfall (Davie et al., 1989). Elevated $R^{36}Cl$ values can result from deep, subsurface (hypogene) production of ^{36}Cl through nuclear reactions involving uranium, thorium and/or their daughter products (Andrews et al., 1986). They can also be produced in the shallow, near-surface (epigene production) as a result of cosmic ray spallation of potassium or calcium and/or neutron capture of ^{35}Cl (Phillips et al., 1983). However, these processes only become significant after very long periods of time, typically on the order of 1 Ma or more. Given that the water samples at Forrest have MTTs of approximately 4 to 10

years, it is more likely that the elevated $R^{36}Cl$ values at Forrest reflect the input of bomb-pulse ^{36}Cl. Thermonuclear testing during the 1950s released large amounts of radionuclides (the 'bomb-pulse') including ^{36}Cl into the atmosphere (Zerle et al., 1997). Subsequent fallout of ^{36}Cl to the earth's surface peaked between 1955 and 1960. $R^{36}Cl$ values in precipitation in the study area at the time of the peak of the bomb pulse are not known. However, ^{36}Cl fallout at the peak of the bomb-pulse was approximately three orders of magnitude higher than it is at present (Bentley et al., 1982; Zerle et al., 1997). Thus, the high $R^{36}Cl$ values in river water at Forrest are most likely the result of mixing of modern and bomb-pulse ^{36}Cl. The bomb-pulse ^{36}Cl may be retained in the catchment due to plant uptake and recycling, which has been previously evidenced over a period of approximately 50 years in the Great Lakes region of North America (Milton et al., 1997; 2003).

$R^{36}Cl$ values decrease downstream from Forrest in each sampling event and attain a nearly constant value of approximately 22 at Winchelsea and Inverleigh (Fig. 4-4f). This is similar to the $R^{36}Cl$ values of groundwater near Lake Murdeduke, which ranged from 22.4 to 53.7 with an average $R^{36}Cl$ value of approximately 27 (Howcroft et al., 2017). Additionally, $R^{36}Cl$ values are inversely correlated with chloride concentrations (Fig. 4-6). Together, these trends suggest that the decrease $R^{36}Cl$ values in river water downstream of Forrest are due to the inflow of older highly saline regional groundwater. Howcroft et al. (2017) showed that this groundwater has a mean residence time of up to 20 ka.

4.5.5. Controls on River Water Chemistry

Together, inflows of groundwater and bank return flow determine the chemistry of river water in the upper Barwon River catchment. The δ^2H and $\delta^{18}O$ values of most of river water samples plot on or close to the MMWL and are distributed around the values of modern Melbourne rainfall (Fig. 4-4). In addition, the δ^2H and $\delta^{18}O$ values of groundwater are distinct from the river water samples. Lastly, ^3H activities are relatively high and fall within the narrow range of 1.76 to 2.66 TU. Together, these data suggest that the river water is

derived primarily from bank storage and return flow and has short residence times, with older groundwater only making a minor contribution to total river discharge.

Groundwater does, however, play an important role in controlling river water chemistry. TDS and major ion concentrations increased downstream during each sampling event (Table 4-1, Fig. 4-4a). This is almost certainly the result of even a small input of groundwater, which has TDS concentrations as high as 44,000 mg/L (Howcroft et al., 2017). However, river salinity is never as high as that of groundwater, which provides further evidence of the importance of bank storage and return flow. Additionally, $\delta^{13}C$ values of DIC in river water are variable at Forrest but remain relatively constant during each sampling event at Kildean, Winchelsea and Inverleigh. $\delta^{13}C$ values at these locations are approximately -15‰ (Table 4-1), which is similar to the average $\delta^{13}C$ value of groundwater near Lake Murdeduke (-14.6‰; Howcroft et al., 2017). Thus, groundwater inflows may provide much of the DIC in the river. This is consistent with the fact that DIC concentrations in groundwater (290 to 920 mg/L) are much higher than they are in the river water (5.7 to 159.8 mg/L) and thus relatively small inflows of groundwater provide much of the DIC. These results are inconsistent with that of Unland et al. (2014), who concluded that bank storage and return flow play little role in determining river water chemistry in the Tambo River of southeast Australia. Together, the results of both studies indicate that the process of bank storage and return flow is, as of yet, still poorly understood.

4.6. Conclusions

The stable and radioactive isotope data, in combination with major ion geochemistry and discharge data, demonstrate that bank storage and return flow is an important process in the upper Barwon River. Bank storage is likely to primarily occur during the winter months, when river discharge is at its highest. This water enters the near-river deposits and mixes with groundwater. There, it has a residence time of several months, if not longer, before returning to the river as bank return flow. Additional bank storage occurs during isolated high flow events; however, its residence times is on the order of weeks rather than months. The input of bank storage and return flow helps maintains river flows, even during the dry,

summer months. In contrast, groundwater inputs into the river have a residence time of up to 20 ka. The fact that the river always has measurable ^{3}H activities, despite the input of very old groundwater, attests to the importance of bank storage and return flow in the upper Barwon River.

River water chemistry is determined by the input of both groundwater and bank storage and return flow. Bank return flow largely determines the river's ^{3}H activities while groundwater inflows strongly influence $\delta^{13}C$ values and $R^{36}Cl$ values. TDS values and major ion concentrations in river water are dependent on both inputs.

The results of this study clearly demonstrate that river water is comprised of both young and old water, which together maintain river flows and influence river water chemistry. In particular, this study shows that bank storage and return flow contributes relatively young, fresh water to rivers while groundwater contributes older, more saline water. Because river salinity is never as high as that of groundwater and ^{3}H activities are always relatively high, bank storage and return flow likely contributes a larger proportion of total river flow than groundwater. This, in turn, explains why about one-third of total river flow globally is derived from precipitation that fell within the past few months.

The results of this study demonstrate that management decisions affecting rivers and near-river environments need to carefully consider the role of both groundwater and bank storage and return flow. For example, construction of flood levees, retaining walls or structures along river banks will result in diminished bank storage and return flow and, therefore, increased river salinity. Conversely, groundwater extraction for water supply, irrigation, or dewatering purpose may decrease groundwater inputs into a river, resulting in river water becoming less saline, which can be harmful to ecosystems.

4.7. Acknowledgements

Field work and laboratory analyses were conducted with the help of Massimo Raveggi, Rachelle Pearson, Kwadwo Osei-Bonsu, Wang Dong and Lei Chu. Funding for this project was provided by Monash University and the National Centre for Groundwater Research and Training (NCGRT). NCGRT is an Australian Government initiative supported by the Australian Research Council and the National Water Commission.

4.8. References

Andrews, J.N., Fontes, J.-Ch., Mechelot, J.L. and D. Elmore, 1986. In-situ neutron flux, ^{36}Cl production and groundwater evolution in crystalline rocks at Stripa, Sweden. Earth and Planetary Science Letters, Vol. 77, pp. 49-58.

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Cendon, D.I., Unland, N.P. and H. Hoffman, 2014. Using ^{14}C and ^{3}H to understand groundwater flow and recharge in an aquifer window. Hydrol. Earth Syst. Sci., Vol. 18, pp. 4951-4964.

Bentley, H.W., Phillips, F.M., Davis, S.N., Gifford, S., Elmore, D., Tubbs, L.E. and H.E. Gove, 1982. Thermonuclear ^{36}Cl pulse in natural water. Nature, Vol. 300, pp. 737-740.

Bentley, H.W., Phillips, F.M., David, S.N., Habermehl, M.A., Airey, P.L., Calf, G.E., Elmore, D., Gove, H.E. and T. Torgersen, 1986a. Chlorine 36 dating of very old groundwater 1. The Great Artesian Basin, Australia. Water Resources Research, Vol. 22 (13), pp. 1991-2001.

Blackburn, G. and S. McLeod, 1983. Salinity of Atmospheric Precipitation in the Murray-Darling Drainage Division, Australia. Australian Journal of Soil Research, Vol. 21, pp. 411-434.

Bourke, S.A., Harrington, G.A., Cook, P.G., Post, V.E. and S. Dogramaci, 2014. Carbon-14 in streams as a tracer of discharging groundwater. J. of Hydrol., Vol. 519, pp. 117-130.

Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Lowenthal, M., Gozzard, E., Newman, J.R. and E.J. Palmer-Felgate, 2015. Characterising phosphorous and nitrate inputs to a rural river using high-frequency concentration-flow relationships. Sci. Total Environ., Vol. 511, pp. 608-620.

Broecker, W.S. and A. Walton, 1959. The geochemistry of ^{14}C in fresh-water systems. Geochimica et Cosmochimica Acta, Vol. 16 (1-3), pp. 15-38.

Bureau of Meteorology (BOM), 2017. http://www.bom.gov.au, last access 13 April 2017.

Cartwright, I., Gilfedder, B. and H. Hoffman, 2013a. Chloride imbalance in a catchment undergoing hydrological change: Upper Barwon River, southeast Australia. Applied Geochemistry, Vol. 31, pp. 187-198.

Cartwright, I., Gilfedder, B. and H. Hoffman, 2013b. Transient hydrological conditions implied by chloride mass balance in southeast Australian rivers. Chemical Geology, Vol. 357, pp 29-40.

Cartwright, I., Gilfedder, B. and H. Hoffman, 2014. Contrasts between estimates of baseflow help discern multiple sources of water contributing to rivers. Hydrol. Earth Syst. Sci., Vol. 18, pp. 15-30.

Cartwright, I. and U. Morgenstern, 2015. Transit times from rainfall to baseflow in headwater catchments estimated using tritium: the Ovens River, Australia. Hydrol. Earth Syst. Sci., Vol. 19, pp. 3771-3785.

Cartwright, I. and U. Morgenstern, 2016. Contrasting transit times of water from peatlands and eucalypt forests in the Australian Alps determined by tritium: implications for vulnerability and the source of water in upland catchments, Hydrol. Earth Syst. Sci., Vol. 20, pp. 4757-4773.

Cartwright, I., Irvine, D., Burton, C. and Morgenstern, U., 2018. Assessing the controls and uncertainties on mean transit times in contrasting headwater catchments. J. Hydrol., Vol. 557, pp. 16-29.

Clark, I.D. and P. Fritz, 1997. Environmental isotopes in hydrogeology. CRC Press/Lewis Publishers, Boca Raton.

Clarke, J.D.A., Lewis, S.J., Fontaine, K., Kilgour, P.L. and Stewart, G., 2015. Regional Hydrogeological Characterisation of the Otway Basin, Victoria and South Australia. Technical report for the National Collaboration Framework, Regional Hydrogeology Project. Geoscience Australia, Record 2015/12.

Coplen, T.B., 1988. Normalisation of oxygen and hydrogen isotope data. Chemical Geology, Vol. 72, pp. 293-297.

Coram, J.E., 1996. Groundwater-surface water interactions around shallow lakes of the Western District Plains, Victoria. Master of Science, University of Melbourne.

Crosbie, R.S., Morrow, D., Cresswell, R.G., Leaney F.W., Lamontagne, S. and M LeFournour, 2012. New insights to the chemical and isotopic composition of rainfall across Australia. CSIRO Water for a Healthy Country Flagship, Australia.

DataSearch Victoria: Victoria Department of Sustainability and Environment Spatial Warehouse, http://services.land.vic.gov.au/SpatialDatamart/index.jsp, last access: 10 June 2015.

Davie, R.F., Kellett, J.R., Fifield, L.K., Evans, W.R., Calf, G.E., Bird, J.R., Topham, S. and T.R. Ophel, 1989. Chlorine-36 measurements in the Murray Basin: preliminary results from the Victorian and South Australian Mallee region. In: BMR Journal of Australian Geology and Geophysics, Vol. 11, pp. 261-272.

Department of Environment, Land, Water and Planning, Water Measurement Information System (WMIS), http://data.water.vic.gov.au/monitoring.htm, last access: 13 April 2017.

Department of Water Resources (DWR), Victoria, 1989. Water Victoria: A Resources Handbook. North Melbourne Victoria Government Printing Office, 311 p.

Doble, R., Brunner, P., McCallum, J. and P.J. Cook, 2011. An analysis of river bank slope and unsaturated flow effects on bank storage. Ground Water, Vol. 50, No. 1, pp. 77-86.

Duvert, C., Stewart, M.K., Cendón, D.I. and M. Raiber, 2016. Time series of tritium, stable isotopes and chloride reveal short-term variations in groundwater contribution to a stream. Hydrol. Earth Syst. Sci. Vol. 20, pp. 257-277.

Fifield, L.K., 1999. Accelerator mass spectrometry and its applications. Reports on Progress in Physics, Vol. 62, pp. 1223-1274.

Fifield, L.K., Tims, S.G., Stone, J.O., Argento, D.C. and M. De Cesare, 2013. Ultra-sensitive measurements of ^{36}Cl and ^{236}U at the Australian National University. Nuclear Instruments and Methods in Physics B, Vol. 294, pp. 126-131.

Gill, B., 1989. Hydrogeological review of salinity problems in the Barwon/Corangamite region. Investigations Branch Report No. 1988/16. Rural Water Commission of Victoria. April 1989, 68 p.

House, W.A. and M.S. Warwick, 1998. Hysteresis of the solute concentration/discharge relationship in rivers during storms. Water Res., Vol. 32, pp. 2279-2290.

Howcroft, W., Cartwright, I., Fifield, L.K. and D.I. Cendon, 2017. Differences in groundwater and chloride residence times in saline groundwater: The Barwon River Catchment of Southeast, Australia. Chem. Geol., Vol. 451, pp. 154-168.

Howcroft, W., Cartwright, I. and U. Morgenstern, 2018. Mean transit times in headwater catchments: insights from the Otway Ranges, Australia. Hydrol. Earth Syst. Sci. Discuss. (in review), doi: 10.5194/hess-2017-219.

Hrachowitz, M., Bohte, R., Mul, M.L., Bogaard, T.A., Savenije, H.H.G. and S. Ulehnbrook, 2011. On the value of combined event runoff and tracer analysis to improve understanding of catchment functioning in a data-scarce semi-arid area. Hydrol. Earth Syst. Sci., Vol. 15, pp. 2007-2024.

Hughes, C.E. and J. Crawford, 2012. A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. Journal of Hydrology, Vol. 464-465, pp. 344-351.

International Atomic Energy Association (IAEA): Global Network of Isotopes in Precipitation, available at: http://www.iaea.org/water, last access: March, 2017.

Jasechko, S., Kirchner, J.W., Welker, J.M. and J.J. McDonnell, 2016. Substantial proportion of global streamflow less than three months old. Nature Geoscience, Vol 9, pp. 126-130.

Jurgens, B.C., Bohkle, J.K. and S.M. Eberts, 2012. TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data. US Geological Survey, Techniques and Methods Report 4-F3, US Geological Survey, Reston VA USA. 60 pp.

Kwicklis, E. and I. Farnham, 2014. Testing the ^{14}C ages and conservative behaviour of dissolved ^{14}C in a carbonate aquifer in Yucca Flat, Nevada (USA), using ^{36}Cl from groundwater and packrat middens. Hydrogeol. Journ., Vol. 22, pp. 1359-1381.

Lin, Y.C. and M.A. Medina Jr., 2003. Incorporating transient storage in conjunctive stream-aquifer modeling. Adv. Water Resour., Vol. 26, pp. 1001-1019.

Lloyd, C.E.M., Freer, J.E., Johnes, P.J. and A.L. Collins, 2016. Technical Note: Testing and Improved Index for analysing storm discharge-concentration hysteresis. Hydrol. Earth Syst. Sci., Vol. 20, pp. 625-632.

McCallum, J.L., Cook, P.G., Brunner, P. and D. Berhane, 2010. Solute dynamics during bank storage flows and implications for chemical base flow separation. Water Resour. Res., Vol. 46, W07541, doi: 10.1029/2009WR008539.

McCallum, J.L., Engdahl, N.B., Ginn, T.R. and P.G. Cook, 2014. Nonparametric estimation of groundwater residence time distributions: What can environmental tracer data tell us about groundwater residence time? Water Resour. Res., Vol. 50, pp. 2022-2048.

McCallum, J.L. and M. Shanafield, 2016. Residence times of stream-groundwater exchanges due to transient stream stage fluctuations. Water Resour. Res., Vol. 52, pp. 2059-2073, doi: 10.1002/2015SWR017441.

McGuire, K.J. and J.J. McDonnell, 2006. A review and evaluation of catchment transit time modelling, J. Hydrol., Vol. 330, pp. 543-563, doi: 10.106/j.jhydrol.2006.04.020.

Milton, J.C.D., Milton, G.M., Andrews, H.R., Chant, L.A., Cornett, R.J.J., Davies, W.G., Greiner, B.F., Imahori, Y., Koslowsky, V.T., Kotzer, T., Kramer, S.J. and J.W. McKay, 1997. A new interpretation of the distribution of bomb-produced chlorine-36 in the environment, with special reference to the Laurentian Great Lakes. Nuclear Instrum. and Methods in Phys. Res. B, Vol. 123, pp 382-386.

Milton, G.M., Milton, J.C.D., Schiff, S., Cook, P., Kotzer, T.G. and L.D. Cecil, 2003. Evidence for chlorine recycling – hydrosphere, biosphere, atmosphere – in a forested wet zone on the Canadian Shield. Applied Geochemistry, Vol. 18, pp. 1027-1042.

Morgenstern, U., and C.B. Taylor, 2009. Ultra low-level tritium measurement using electrolytic enrichment and LSC, Isot. Environ. Health Stud., 45, 96-117.

Morgenstern, U., Stewart, M.K., and R. Stenger, 2010. Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit times with streamflow, Hydrol. Earth Syst. Sci., Vol. 14, pp. 2289-2301.

Petrides, B. and I. Cartwright, 2006. The hydrogeology and hydrogeochemistry of the Barwon Downs Graben aquifer, southwestern Victoria, Australia. Hydrogeology Journal, Vol. 14, pp. 809-826.

Phillips, F.M., Smith, G.I., Bentley, H.W., Elmore, D. and H.E. Gove, 1983. Chlorine-36 dating of sediments: preliminary results from Searles Lake, California. Science, New Series, Vol. 222 (4626), pp. 925-927.

Roderick, P., 1988. Investigation of highly saline groundwater inflows between Winchelsea and Inverleigh. Investigations Branch Report No. 1988/7. Rural Water Commission of Victoria. August 1989, 27 p.

Soulsby, C., Malcolm, R., Helliwell, R., Ferrier, R.C. and A. Jenkins, 2000. Isotope hydrology of the Allt a' Mharcaidh catchment, Cairngorms, Scotland: implications for hydrological pathways and residence times. Hydrol. Process., Vol. 14, pp. 747-762.

Squillace, P.J., 1996. Observed and Simulated Movement of Bank-Storage Water. Ground Water, Vol. 34, No. 1, pp. 121-134.

Stewart, M.K. and J.T. Thomas, 2008. A conceptual model of flow to the Waikoropupa Springs, NW Nelson, New Zealand, based on hydrometric and tracer (^{18}O, Cl, ^{3}H and CFC) evidence. Hydrol. Earth Syst. Sci., Vol. 12, pp. 1-19.

Stewart, M.K., Morgenstern, U., and J.J McDonnell, 2010. Truncation of stream residence times: how the use of stable isotopes has skewed our concept of streamwater age and origin, Hydrol. Process., Vol. 24, pp. 1646-1659, doi: 10.1002/hyp.7576.

Tadros, C.V., Hughes, C.E., Crawford, J., Hollins, S.E., and R. Chisari, 2014. Tritium in Australian precipitation: a 50 year record, J. Hydrol., Vol. 513, pp. 262-273, doi: 10.1016/j.jhydrol.2014.03.031.

Taylor, C.B., 1997. On the isotopic composition of dissolved inorganic carbon in rivers and shallow groundwater: a diagrammatic approach to process identification and a more realistic model of the open system. Radiocarbon, Vol. 39 (3), pp. 251-268.

Tickell, S.J., Cummings, S., Leonard J.G. and J.A. Withers, 1991. Colac: 1:50 000 Map Geological Report. Geological Survey Report No. 89, Victoria Department of Manufacturing and Industry Development.

Torgersen, T., Habermehl, M.A., Phillips, F.M., Elmore, D., Kubik, P., Geoffrey Jones, B., Hemmick, T. and H.E. Gove, 1991. Chlorine 36 Dating of Very Old Groundwater. 3. Further Studies in the Great Artesian Basin, Australia. Water Resour. Res., Vol. 27, No. 12, pp. 3201-3213.

Unland, N.P., Cartwright, I., Cendon, D.I. and R. Chisari, 2014. Residence times and mixing of water in river banks: implications for recharge and groundwater-surface water exchange. Hydrol. Earth Syst. Sci., Vol. 18, pp. 5109-5124.

Whiting, P.J. and M. Pomeranets, 1997. A numerical study of bank storage and its contribution to streamflow. J. Hydrol., Vol. 202, pp. 121-136.

Williams, G.P., 1989. Sediment concentration versus water discharge during single hydrologic events in rivers. J. Hydrol., Vol. 111, pp. 9-106.

Zerle, L., Faestermann, T., Knie, K., Korschinek, G. And E. Nolte, 1997. The ^{41}Ca bomb pulse and atmospheric transport of radionuclides. Journ. Of Geophys. Research, Vol. 102, No. D16, pp. 19,517-19,527.

Chapter 5
Conclusions

5.1. Key Research Findings

In Chapter 2, differences in groundwater and chloride residence times and mean residence times (MRTs) of groundwater in the Barwon River Catchment were evaluated using groundwater levels, major ion concentrations, stable and radioactive isotopes, the radioactive decay formula, the Piston Flow Model (PFM) and the Exponential Piston Flow Model (EPM) within TracerLPM, and a range of input parameter values. Key findings from this study comprise the following:

- Chloride residence times in groundwater downgradient of Lake Murdeduke are, in many cases, greater than the corresponding residence times of the groundwater itself. This difference is due to the recycling of chloride at Lake Murdeduke and other regional saline lakes in response to environmental change. The implication of this finding is that if groundwater recharge in this region, or other regions like it, was estimated using the chloride mass balance method, that estimate would be less than the true value. This demonstrates the importance of having a good conceptual hydrogeological understanding of a study area when applying the chloride mass balance method to estimate recharge.
- Elevated groundwater salinity in the region is primarily due to through-flow of hyper saline lake water at Lake Murdeduke and other nearby lakes into the underlying groundwater system. This groundwater flows south-easterly from the area of Lake Murdeduke and discharges into the Barwon River, resulting in elevated salinity within the river as well. Additional contributions to salinity result from halite dissolution and mineral weathering; however, these processes are relatively minor in importance compared to the through-flow from Lake Murdeduke.
- Decreases in $\delta^{13}C$, $a^{14}C$, TDS and deuterium excess in the direction of groundwater flow southeast of Lake Murdeduke suggest a progressive increase in evaporation

over time in response to environmental change. These results further suggest that $\delta^{13}C$ may be enriched as a result of evaporation which, before this study, has only been observed in the laboratory.

- Groundwater residence times estimated using the radioactive decay formula, with the correction factor q allowed to vary from 0.85 to 0.95, ranged from Modern (<200 years) to 21,860 years. Mean residence times (MRTs) estimated using the Piston Flow Model (PFM) were similar (generally <10% difference) to those derived using the radioactive formula. MRTs estimated using the Dispersion Model (DM), with the Dispersion Parameter (D_p) set equal to 0.05, were slightly longer, but not significantly so, than those determined using the radioactive decay formula or the PFM. Significant differences in the MRT estimates only became apparent when D_p was set equal to 0.5, leading to MRTs at high as 57,510 years. These results demonstrate the uncertainty in using radioactive tracers to determine groundwater residence times.
- The regional horizontal hydraulic conductivity of the Newer Volcanics basalt is estimated to be approximately 10^{-2} m day^{-1}. The vertical hydraulic conductivity is of the basalt estimated to be within the range of 10^{-5} to 10^{-4} m day^{-1}.
- Elevated groundwater $R^{36}Cl$ values, above that expected and measured within modern regional precipitation, suggest that $R^{36}Cl$ values in rainfall during the past were higher than they are at present, as a result of environmental change. For example, during the last glacial maximum, the coast line would have likely been much further away from the study area than it is at present. As a result, chloride concentrations in rainfall would likely have been lower and, therefore, $R^{36}Cl$ values higher. Very high $R^{36}Cl$ values within groundwater at two observation bores are likely due to bomb-pulse ^{36}Cl still being retained in the environment.

In Chapter 3, mean transit times (MTTs) in six headwater catchments within the Otway Ranges were evaluated using ^{3}H activities and major ion concentrations in river water, streamflow data, the Exponential Piston Flow Model (EPM) and the Dispersion Model

(DM) within TracerLPM, and a range of input parameter values. Key findings from this study comprise the following:

- MTTs ranged from approximately 7 to 230 years and, at low streamflows, are far longer than in most headwater catchments globally. The reason(s) for the unusually long MTTs is not known with certainty but may be due to low rainfall in combination with high evapotranspiration rates, which limit recharge.
- The long MTTs suggest that there are long-lived stores of water within the catchments that can sustain streamflow during drought periods lasting up to a few years. However, longer-term changes such as land use or climate change may eventually affect streamflow.
- MTTs derived from the various models were relatively similar when ^{3}H activities were greater than 1.0 TU. However, as ^{3}H activities in river water decrease below this value, the relative difference between model estimates increases. At the lowest ^{3}H activity of 0.20 TU, MTTs varied by as much as 164 years.
- Calculated MTTs may be lower than true MTTs due to the possibility of macroscopic mixing (aggregation). Evaluation of this error at Love Creek Kawarren suggests that, during the summer, low streamflow conditions, aggregation may be insignificant. At other times of the year, calculated MTTs may underestimate true MTTs by nearly 40%.
- The relative difference between MTTs calculated from three different ^{3}H records in rainfall is highest when ^{3}H activities exceed 1.0 TU. For H activities <0.5 TU, however, MTTs vary by less than 5%.
- There is a strong correlation between ^{3}H activities and streamflow across all catchments, despite differences in geology, size, slope and land use. This suggests that MTTs at high streamflows reflect the input of water from shallower water stores that are largely independent of catchment attributes.
- Within several of the catchments, there is a strong correlation between ^{3}H activities and nitrate and/or sulphate concentrations at high streamflows. This

suggests the input of contaminants to the streams from recent agricultural activities via young groundwater that is mobilised at those times

In Chapter 4, the residence times of bank storage and return flow and its influence on river water chemistry in the upper Barwon River were investigated using stable ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C$) and radioactive (^{3}H and ^{36}Cl) isotopes, major ion geochemistry, streamflow data, and EC-discharge hysteresis loops. Key findings from this study comprise the following:

- Downstream increases in ^{3}H activities following seasonal high, winter river flows indicate that bank storage and return flow contributes to river discharge for a period of at least several months, if not longer.
- Hysteresis patterns in the EC-discharge record indicate that individual storm events can make additional contributions to bank storage and return flow throughout the year, with residence times on the order of a few weeks.
- High ^{3}H activities (>1.75 TU) in the river throughout the year suggest that the older groundwater contribution to streamflow is probably minor in comparison to bank storage and return flow.
- Downstream increases in total dissolved solids (TDS) concentrations, $\delta^{13}C$ values and $R^{36}Cl$ values demonstrate that groundwater inputs are instrumental in determining river water chemistry.
- Elevated $R^{36}Cl$ values in river water in the uppermost portion of the catchment are likely due to plant uptake and recycling of bomb-pulse ^{36}Cl.

5.2. Review of Research Objectives

As outlined in Chapter 1, the broad objective of this research was to employ residence times as a means of gaining further understanding of river catchment functioning and groundwater-surface water interaction. More specifically, using the Barwon River and Otway Catchments as a study area, this study sought to help answer five research questions:

1. Are water and chloride residence time equivalent?
2. What are the sources of water contributing to streamflow, and are those sources the same in headwater streams as they are in lowland rivers?
3. What is the residence time of bank storage and return flow?
4. Are residence times in headwater catchments similar to those of lowland rivers?
5. What are the effects of using different models to estimate residence times?

In Chapter 2, it was shown that groundwater and chloride residence times are not always equal. In fact, at about half of the observation bores sampled in the vicinity of Lake Murdeduke, estimate chloride residence (accession) times exceeded the mean residence times of the groundwater in which the solute was contained. This observation is interpreted to be the result of the recycling of chloride at Lake Murdeduke and other permanent and semi-permanent saline lakes within the catchment. The implication of this observation is that, if groundwater recharge was estimated using chloride concentrations at these bores, the calculated recharge rate would underestimate the true value. This conclusion demonstrates the importance of having a good conceptual hydrogeologic understanding of a region before applying the chloride mass balance technique of estimating recharge.

In Chapter 3, it was demonstrated that groundwater inputs make an important contribution to headwater streams at low streamflows. At high streamflows, however, younger water stores, such as soil water or regolith water, are mobilised and make an increasingly more important contribution to streamflow. In Chapter 4, it was demonstrated that, in lowland rivers such as the upper Barwon River, one of the most important inputs to streamflow is bank storage and return flow. The implications of these conclusions are that: 1) impacts to shallow, young water stores, which are most vulnerable to contamination, can affect headwater stream water quality over a period lasting years to decades, and 2) engineering controls along lowland rivers, such as flood control barriers, can result in increased river salinity.

In Chapter 4, it was demonstrated that bank storage and return flow during high winter flows can have residence times of at least several months, if not longer. In addition, during

other times of the year, individual storm events can make additional contributions to bank storage and return flow, with residence times on the order of a few weeks. The implications of this research is that water within lowland rivers is comprised of a significant fraction of young (<1 year) water. Hence, managing lowland rivers and their near-river environments requires careful consideration of bank storage and return flow.

In Chapters 3 and 4, it was demonstrated that transit times in headwater catchments and lowland rivers such as the upper Barwon River can vary considerably. For example, within the headwater catchments of the Otway Ranges, transit times ranged from approximately 7 to 230 years, depending on streamflow. In contrast, transit times within the upper Barwon River, located just a short distance (<50 km) away, were estimated to be less than or equal to about 10 years, regardless of streamflow. The implications of this conclusion is that streamflow within headwater catchments can be fed by long-lived stores of water that can sustain the streams for a period of up to at least a few years. In contrast, streamflows in lowland rivers are much more likely to be impacted by longer-term changes, such as drought or climate change.

In Chapters 2, 3 and (to a lesser degree) Chapter 4, it was demonstrated that there exists considerable uncertainty in using radioactive tracers to estimate residence times (and transit times) of groundwater and river water. In groundwater, residence time estimated using the radioactive decay equation and the piston-flow model (PFM) were relatively similar. However, when using the Exponential Flow Model (EPM) or the Dispersion Model (DM), transit times varied considerably. Likewise, in river water, residence times varied considerably depending on the model employed. However, these differences are insignificant when tracer concentrations (e.g. ^{3}H) are relatively high. Other uncertainties exist however, including the tracer input history, macroscopic mixing, and analytical uncertainty.

5.3. Broad Implications of Research

In these investigations, the concept of residence time has been shown to be a valuable tool towards gaining better understanding groundwater-surface water interaction. Combined with aqueous geochemistry, stable isotopes, streamflow and water quality data, catchment characteristics, and groundwater levels, this study has shown that residence times can provide valuable information on geochemical processes, water-rock interaction, environmental change, catchment functioning, anthropogenic impacts, and sources of baseflow. In water-scarce regions, both surface water and groundwater are vitally important to the economic wellbeing of the communities that exist there, as well as to the ecosystems that depend on that water for their survival. It is therefore hoped that the results of this work can be applied to similar river systems globally, not just within the Barwon River and Otway Catchments of southeast Australia.

Much of water in the Barwon River and Otway Catchments is characterised by high salinity. This includes Lake Murdeduke and other nearby lakes, shallow groundwater downgradient of Lake Murdeduke, and stretches of the upper Barwon River. As evidenced in the studies described herein, the region appears to have been undergoing environmental change for many thousands of years, with a slow but steady progression to more evaporative conditions. This has, in turn, no doubt contributed to the development of highly saline water within the Barwon River Catchment. While these processes cannot easily be reversed, having a better understanding of groundwater-surface water interaction may certainly help the problem from getting worse. For example, these investigations have demonstrated the importance of bank storage and return flow in controlling river salinity. Thus, the floodplain deposits along the Barwon River need to be protected, as they contribute relatively fresh water to the river throughout much of the year. Large-scale developments on these deposits, or construction of roadways or retention walls, can impact the ability of the sediments to both receive and then release storm event water. This, in turn, could then result in greater salinisation of the Barwon River. Likewise, any development that affects the highly saline groundwater system needs to carefully consider

how that development might affect groundwater flow patterns, for a change in groundwater flow direction might cause other surface water bodies to become salinised. In addition, any groundwater extraction needs to consider how the highly saline groundwater will be managed.

Unlike the nearby Barwon River, headwater streams within the Otway Ranges are characterised by low salinity. However, these investigations have shown that water quality within a few of the catchments has already been impacted by anthropogenic activities in the form of high nitrate and sulphate concentrations at high streamflows. Further, these largely forested pristine catchments are prone to changes that include deforestation, agricultural development, bushfires, drought, urbanisation and contaminant loading. In these studies, it was shown that such changes, should they occur, would not likely fully manifest themselves within the headwater streams for at least a few years. This timeframe provides a buffer with which resource managers can plan for potential impacts to river water quality and quantity. However, it also allows for complacency, as the effects of such changes will not become immediately apparent.

5.4. Suggestions for Further Study

This study has revealed some valuable insight into the processes and timescales of groundwater-surface water interaction. However, these investigations have also revealed additional gaps that further studies might address. These include:

- Differences in chloride and groundwater residence time suggest that groundwater recharge estimates based on the chloride mass balance method would underestimate the actual value. This could be evaluated through use of an alternative solute such as bromide, which is likely to be more conservative than chloride due to its larger ionic radius and hence exclusion in halite formation.
- These investigations have provided evidence of fractionation of $\delta^{13}C$, which has been scarcely examined in the scientific literature. Additional sampling and analysis of

groundwater from areas adjacent to Lake Murdeduke for $\delta^{13}C$, $\delta^{18}O$, $\delta^{2}H$ and $a^{14}C$ could lend credence to this hypothesis.

- Evidence of environmental change appears to be preserved within groundwater located hydrologically downgradient of Lake Murdeduke, a hyper-saline through-flow lake. Similar environments might yield additional climate change information.
- Downstream increases in ^{3}H activities in the upper Barwon River suggest that bank storage and return flow can have a residence time of several months, if not longer. This could be further evaluated through a more thorough sampling and analysis regime, not only within the river but from bores installed within adjacent alluvial sediments.
- Elevated $R^{36}Cl$ values in groundwater and in surface water appear to be due to bomb-pulse ^{36}Cl still being retained within the environment. This could be confirmed through additional sampling and analysis, including from other rivers in the region.
- A strong correlation was noted between ^{3}H activities and EC and TDS concentrations at Porcupine Creek, and between ^{3}H activities and TDS at Lardners Gauge. These correlations allow ^{3}H activities and, therefore, MTTs to be estimated from a simple water quality measure. However, these correlations are based upon a limited number (five) of samples. Further sampling and analysis at these locations would confirm and perhaps strengthen these relationships.