Dynamics of stream and groundwater exchange using environmental tracers

submitted by

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TABLE OF CONTENTS

TABLE OF CONTENTS .... **I**

LIST OF FIGURES .... **VIII**

LIST OF TABLES .... **XVII**

LIST OF SYMBOLS .... **XIX**

ABSTRACT .... **XXII**

DECLARATION OF ORIGINALITY .... **XXIV**

PUBLICATIONS ASSOCIATED WITH THIS THESIS .... **XXV**

ACKNOWLEDGEMENTS .... **XXVIII**

1 INTRODUCTION **1**

1.1 SCOPE 1

1.1 PREVIOUS WORK 2

1.2 AIMS OF THE THESIS 3

1.3 APPLICATION OF ENVIRONMENTAL TRACERS 4

1.4 OUTLINE OF ENVIRONMENTAL TRACERS USED 6

1.4.1 Chloride *6*

1.4.2 Radon-222 .... *7*

1.4.3 Stable isotopes of water *10*

1.4.4 Strontium isotopes and concentrations *12*

1.4.5 Tracer comparison *14*

1.5 STUDY AREA OVERVIEW 16

1.5.1 Physical Setting *16*

1.5.2 Climate *16*

1.5.3 Hydrology *20*

1.5.4 Hydrogeology *21*

1.5.5 Land use *22*

1.6 CHAPTER DESCRIPTIONS 22

1.6.1 Chapter 1: Introduction *22*

1.6.2 Chapter 2: Methods *23*

1.6.3 Chapter 3: Dynamics of stream and groundwater exchange using ^{222}*Rn* . *23*

1.6.4 Chapter 4: Quantifying groundwater discharge to streams using ^{222}*Rn* .. *24*

1.6.5 Chapter 5: Sources of water to streams using tracer techniques *24*

1.6.6 Chapter 6: Reach scale interpretation of tracer data *25*

1.6.7 Chapter 7: Conclusions *25*

2 SAMPLING AND ANALYTICAL METHODS 26

2.1 SITE SELECTION 26

2.2 BORE AND PIEZOMETER NETWORK 26

2.3 RUN OF RIVER SITES 30

2.4 TIME SERIES SITE 36

2.5 SURFACE WATER AND GROUNDWATER MONITORING 37

2.6 SAMPLING METHODOLOGY 39

2.6.1 Groundwater sampling *39*

2.6.2 Surface water sampling *40*

2.6.3 Soil and unsaturated zone pore water sampling *41*

2.7 SAMPLE PRESERVATION 42

2.7.1 Major ion chemistry *42*

2.7.2 Radon *42*

2.7.3 Stable isotopes of water *43*

2.7.4 Strontium *44*

2.8 ANALYTICAL TECHNIQUES 44

2.8.1 Field analysis *44*

2.8.2 Major ion chemistry *44*

2.8.3 Radon *46*

2.8.4 Stable isotopes of water *47*

2.8.5 Strontium *48*

2.8.6 Soils *49*

2.9 RESULTS 51

3 DYNAMICS OF EXCHANGE BETWEEN STREAM WATER, ALLUVIAL GROUNDWATER AND REGIONAL GROUNDWATER USING ^{222}Rn 52

3.1 INTRODUCTION 52

3.2 RESULTS 54

3.2.1 Water level gradients *54*

3.2.2 End-member ^{222}Rn concentrations *57*

3.2.3 Flood recession and baseflow ^{222}Rn concentrations *58*

3.2.4 Emanation of ^{222}Rn from alluvial aquifer material *64*

3.3 DISCUSSION 65

3.3.1 Origin of ^{222}Rn in alluvial aquifer *65*

3.3.2 Extent of surface water influx to alluvial aquifer *70*

3.3.3 Regional groundwater leakage into the alluvial aquifer *78*

3.4 CONCLUSIONS 81

4 QUANTIFYING GROUNDWATER DISCHARGE TO STREAM FLOW USING ^{222}Rn 84

4.1 INTRODUCTION 84

4.2 BACKGROUND THEORY 86

4.2.1 Estimating groundwater discharge to stream flow *86*

4.2.2 Percentage groundwater discharge to stream flow *93*

4.3 FIELD RESULTS 94

4.3.1 End-member characteristics *94*

4.3.2 In-stream transects ... *95*

4.4 PARAMETERS FOR ESTIMATING ^{222}Rn PERSISTENCE IN STREAM WATER ... 98

4.4.1 Stagnant film thickness ... *98*

4.4.2 Background ^{222}Rn concentration in stream water ... *100*

4.5 MODELLING ^{222}Rn PERSISTENCE IN STREAM WATER ... 101

4.5.1 Introduction ... *101*

4.5.2 Predicting downstream ^{222}Rn concentrations in stream water ... *104*

4.5.3 Background ^{222}Rn concentration in stream water ... *107*

4.5.4 Distance of ^{222}Rn persistence in stream water ... *109*

4.5.5 Constraining groundwater discharge to stream flow ... *114*

4.5.6 Optimal intervals for sampling ^{222}Rn in stream water ... *126*

4.6 CONCLUSIONS ... 132

5 APPLICATION OF TRACER TECHNIQUES TO IDENTIFY SOURCES OF WATER TO STREAM FLOW DURING BASEFLOW & FLOOD RECESSION ... 134

5.1 INTRODUCTION ... 134

5.1.1 Background ... *134*

5.1.2 Objectives ... *136*

5.1.3 Sampling Strategy ... *137*

5.2 RESULTS ... 139

5.2.1 Stream hydrograph ... *139*

5.2.2 Chloride ... *141*

5.2.3 Radon-222 ... *142*

5.2.4 Stable isotopes of water ... *145*

5.2.5 Strontium and ^{87}Sr/^{86}Sr ... *155*

5.2.6 Time series data ... *158*

5.3 METHODOLOGY FOR USE OF ENVIRONMENTAL TRACERS TO IDENTIFY SOURCES OF GROUNDWATER DISCHARGE TO STREAM FLOW 161

5.3.1 Stream water salinity as an indicator of groundwater discharge to stream flow 161

5.3.2 Radon-222 in stream water as an indicator of groundwater discharge to stream flow 163

5.3.3 Stable isotopes of water as indicators of groundwater discharge to stream flow 170

5.3.4 Strontium and $^{87}Sr/^{86}Sr$ as indicators of groundwater discharge to stream flow 176

5.4 SOURCES OF GROUNDWATER DISCHARGE TO STREAM FLOW...................... 179

5.4.1 Long-term monitoring 179

5.4.2 Flood recession 183

5.4.3 Baseflow 188

5.5 SPATIAL DISTRIBUTION OF ALLUVIAL GROUNDWATER AND REGIONAL GROUNDWATER CONTRIBUTIONS TO STREAM FLOW 193

5.6 CONCLUSIONS 197

6 REACH-SCALE INTERPRETATION OF TRACER DATA...................... 200

6.1 INTRODUCTION...................... 200

6.2 FLOOD RECESSION...................... 202

6.2.1 Stations 13 to 12...................... 202

6.2.2 Stations 12 to 11...................... 204

6.2.3 Stations 11 to 10...................... 205

6.2.4 Stations 10 to 9...................... 207

6.2.5 Stations 9 to 8...................... 209

6.2.6 Stations 8 to 7...................... 210

6.2.7 Stations 7 to 4...................... 210

6.2.8 Stations 4 to 3 .... *212*

6.2.9 Stations 3 to 2 .... *214*

6.2.10 Stations 2 to 1 .... *216*

6.3 BASEFLOW 218

6.3.1 Stations 13 to 12 .... *218*

6.3.2 Stations 12 to 11 .... *222*

6.3.3 Stations 11 to 10 .... *224*

6.3.4 Stations 10 to 9 .... *227*

6.3.5 Stations 9 to 8 .... *231*

6.3.6 Stations 8 to 7 .... *233*

6.3.7 Stations 7 to 5 .... *235*

6.3.8 Stations 5 to 4 .... *236*

6.3.9 Stations 4 to 3 .... *239*

6.3.10 Stations 3 to 2 .... *244*

6.3.11 Stations 2 to 1 .... *248*

6.4 SPATIAL DISTRIBUTION OF GROUNDWATER DISCHARGE TO STREAM FLOW 250

6.5 CONCLUSIONS 254

7 CONCLUSIONS........ 257

7.1 OVERVIEW 257

7.2 STREAM WATER AND GROUNDWATER EXCHANGE PROCESSES 258

7.2.1 Extent of stream water and groundwater interaction in alluvial aquifers 258

7.2.2 Regional groundwater contribution to alluvial aquifers *258*

7.2.3 Groundwater contribution to stream flow *259*

7.3 METHOD DEVELOPMENT FOR INVESTIGATING SURFACE WATER AND GROUNDWATER EXCHANGE 261

7.3.1 Surface water and groundwater exchange *261*

7.3.2 Groundwater discharge to stream flow 262

REFERENCES 265

APPENDIX A: SURFACE WATER & GROUNDWATER CHEMISTRY 282

APPENDIX B: PHREEQC GEOCHEMICAL MODELLING OUTPUT 308

APPENDIX C: PREDICTED COMPARED TO MEASURED ^{222}Rn CONCENTRATIONS IN STREAM WATER 359

LIST OF FIGURES

Figure 1.1 Location map of the Wollombi Brook Catchment.

Figure 1.2 Satellite image of Wollombi Brook Catchment (Wollombi township marker: 32º57’00’00” S, 151º08’00” E).

Figure 1.3 Average monthly rainfall (1889 to 2002) and potential evaporation (1972 to 2002) at Broke (lower Wollombi Brook).

Figure 1.4 Stream discharge (m^3 d^{-1}) in the lower Wollombi Brook (Warkworth) and in a mid-catchment tributary (Brickmans).

Figure 2.1 Location of catchment-scale surface water, 'run of river' sampling sites from the Wollombi Brook and its tributaries and locations of piezometer networks and bores.

Figure 2.2 Groundwater monitoring sites: (*a*) Warkworth (site 1), (*b*) Fordwich (site 3) and (*c*) Wollombi (site 10).

Figure 2.3 Cross-sections of the piezometer and bore network set-up at (*a*) Warkworth (site 1, lower Wollombi Brook), (*b*) Fordwich (site 3, lower Wollombi Brook) and (*c*) Wollombi (site 10, mid to upper Wollombi Brook).

Figure 2.4 Surface water sampling stations (*a*) 21, and (*b*) 20, located along the Watagan branch of the Wollombi Brook.

Figure 2.5 Timing of field trips compared to daily rainfall at Broke and stream discharge at Warkworth (site 1).

Figure 3.1 Water levels in the Wollombi Brook and adjacent alluvial aquifer compared to groundwater levels in deep and shallow bores in the lower (Warkworth site 1 and Fordwich site 3) and mid to upper (Wollombi site 10) Wollombi Brook measured during flood recession (*a*, *b*, *c*, Mar-01) and baseflow (*d*, *e*, *f*, Nov-01) conditions.

Figure 3.2 The 10th, 25th, 75th and 90th percentiles represent the variation throughout the two-year sampling period (2000-01) of ^{222}Rn measured in stream water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 3.3 Warkworth (site 1): ^{222}Rn activity (Bq L^{-1}) of groundwater sampled from piezometer network during flood recession (*a*) May-00, (*b*) Mar-01 and (*c*) low flow conditions (baseflow) Nov-01.

Figure 3.4 ^{222}Rn activity (Bq L^{-1}) in alluvial groundwater (AW) relative to distance (*x*) from the stream channel (m) during (*a*) May-00 flood recession, (*b*) Mar-01 flood recession and (*c*) Nov-01 baseflow.

Figure 3.5 Fordwich site: ^{222}Rn activity (Bq L^{-1}) of groundwater sampled from piezometer network during (*a*) Mar-01 flood recession and (*b*) Nov-01 low flow (baseflow).
Figure 3.6 Wollombi site: ^{222}Rn activity (Bq L^{-1}) of groundwater sampled from piezometer network during (*a*) Mar-01 flood recession and (*b*) Nov-01 low flow (baseflow) conditions.
Figure 3.7 Steady state ^{222}Rn activity (C_{ss}, Bq L^{-1}) in alluvial aquifer sediment profiles located distances of 0, 4 and 23 m from the stream channel at Warkworth.
Figure 3.8 Residence time (T) of water within the alluvial aquifer and the fraction of ^{222}Rn ingrowth represented by the ^{222}Rn concentration measured in the alluvial aquifer ($^{222}R_{meas}$) divided by the steady state ^{222}Rn emanation from alluvial aquifer material (C_{ss}).
Figure 3.9 Residence time (days) of stream water in the alluvial aquifer at Warkworth during the (*a*) May-00 and (*b*) Mar-01 flood recessions and during the (*c*) Nov-01 low stream flow (baseflow) conditions based on ^{222}Rn ingrowth estimates.
Figure 3.10 Residence time (days) of stream water in the alluvial aquifer at Fordwich during the (*a*) May-00 flood recession and (*b*) Nov-01 low flow (baseflow) conditions based on ^{222}Rn ingrowth estimates.
Figure 3.11 Residence time (days) of stream water in the alluvial aquifer at Wollombi during the (*a*) Mar-01 flood recession and the (*b*) Nov-01 low stream flow (baseflow) conditions based on ^{222}Rn ingrowth estimates.
Figure 4.1 Stream cross-section, where the radon concentration in stream water ($^{222}Rn_{sw}$) is much higher than the radon concentration in the atmosphere ($^{222}Rn_{atm}$) and radon transfer occurs via molecular diffusion across the hypothetical stagnant boundary layer (z).
Figure 4.2 Stream section showing parameters measured for estimation of stagnant film thickness (z, equation 4.1) in a section of the stream in which there is no groundwater discharge to stream flow.
Figure 4.3 The 10th, 25th, 75th and 90th percentiles represent the variation throughout the two-year sampling period (2000-01) of radon (^{222}Rn) measured in stream water (SW), alluvial groundwater (AW) and regional groundwater (GW) sampled across the Wollombi Catchment.
Figure 4.4 ^{222}Rn concentrations (mBq L^{-1}) measured in the upper Wollombi Catchment during baseflow conditions (Nov-01).

Figure 4.5 Radon (^{222}Rn) activities (Bq L^{-1}) in stream water measured during flood recession (May-00 & Mar-01) and baseflow (Nov-01) in the Wollombi Brook and tributaries compared background levels.

Figure 4.6 The downstream ^{222}Rn concentration was predicted (C_{TR}^{n} , equation 4.8) for n progressively smaller intervals of x until C_{TR}^{n} converged.

Figure 4.7 Example of model output. The predicted ^{222}Rn concentration (C_{TR}^{n}) in stream water converged at approximately 40 mBq L^{-1} where C^{0} = 280 mBq L^{-1}, x = 4.5 km (divided into >100 equal intervals, i), v = 0.05 m s^{-1}, h = 0.93 m, z = 6.7 × 10^{-5} m.

Figure 4.8 ^{222}Rn concentrations (mBq L^{-1}) measured in stream water (C^{0}) during (*a*) the March-2001 flood recession and (*b*) under baseflow conditions (Nov-2001) compared to predicted ^{222}Rn concentrations (C_{TR}^{n}), based on upstream ^{222}Rn concentrations and gas exchange and radioactive decay ^{222}Rn losses.

Figure 4.9 Minimum percentages of (*a*) alluvial groundwater ($\%AGW_{\min}$) and (*b*) regional groundwater ($\%RGW_{\min}$) discharges to stream flow during flood recession (Mar-01) and baseflow (Nov-01).

Figure 4.10 ^{222}Rn activities (mBq L^{-1}) during (*a*) flood recession (Mar-01) and (*b*) baseflow (Nov-01) compared to predicted ^{222}Rn activities ($C_{\max}^{0}$) required at the upstream sampling station (due to gas exchange and radioactive decay losses) to reproduce actual ^{222}Rn activities downstream (C^{n}).

Figure 4.11 Maximum and minimum percentages of alluvial groundwater contribution to stream flow during (*a*) flood recession (Mar-01) and (*b*) baseflow (Nov-01).

Figure 4.12 Maximum and minimum percentages of regional groundwater contribution to stream flow during (*a*) flood recession (Mar-01) and (*b*) baseflow (Nov-01).

Figure 4.13 Relationships between average stream velocity (v), average stream height (h) and distance between sampling stations (x) for constraining limits of alluvial and regional groundwater discharge to stream flow.

Figure 5.1 Conceptual diagram of alluvial groundwater (AW) and regional groundwater (RW) discharge to stream flow.

Figure 5.2 Stream discharge (m^{3} d^{-1}) hydrographs monitored in the lower Wollombi Brook (Warkworth and Bulga) and in a mid-catchment tributary (Brickman's Bridge).

Figure 5.3 Chloride (Cl^-) concentrations (mg L^{-1}) in stream water measured during flood recession (Mar-01) and baseflow (Nov-01) in the Wollombi Brook and tributaries. The 10th, 25th, 75th and 90th percentiles represent the variation throughout a two-year sampling period (2000-01) of Cl^- measured in surface water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 5.4 Radon (^{222}Rn) activities (Bq L^{-1}) measured in stream water during flood recession (Mar-01) and baseflow (Nov-01) in the Wollombi Brook and tributaries compared to background concentrations. The 10th, 25th, 75th and 90th percentiles represent the variation throughout a two-year sampling period (2000-01) of ^{222}Rn measured in surface water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 5.5 (*a*) Oxygen-18 ($\delta^{18}O$) and (*b*) deuterium (δ^2H) values (‰ VSMOW) in stream water measured during flood recession (Mar-01) and baseflow (Nov-01) in the Wollombi Brook and tributaries. The 10th, 25th, 75th and 90th percentiles represent the variation throughout a two-year sampling period (2000-01) of $\delta^{18}O$ and δ^2H measured in surface water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 5.6 Deuterium excess (*d*-excess) values in stream water measured during flood recession (Mar-01) and baseflow (Nov-01) in the Wollombi Brook and tributaries compared to the Global Meteoric Water Line (GMWL). The 10th, 25th, 75th and 90th percentiles represent the variation throughout a two-year sampling period (2000-01) of *d*-excess measured in surface water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 5.7 Soil moisture content and δ^2H signature in unsaturated soils located (*a*) 2 m, (*b*) 6 m, (*c*) 21 m, (*d*) 4 m, (*e*) 10 m and (*f*) 23 m from the stream channel at sampling station 1 (Warkworth) during (*a, b, c*) flood recession (Mar-01) and (*d, e, f*) baseflow (Nov-01) conditions.

Figure 5.8 Soil moisture content and *d*-excess in unsaturated soils located (*a*) 2 m, (*b*) 6 m, (*c*) 21 m, (*d*) 4 m, (*e*) 10 m and (*f*) 23 m from the stream channel at sampling station 1 (Warkworth) during (*a, b, c*) flood recession (Mar-01) and (*d, e, f*) baseflow (Nov-01) conditions.

Figure 5.9 The strontium concentration (Sr^{2+} mg L^{-1}) in stream water measured during baseflow (Nov-01) separated into the main stem (Brook), two major branches (Watagan and South) and tributaries. The 10th, 25th, 75th and 90th percentiles represent the variation throughout a two-year sampling period (2000-01) of Sr^{2+} measured in surface water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 5.10 Strontium isotope ratios ($^{87}Sr/^{86}Sr$) in stream water measured during baseflow (Nov-01) separated into the main stem (Wollombi Brook) and two major branches (Watagan and South). The 10th, 25th, 75th and 90th percentiles represent the variation throughout a two-year sampling period (2000-01) of $^{87}Sr/^{86}Sr$ measured in surface water (SW), alluvial groundwater (AW) and regional groundwater (RW) sampled across the Wollombi Catchment.

Figure 5.11 'Long-term' changes in (*a*) Cl^- concentrations, (*b*) δ^2H and $\delta^{18}O$, and (*c*) *d*-excess in the Wollombi Brook in comparison to (*d*) stream water discharge at Brickman's Bridge (site 'TB', tributary to the Wollombi Brook) and daily rainfall at Broke (site '4').

Figure 5.12 Conceptual diagram of ^{222}Rn loss and gain from the Wollombi Brook between surface water sampling stations 0 and *n*.

Figure 5.13 Schematic δ^2H-$\delta^{18}O$ plot demonstrating the difference in slope (*m*) between surface water and groundwater evaporation lines in a temperate climate.

Figure 5.14 Conceptual diagram demonstrating that similar changes in the *d*-excess of stream water can be caused by different processes (indicated by arrows).

Figure 5.15 Conceptual shifts in stream water δ^2H-$\delta^{18}O$ slopes (*m*) and δ^2H between consecutive surface water sampling stations (from point 1 to 2), or between successive sampling times.

Figure 5.16 Conceptual changes in stream water $^{87}Sr/^{86}Sr$ and Sr^{2+} concentration in response to evaporation from the stream channel, rainfall dilution and groundwater discharge from basalt and silicate aquifers.

Figure 5.17 Strategy used for identifying sources of water to stream flow between sampling periods based on δ^2H-$\delta^{18}O$ and Cl^- data.

Figure 5.18 Major sources of water to the Wollombi Brook at the "time series" surface water sampling station between October 2000 and January 2002 in response to daily rainfall (at Broke) and changes in stream discharge (at Brickman's).

Figure 5.19 Surface water δ^2H-δ^{18}O evaporation lines for long-term “time series” sampling, and “snapshot” flood recession (Mar-01) and baseflow (Nov-01) sampling.

Figure 5.20 δ^2H-δ^{18}O signatures measured in alluvial groundwater (AW), regional groundwater (RW), the Wollombi Brook (Brook) and tributaries in relation to the Global Meteoric Water Line (GMWL) during (*a*) flood recession (Mar-01) and (*b*) baseflow (Nov-01) conditions.

Figure 5.21 Unsaturated zone (UZ) δ^2H-δ^{18}O signatures compared to δ^2H-δ^{18}O signatures in the Wollombi Brook (Brook), alluvial groundwater (AW), regional groundwater (RW) and the Global Meteoric Water Line (GMWL) during (*a*) flood recession (Mar-01, located 2, 6 and 21 m from the stream channel) and (*b*) baseflow (Nov-01, located 4, 10 and 23 m from the stream channel) conditions.

Figure 5.22 Alluvial groundwater (AW) δ^2H-δ^{18}O evaporation line at Fordwich (station site 3) during flood recession (Mar-01) in relation to the Global Meteoric Water Line (GMWL).

Figure 5.23 ^{87}Sr/^{86}Sr versus inverse Sr^{2+} concentration of stream water (Brook), alluvial groundwater (AW) and regional groundwater (RW) during (*a*) flood recession (Mar-01) and (*b*) baseflow (Nov-01) conditions. Theoretical mixing lines were constructed between stream water and regional groundwater end-members demonstrating potential percentages of regional groundwater discharge to stream flow.

Figure 5.24 Conceptual diagram of changes in stream channel morphology and discharge characteristics from the upper to the lower Wollombi Brook.

Figure 6.1 Schematic diagram of two-component end-member mixing.

Figure 6.2 δ^2H and δ^{18}O (‰ VSMOW) composition of stream water (stations 13 and 12), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during flood recession (Mar-01).

Figure 6.3 δ^2H and δ^{18}O (‰ VSMOW) composition of stream water (stations 11 and 10) and tributaries, alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during flood recession (Mar-01).

Figure 6.4 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 7, 5 and 4), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during flood recession (Mar-01).

Figure 6.5 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 4 and 3), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during flood recession (Mar-01).
Figure 6.6 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 3 and 2), tributary “T1”, alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during flood recession (Mar-01).
Figure 6.7 Changes in the strontium isotope ratio (^{87}Sr/^{86}Sr) and inverse strontium concentration (1/Sr^{2+}, L mg^{-1}) in the Wollombi Brook between stream water sampling stations 3 and 1 in comparison to alluvial groundwater (AW) and regional groundwater (RW) values during flood recession (Mar-01). Theoretical mixing lines were constructed between stream water at sampling station 3 and (*a*) alluvial groundwater, and (*b*) regional groundwater, to estimate the potential proportions of groundwater discharge to stream flow between stations 3 and 1.
Figure 6.8 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 2 and 1), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during flood recession (Mar-01).
Figure 6.9 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 13 and 12), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during baseflow (Nov-01).
Figure 6.10 Change in ^{87}Sr/^{86}Sr and inverse Sr^{2+} concentration of stream water (SW) in between stations 13 and 11 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 13, RW and (*a*) maximum AW, and (*b*) minimum AW to estimate the proportions of each water source present in stream water at sampling station 11.
Figure 6.11 Schematic diagram of three-component end-member mixing.
Figure 6.12 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 12 and 11), tributaries (T8, T9 and T10) alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during baseflow (Nov-01).
Figure 6.13 δ^2H and δ^{18}O (‰ VSMOW) values in stream water (stations 11 and 10), tributary water (14 and T6), alluvial groundwater (AW) and regional

groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during baseflow (Nov-01).

Figure 6.14 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) between stations 11 and 10 compared to tributary water (14) alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 11, tributary 14 and (*a*) maximum AW, and (*b*) minimum AW values to estimate proportions of each water source present in stream water at sampling station 10.

Figure 6.15 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 10 and 9 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 10, (*a*) maximum AW and minimum RW values, and (*b*) minimum AW and maximum RW values to estimate proportions of each water source present in stream water at sampling station 9.

Figure 6.16 δ^2H and $\delta^{18}O$ (‰ VSMOW) values in stream water (stations 9 and 8), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during baseflow (Nov-01).

Figure 6.17 δ^2H and $\delta^{18}O$ (‰ VSMOW) values in stream water (stations 8 and 7), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during baseflow (Nov-01).

Figure 6.18 δ^2H and $\delta^{18}O$ (‰ VSMOW) values in stream water (stations 5 and 4), alluvial groundwater (AW) and regional groundwater (RW) in relation to the Global Meteoric Water Line (GMWL) during baseflow (Nov-01).

Figure 6.19 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 9 and 4 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 9 and (*a*) shallow AW, and (*b*) shallow RW to estimate the potential proportions of each water source present in stream water at sampling station 4.

Figure 6.20 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 9 and 4 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 9 and (*a*) minimum deep AW, and (*b*) maximum deep AW values to estimate the potential proportion of deep AW present in stream water at sampling station 4.

Figure 6.21 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 9 and 4 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 7 and shallow RW to estimate potential shallow RW discharge to stream flow between stations 7 and 4.

Figure 6.22 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 9 and 4 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 7 and (*a*) minimum, and (*b*) maximum deep AW values to estimate potential deep AW discharge to stream flow between stations 7 and 4.

Figure 6.23 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 4 and 3 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 4, shallow AW, deep AW and shallow RW to estimate potential proportions of groundwater discharge to stream flow between stations 4 and 3.

Figure 6.24 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 3 and 2 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 3 and shallow AW to estimate potential proportions of groundwater discharge to stream flow between stations 3 and 2.

Figure 6.25 Change in $^{87}Sr/^{86}Sr$ and inverse Sr^{2+} concentration in stream water (SW) in between stations 2 and 1 compared to alluvial groundwater (AW) and regional groundwater (RW) values. Theoretical mixing lines were constructed between SW at station 2, deep AW and RW to estimate potential proportions of groundwater discharge to stream flow between stations 2 and 1.

Figure 6.26 Estimated ranges of alluvial groundwater (AW), and regional groundwater (RW) discharge to stream flow during (*a* and *b*) flood recession (Mar-01), and (*c* and *d*) baseflow (Nov-01).

LIST OF TABLES

Table 1.1 ^{222}Rn activity of groundwater from sedimentary and alluvial aquifers (adapted from Faure 1986).

Table 1.2 Atmospheric ^{222}Rn concentrations.

Table 1.3 Estimated dissolution times and likely ranges of ^{87}Sr/^{86}Sr assuming an initial ratio of 0.705 and Rb/Sr typical for Palaeozoic granites of eastern Australia (0.3 – 2.0). Modified from Douglas *et al*. (1995).

Table 1.4 Advantages and limitations of Cl^-, ^{222}Rn, δ^2H & $\delta\,^{18}$O and Sr^{2+} & ^{87}Sr/^{86}Sr for distinguishing between water reservoirs and for interpreting stream and groundwater interactions.

Table 1.5 Average monthly and annual relative humidity (%) measured daily at 9 am and 3 pm.

Table 2.1 Average stream height (h), average stream velocity (v) and stream discharge (Q) measured at selected sites using a pycnometer.

Table 3.1 Steady state ^{222}Rn concentration (C_{ss}, Bq L^{-1}) in alluvial aquifer material at Warkworth (site 1).

Table 4.1 Stagnant film thickness (z) estimates and variable parameters (upstream and downstream ^{222}Rn concentrations; C^0 , C_T^n , distance and travel time between sampling stations; x , t , average stream height and velocity; h , v) for each run of river transect in the Wollombi Brook (flood recessions May-00 and Nov-01, and baseflow Mar-01) based on ^{222}Rn gas exchange equation (4.1).

Table 4.2 Background ^{222}Rn concentrations in stream water (C^B) due to sediment flux (Bq L^{-1}).

Table 4.3 Background ^{222}Rn concentrations (C^B) in stream water (Bq L^{-1}) estimated using equation (4.9).

Table 4.4 Summary of parameters required for estimation of the distance of ^{222}Rn persistence (x) in stream water following groundwater discharge based on ^{222}Rn gas exchange with the atmosphere (equation 4.10).

Table 4.5 Summary of the distance of ^{222}Rn persistence in stream water estimates (x km) for the upper Wollombi Brook during flood recession (Wollombi, site 10, Mar-01) and the lower Wollombi Brook during baseflow (Fordwich, site 3, Nov-01).

Table 4.6 Summary of steady state ^{222}Rn emanation from alluvial aquifer material, maximum and minimum ^{222}Rn concentrations measured in regional groundwater in the lower, mid and mid-upper regions of the Wollombi Brook Catchment.

Table 4.7 Comparison of empirical (equation 4.18) and numerical (equations 4.20 and 4.21) estimates of the maximum distance (x) in between stream water ^{222}Rn sampling stations such that estimates of maximum groundwater (equations 4.16 and 4.17) contribution to stream flow are well constrained (<100%).

Table 6.1 Summary of the percentages of alluvial groundwater (AGW) and regional groundwater (RGW) discharges to stream flow between consecutive stream water sampling stations (1 to 13) during flood recession (Mar-01) and baseflow (Nov-01).

LIST OF SYMBOLS

C^0	^{222}Rn activity upstream	(Bq L^{-1})
$C^0_{\max}$	Maximum predicted upstream ^{222}Rn activity	(Bq L^{-1})
C_{ss}	Steady state ^{222}Rn activity of groundwater	(Bq L^{-1})
C_{ss}^{AGW}	Steady state ^{222}Rn emanation from alluvial aquifer sands	(Bq L^{-1})
C^B	Background ^{222}Rn activity in stream water	(Bq L^{-1})
$C_{\max}^{RGW}$	Maximum ^{222}Rn activity measured in regional groundwater	(Bq L^{-1})
$C_{\min}^{RGW}$	Minimum ^{222}Rn activity measured in regional groundwater	(Bq L^{-1})
C^{gw}	^{222}Rn activity of groundwater	(Bq L^{-1})
C^{i-1}	^{222}Rn activity upstream of a distance interval, i	(Bq L^{-1})
C_R^i	^{222}Rn activity downstream of a distance interval, i, due to radioactive decay losses	(Bq L^{-1})
C_T^i	^{222}Rn activity downstream of a distance interval, i, due to turbulent losses	(Bq L^{-1})
$C_{\min}^{i}$	Minimum ^{222}Rn activity of groundwater input to streamflow	(Bq L^{-1})
C^j	^{222}Rn activity of stream water lost to the adjacent aquifer	(Bq L^{-1})
c_m	^{222}Rn activity within aquifer matrix	(Bq L^{-1})
C_m	Cl^- concentration of mixed pore water and deionised water	(mg L^{-1})
C_{pw}	Cl^- concentration of pore water	(mg L^{-1})
C^n	^{222}Rn activity downstream	(Bq L^{-1})
C_R^n	^{222}Rn activity downstream due to radioactive decay	(Bq L^{-1})
C_T^n	^{222}Rn activity downstream	(Bq L^{-1})
C_{TR}^n	Predicted ^{222}Rn activity downstream after turbulent and radioactive losses	(Bq L^{-1})
C^{222}	The ^{222}Rn concentration in a closed system	(Bq L^{-1})
C^{226}	^{222}Rn concentration produced by the radioactive decay of ^{226}Ra	(Bq L^{-1})
D	Molecular diffusivity of ^{222}Rn	(at 23°C 1.2×10^{-9} m^2 s^{-1})

E	^{222}Rn emanation rate	(Bq kg^{-1})
ε	Porosity	(cm^{3} cm^{-3})
f	Fraction of surface water lost to the adjacent aquifer	
f_{aq}	Porosity of aquifer material (expressed as a fraction)	
f^{0}	Fraction of surface water lost to the adjacent aquifer that originates from Q^{0}	
$1-f^{0}$	Fraction of surface water lost to the adjacent aquifer that originates from Q^{gw}	
h	Average depth of stream	(m)
h_{eq}	Equivalent freshwater head	(m)
h_{m}	Measured head	(m)
i	Interval number, integer fraction of n	
L_{n}^{0}	^{222}Rn loss from stream water between consecutive surface water sampling stations (i.e. between *0* and *n*)	(Bq L^{-1})
L_{n}^{gw}	^{222}Rn loss from groundwater that contributes to stream flow between consecutive surface water sampling stations (i.e. between *0* and *n*)	(Bq L^{-1})
L_{j}^{0}	^{222}Rn loss from stream water before it discharges to the adjacent aquifer	(Bq L^{-1})
L_{j}^{gw}	^{222}Rn loss from groundwater that contributes to stream flow and later recharges the adjacent aquifer	(Bq L^{-1})
λ	^{222}Rn decay constant	(2.098×10^{-5} s^{-1})
M_{cw}	Mass of wet soil and chipette	(g)
M_{cd}	Mass of dry soil and chipette	(g)
M_{c}	Mass of chipette	(g)
M_{d}	Mass of oven-dried soil	(g)
M_{dw}	Mass of deionised water	(g)
M_{pw}	Mass of pore water ($M_{pw} = \theta_{g} \times M_{w}$)	(g)
M_{w}	Mass of wet soil	(g)
n	Number of equal sections over a constant distance, x	
Q^{0}	Stream discharge at upstream sampling station	(m^{3} s^{-1})

Q^j	Stream water discharged (lost) to the adjacent aquifer	(m^3 s^{-1})
Q^n	Stream discharge at downstream sampling station	(m^3 s^{-1})
Q^{gw}	Groundwater discharged to stream flow	(m^3 s^{-1})
Q^{sw}	Stream discharge	(m^3 s^{-1})
Q^{gw}/Q^{sw}	Fraction of groundwater in stream water at downstream sampling station	
$^{222}R_{meas}$	^{222}Rn activity measured in groundwater	(Bq L^{-1})
ρ_b	Bulk density	(g cm^{-3})
ρ_{fw}	Density of freshwater	(1 kg m^{-3})
ρ_m	Density of measured groundwater	(kg m^{-3})
ρ_s	Particle density	(g cm^{-3})
θ_g	Gravimetric water content of soils	(g^{-1} g^{-1})
t	Travel time between consecutive sampling stations	(s)
T	Time of ^{222}Rn ingrowth	(s)
TDS	Total dissolved solids	(mg L^{-1})
TDS_m	Total dissolved solids measured in groundwater	(kg m^{-3})
v	Velocity of stream water	(m s^{-1})
V	Volume of soil core	(cm^{-3})
V^{gw}	Volume of groundwater discharged to the stream channel	(L)
x	Distance between sampling stations	(m)
z	Thickness of stagnant film	(m)
$\%AGW_{\min}$	Minimum percentage of stream water sourced from alluvial groundwater	
$\%RGW_{\min}$	Minimum percentage of stream water sourced from regional groundwater	
$\%AGW_{\max}$	Maximum fraction of stream water sourced from alluvial groundwater	
$\%RGW_{\max}$	Maximum fraction of stream water sourced from regional groundwater	

ABSTRACT

Regions of surface water and groundwater exchange are major sites for the transfer and transformation of solutes and nutrients between stream and subsurface environments. Conventional stream and groundwater exchange investigations are limited by methodologies that require intensive field investigations and/or the set-up of expensive infrastructure. These difficulties are exacerbated where hydraulic gradients are very low and stream discharge highly variable. This thesis uses a suite of environmental tracers (Cl^-, ^{222}Rn, δ^2H & $\delta^{18}O$, $^{87}Sr/^{86}Sr$) to characterise the extent of stream and groundwater exchange between a sand bed stream and adjacent alluvial aquifer in a subtropical catchment (the Wollombi Brook) of eastern Australia. The aims were to identify sources and relative contributions of different sources of groundwater to stream discharge and specifically to improve the methodology of using ^{222}Rn to obtain quantitative estimate of groundwater fluxes.

The sensitivity of the ^{222}Rn technique for identifying groundwater discharge based on the ^{222}Rn concentration in stream water was improved via an iterative numerical approach to account for ^{222}Rn loss from stream water via turbulent gas exchange and radioactive decay. Optimal distances between stream sampling points for defining the magnitude of groundwater discharge to stream flow based on ^{222}Rn concentrations in stream water is a function of average stream velocity and water depth. The maximum allowable distance between sampling points for determining the magnitude of groundwater discharge to the Wollombi Brook was 2 km. This work showed that groundwater discharged to all reaches of the Wollombi Brook during baseflow and flood recession conditions. Alluvial groundwater contributed <30% of water to stream flow in the mid Wollombi Brook catchment.

Dilution of steady-state ^{222}Rn concentrations measured in transects from the stream to the alluvial sediments showed that significant surface water and groundwater exchange occurs even when gradients between surface water and groundwater are low. Lateral stream water influx to the adjacent alluvial aquifer was more extensive in the lowland areas of the Wollombi Catchment during low flow than flood recession conditions. Extensive stream water influx to the adjacent alluvial aquifer occurs contrary to the net direction of surface water and groundwater flux (as indicated by hydraulic gradients toward the stream channel). The rate of stream and groundwater exchange within the adjacent alluvial aquifer appears to be greatest during baseflow conditions. Fresh alluvial groundwater appeared to provide a buffer against higher salinity regional groundwater discharge to the alluvial aquifer in some reaches of the Wollombi Brook catchment. Pumping of the alluvial aquifer and diversions of surface water may jeopardise the water quality and volume of the alluvial aquifer and induce water flow from the regional aquifer toward the stream, potentially salinising the fresh alluvial aquifer and subsequently the stream.

The change in the Cl^- concentration and the variation in slope of the δ^2H-δ^{18}O line between consecutive stream sampling points could be used to differentiate between regional and alluvial groundwater discharge to stream flow. Incorporating this information with three-component end-member mixing using [Sr^{2+}] and ^{87}Sr/^{86}Sr showed that stream and alluvial groundwater exchange within the stream channel was highest in the lowland floodplains during low flow conditions. The least stream and alluvial groundwater exchange occurred in the low streambed gradient mid reaches of the Wollombi Brook regardless of stream stage. The greatest difference in the degree of stream and alluvial groundwater exchange between high and low stream stages occurred in the lowland floodplains of the Wollombi Brook.

DECLARATION OF ORIGINALITY

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by any other person except where due reference is made in the text.

Jodie Lee Pritchard
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PUBLICATIONS ASSOCIATED WITH THIS THESIS

JOURNAL PAPERS

Lamontagne S, Herczeg A L, Dighton J C, Jiwan J S, **Pritchard J L** (2005). Patterns in nitrogen concentration in the floodplain of a subtropical stream (Wollombi Brook, New South Wales). *Biogeochemistry*, **72(2)**: 169-190.

Pritchard J L, Herczeg A L (in prep). Dynamics of exchange of water between alluvial groundwater ↔ regional groundwater and surface water ↔ alluvial groundwater: Testing conceptual flow processes in near-stream subsurface. Journal of Hydrology.

Pritchard J L, Herczeg A L, Lamontagne S (in prep). Comparison of sources of water to stream flow during baseflow and flood recession. Hydrological Processes.

TECHNICAL REPORTS

Lamontagne S, Herczeg A, Dighton J C, **Pritchard J L**, Jiwan J S, Ullman W J (2003). Groundwater-surface water interactions between streams and alluvial aquifers: Results from the Wollombi Brook (NSW) study (Part II – Biogeochemical processes). CSIRO Land and Water, Technical Report 42/03, July 2003, pp. 64.

CONFERENCE PAPERS

Pritchard J, Herczeg A, Lamontagne S (2003). Comparison of environmental isotopes for tracing groundwater-surface water interactions in a sand-bed stream. Proceedings from the International Symposium on Isotope Hydrology and Integrated Water Resources Management, IAEA, May 19 - 23, Vienna, Austria: 153-154.

Pritchard J L, Herczeg A L (2003). Tracing sources of water to an alluvial aquifer using strontium isotopes and radon. Proceedings from the EGS - AGU - EUG Joint Assembly, April 7 - 11, Nice, France: 297.

Pritchard J, Herczeg A, Lamontagne S (2003). Tracing seasonal groundwater contributions to stream flow using a suite of environmental isotopes. Proceedings from the EGS - AGU - EUG Joint Assembly, April 7 - 11, Nice, France: 295.

Pritchard J, Herczeg A, Lamontagne S (2002). The use of environmental tracers for estimating the seasonal contributions of groundwater to streamflow. Proceedings from the International Conference on balancing the water budget, IAH, May 12 – 17, Darwin, NT, Australia. pp 6.

Pritchard J, Herczeg A, Lamontagne S (2001). Tracing exchange of water between streams and alluvial aquifers using environmental isotopes. Proceedings from the 7th Australasian conference on Isotopes in the Environment, 24 - 26 September 2001, Robertson, NSW, Australia: 37-38.

Lamontagne S, Herczeg A, Leaney F, Dighton J, **Pritchard J**, Ullman W, Jiwan J (2001). Nitrogen attenuation by stream riparian zones: Prospects for Australian landscapes. Proceedings of the 8th Murray-Darling Basin groundwater workshop 2001, 4 – 6 September 2001, Victor Harbour, SA, Australia.

Herczeg A, Lamontagne S, **Pritchard J**, Leaney F, Dighton J, Jiwan J, Smith P (2001). Groundwater – surface water interactions: testing conceptual models with environmental tracers. Proceedings of the 8th Murray-Darling Basin groundwater workshop 2001. 4 – 6 September 2001, Victor Harbour, SA, Australia.

Lamontagne S, Herczeg A, Conway C, **Pritchard J**, Leaney F, Dighton J, Jiwan J (2001). Exchange of water and nutrient transformations in a sub-tropical stream-alluvial aquifer system. 28th congress of the International Society for Limnology, 4-10 February 2001, Melbourne, Vic, Australia.

Pritchard J L, Lamontagne S, Herczeg A L (2001). Tracing exchange of water between streams and alluvial aquifers using stable isotopes of water. 28th congress of the International Society for Limnology, 4-10 February 2001, Melbourne, Vic, Australia.

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