Interaction of Surface Water and Groundwater in the Lower Peel Valley

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Honours Thesis

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Declaration

The research for this thesis was undertaken while a full-time student at the Research School of Earth Sciences at the Australian National University, Canberra. This thesis is submitted as part of the requirements for the degree of Bachelor of Science (Honours).

I, Carl Thomas Zimmermann, hereby declare that to the best of my knowledge, the results and interpretation incorporated in this thesis are my own, except where otherwise acknowledged in the text. This work has not been used as credit towards any other degree.

27th day of October, AD 2010

Abstract

Understanding the interaction of surface and groundwater in highly connected river reaches is vital to managing water resources. The Lower Peel River, a tributary of the Namoi River and an upper tributary of the Murray-Darling Basin system, is highly connected to an alluvial groundwater system. Irrigation water is extracted from both the river and the aquifer. Complementary use is made of hydrograph and hydraulic head analysis and chemical tracers, to understand the interaction between the river and the alluvial aquifer over different spatial and temporal scales. This work includes the first detailed study of the chemistry of the region's groundwater.

Analysis of river hydrographs over the same period as water samples were taken indicated that the river was gaining 10 ± 6.5 % due to baseflow between the gauges at Appleby (419073) and Somerton (419075), which are ~ 40 km apart. Over the same river reach, stable water isotopes indicated groundwater discharge increased river flow by 14.5 ± 6.5 %, giving confidence in the baseflow separation technique. Applying the same baseflow filter to a period of years indicates this river reach is variably gaining-losing, with an average gain due to groundwater discharge of ~ 4 %, with bank storage also likely to be important over this river reach.

Increases in riverine chloride concentration and bore hydrographs suggest that groundwater flow is parallel to the Peel River for several kilometres between Moore Creek and Attunga Creek, with recharge from the Peel near Moore Creek and discharge near Attunga Creek. Over this distance, substantial transpiration, though not evaporation, is found to occur.

The detailed understanding of the system, and the degree of confidence in the results, has only been possible through the complementary application of physical methods and chemical tracers, demonstrating the importance of uniting these approaches when investigating surface water/groundwater interaction. This work will improve management by giving decision-makers better understanding of how water extracted from the groundwater system affects river flow and by giving a better understanding of the causes of salinity in the area.

Acknowledgements

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Chapter 1. Introduction

General Introduction

Where surface and groundwater systems are connected, there exists the potential for significant interaction between the systems. This interaction has important implications not only for sustainable water extraction rates, but also for water quality. Despite this, connected surface and groundwater systems are largely managed as separate regimes in Australia (Kelly *et al.* 2007). This is partly because the interaction between surface water and groundwater has until recently been largely neglected (Winter *et al.* 1998, Kelly *et al.* 2007, Acworth 2009).

Approaches to the interaction of surface water and groundwater that use independent methods to verify findings are desirable, as they reduce uncertainties and lessen the chance of misinterpretation that exists when using only a single approach. Additionally, utilisation of different methods can allow investigation over a greater variety of spatial and timescales (Halford & Mayer 2000, Cook *et al.* 2003, Kalbus *et al.* 2006).

Baseflow recession curves, where groundwater discharge is calculated from stream hydrographs, have long held a central place in groundwater flux estimates (Freeze & Cherry 1979, Kalbus *et al.* 2006, NOW 2010d). The sparseness of gauges on many rivers limits the resolution of this approach. Additionally, inputs of water from other sources can result in surface inflows wrongly being attributed to groundwater discharge (Kalbus *et al.* 2006). Hydrograph separation is sometimes aided by use of chemical tracers to distinguish baseflow from rain event flow. Cey *et al.* (1998) for example, used electrical conductivity and ^{18}O to separate hydrographs of a small stream in Ontario, and then used the calculated baseflow as a quantitative estimate of groundwater discharge.

Darcy's Law flow calculations are also routinely used to determine groundwater discharge. The major difficulty in use of Darcy's Law calculations is poor constraints of hydraulic conductivity, with ranges of three orders of magnitude common for a single sediment type (Fetter 2001). Hannula *et al.* (2003) used groundwater flux calculated by baseflow recession combined with Darcy's Law to constrain aquifer properties for use in further calculations for different flow conditions.

Modern instrumental analysis has made such broad-ranging collection of chemical data relatively easy and routine (*e.g.* Meredith *et al.* 2009, Cartwright *et al.* 2010). Chloride

and bromide have been found to be generally conservative water tracers, with Cl/Br ratios providing an important means of elucidating halite precipitation/dissolution (which makes Cl a non-conservative tracer, if it occurs) (Cartwright *et al.* 2006, Cartwright *et al.* 2010). Herczeg *et al.* (1997) used a combined mass balance approach, in which chloride concentration data are combined with stable water isotope signatures to identify the relative importance of different water end-members to mixing in a karst aquifer in South Australia.

Other major ions in natural waters are reactive, so provide less clear tracers of groundwater movement. However, hydrochemical similarity between groundwater bodies or river and groundwater can be taken as evidence of a common source. Baskaran *et al.*(2009) used this approach to qualitatively assess groundwater/surface water interaction in the Border Rivers area of northern New South Wales.

Introduced tracers may be used in the same way. A salt such as calcium chloride, or a dye, may be introduced to a well, and its appearance in a connected stream then observed. The groundwater velocity and potentially, flux can be computed from this (Kalbus *et al.* 2006). Otz *et al.* (2003) used injected dye into rivers and a lake in Switzerland to demonstrate hydraulic connection with multiple aquifers and the timescale of that interaction.

The isotopic signature of the water itself is ideal as a tracer, since it is negligibly affected by chemical processes (Clark & Fritz 1997). Importantly, and unlike solutes, stable isotopes provide a tracer unaffected by transpiration (Turner *et al.* 1987, Clark & Fritz 1997). Using the differing stable water isotope signatures of groundwater and river water, Andersen *et al*. (2008) were able to demonstrate the loss of river water to a shallow groundwater system in Maule's Creek, in the Namoi Basin in northern New South Wales.

The ratio of two stable isotopes of strontium, $^{87/86}$Sr has been used as another tracer of groundwater mixing. Water that has passed through rock rich in ^{87}Rb, which partitions with K, will be enriched in the daughter isotope ^{87}Sr. The result is that water passing through different rock types will have different $^{87/86}$Sr ratios. This was used by Lyons *et al.* (1995) to trace mixing between two distinct groundwater bodies around Lake Tyrrell in Victoria. The same principle could be applied to mixing between river and groundwater.

A heat balance approach has successfully been applied to flux of water from or to a groundwater system. Rau *et al.* (2008) successfully applied this approach to quantitatively estimate the flux of groundwater to Maules Creek at Elfin Crossing in the Namoi Basin. Extraneous factors affecting the temperature in both the river and the groundwater can be difficult to control for (Blume *et al.* 2008). It also requires temperature monitoring at the

actual site of groundwater discharge, or recharge (Rau 2008), so this technique is most appropriate to areas where groundwater flux is known to be confined to a short river reach.

Age-based approaches

A number of approaches have been developed that focus on atmospherically derived tracers that have varied in concentration over time. Concentrations in groundwater recharged years, decades, or centuries ago will be different to those in modern surface water, or more recently recharged groundwater. These and other tracer-based methods of elucidating mixing of groundwater with surface water are often equally applicable to determining mixing of different groundwater bodies, so the following discussion includes some studies that have focussed on this rather than on groundwater/surface water interaction.

Chlorofluorocarbons are found in groundwater and surface water in proportion to the atmospheric concentrations at the time of recharge. These have been used as tracers of groundwater movement, but their phase-out under the Montreal Protocol has caused atmospheric levels to plateau and decline (Prinn *et al.* 2000). This means that CFCs are less useful for water recharged since about the early 1990s (Plummer *et al.* 2006).

Cook *et al.* (2003) used this approach, in conjunction with ^{222}Rn. ^{222}Rn is produced by decay of uranium-series elements and has a half-life of only 3.8 days and is quickly lost from water open to the atmosphere. Making combined use of ^{222}Rn and CFCs, Cook *et al.* (2003) modelled mixing between the Daly River in the Northern Territory to quantify groundwater discharge.

^{85}Kr, an isotope with a half-life of 10.76 years, has increased steadily in atmospheric concentration over the past decades, largely as a result of nuclear fuel reprocessing (Achkasov *et al.* 1991, Ekwurzel *et al.* 1994). This has previously been used to date groundwater (Ekwurzel *et al.* 1994) and can be used in a similar way to CFCs to trace groundwater/surface water interaction, or the mixing of groundwaters. Ekwurzel *et al.* (1994) made combined use of ^{85}Kr with CFCs to date groundwaters. From the agreement of ages based on the different tracers, they were able to conclude mixing of different groundwater bodies was negligible in their study area of the Delmarva Peninsula the eastern coast of the United States.

Sulfur hexafluoride, an inert gas that has increased almost linearly in atomspheric concentration since the mid-1970s, may similarly be used for dating groundwater recharge and mixing between older and younger water. SF_6 is also potentially useful for discriminating between groundwaters recharged too recently for CFCs to discriminate between them

(Gooddy *et al.* 2006). Goody *et al.* (2006) made use of CFCs in conjunction with SF_6 to elucidate mixing between bodies of water with different recharge ages in the chalk aquifer of southeast England.

Despite the broad array of techniques available for elucidating the interaction of surface and groundwater, there is scope for better complementary use of chemical tracers and physical methods. Particularly, relatively little of the existing literature concentrates on quantitative evaluation of the interaction of groundwater and surface water combined with an estimate of the uncertainty of this evaluation.

Lower Peel as a suitable study area

Both data availability and the likely nature of the system make the Lower Peel Valley (*i.e.* the section below Tamworth, introduced in detail in Chapter 2) a suitable area for the complementary use of physical measurements and chemical tracers. The Lower Peel River is in hydraulic connection to a shallow alluvial aquifer and has been noted previously as interacting with the alluvial groundwater system (CSIRO 2007, Ivković *et al.* 2009). The flow in this river-stretch is gauged at two gauging stations and approximately monthly hydraulic head measurements spanning the past decade have been made at a network of piezometers in the alluvial aquifer. The piezometers provide groundwater sampling points that are not only readily accessible, but are of high-quality construction, with a defined screened interval. Drillers' logs are also available for these bores, aiding in interpretation of the results.

In addition to the suitability of the Lower Peel Valley as an area for investigating the combined use of chemical tracers and physical hydrogeology, the area is of interest in its own right. The Lower Peel (*i.e.* between Tamworth and the River's confluence with the Namoi) has been classified as under medium hydrological stress, with water extraction moderately likely to be contributing to this (DLWC 1998). Salinity and nitrate concentrations are part of this environmental stress, with levels higher than in most other parts of the Namoi Basin (Nancarrow 1998). Additionally, as an important small upper-catchment area of the Murray-Darling Basin, understanding of the interaction of different parts of the hydrological system in this area and other similar ones is important in developing policies to improve the health of the Basin as a whole, such as the present draft Basin Plan (MDBA 2010b). Despite this, the Peel Valley's groundwater has not previously been the subject of a concerted hydrochemical investigation (Kelly *et al.* 2007). Most previous work undertaken interpreting of physical hydrological measurements has been a small and peripheral part of larger projects (Crapper *et*

al. 1999, Braaten & Gates 2002, Ivković 2006, CSIRO 2007). Previous publications, by the NSW Office of Water and antecedents, focusing explicitly on the Peel Valley's hydrogeology are lacking in detail (WCIC 1970, WRC 1986, NOW 2010d). The results of this study will yield better parameters for undertaking further modelling work and may have implications for management of water resources in the Valley.

In the present study, complimentary use will be made of hydrograph analysis, soluble natural chemical tracers and stable water isotopes. Some other chemical tracers were considered, but ultimately rejected for this study, as a well-developed sampling strategy would require more information on the area's hydrogeochemistry than was known prior to the present research. This is particularly true of the age-based tracer techniques. They may be useful tracers if a follow-up study is conducted to examine interaction of the bedrock aquifer.

Aims

In this thesis, complementary use will be made of stream and bore hydrographs and chemical tracers, both solutes and water isotopes, to quantitatively estimate the interaction of surface and groundwater in a section of the Lower Peel River. It is further aimed to advance the conceptual understanding of the hydrological regime in the region.

It is hoped that the understanding of the Lower Peel's hydrogeology may be used to inform modelling of the Namoi Basin's hydrology, including the models of the Centre for Integrated Catchment Management at the ANU's Fenner School.

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Thesis Overview

Following from this Introduction, the context of the study area is introduced in greater detail in the Background chapter. In Chapter 3, the sampling strategy and details of sampling and analytical procedures are outlined. Following from this, the results from the physical hydrogeological analyses are presented and discussed. In Chapter 5, the results of analyses of chemical tracers are presented and discussed in the context of the findings outlined in the previous chapter. The thesis concludes with a chapter of conclusions and recommendations for further work.

Chapter 2. Site Background

Peel Valley: Geomorphology

The Peel River catchment is approximately 4 700 km^2 in area, which is about10 percent of the Namoi River catchment area (Crean *et al.* 2000, CSIRO 2007, NOW 2010c).

The Peel River is typical in its hydrology of an upper catchment tributary stream to a major Australian river system. The upper reaches of many rivers are generally hydraulically connected to unconfined aquifers, as topographic constraints on the extent of the alluvium limit water flow to a relatively narrow and shallow band. In the middle-reaches, rivers flow out onto wide flood-plains with deep and wide alluvium and the water table drops below the level of the riverbed (Braaten & Gates 2003). The Peel, a major tributary of the Namoi River in northern New South Wales (Figure 2-1) shows this pattern as it flows out of its relatively narrow, confined valley into the broader floodplain environment of the Namoi River. The Peel River is hydraulically connected to its associated alluvial groundwater system (NOW 2010d). The Namoi river is a loosing river from above its confluence with the Peel, becoming disconnected in its lowest reaches around Wee Waa (Ivković 2006). Similar patterns are observed at smaller scale with some sub-catchments, including the catchment of the Mooki River, another tributary Namoi River, with a confluence approximately 40 km downstream of the Peel's confluence (see Figure 2-1) (Braaten & Gates 2003).

The study area is located downstream of Tamworth and upstream of Keepit Dam (Figure 2-1). The catchment is bounded to the north by the Moonbi Range, to the south by the Great Dividing Range and to the south-east by the Peel Range. Elevation falls from about 1 000 m along the Moonbi Range to 287 m at Carroll Gap, on the Peel River close to its confluence with the Namoi River (WCIC 1970, NOW 2010c). The Cockburn River flows into the Peel approximately 5 km upstream of Tamworth and Goonoo Goonoo Creek flows into the Peel in Tamworth (WCIC 1970, AUSLIG 2001). Tagaratta Creek, Moore Creek and Attunga Creek all flow (ephemerally) into the Peel in the area selected for the present study (Figure 2-1, Figure 2-7).

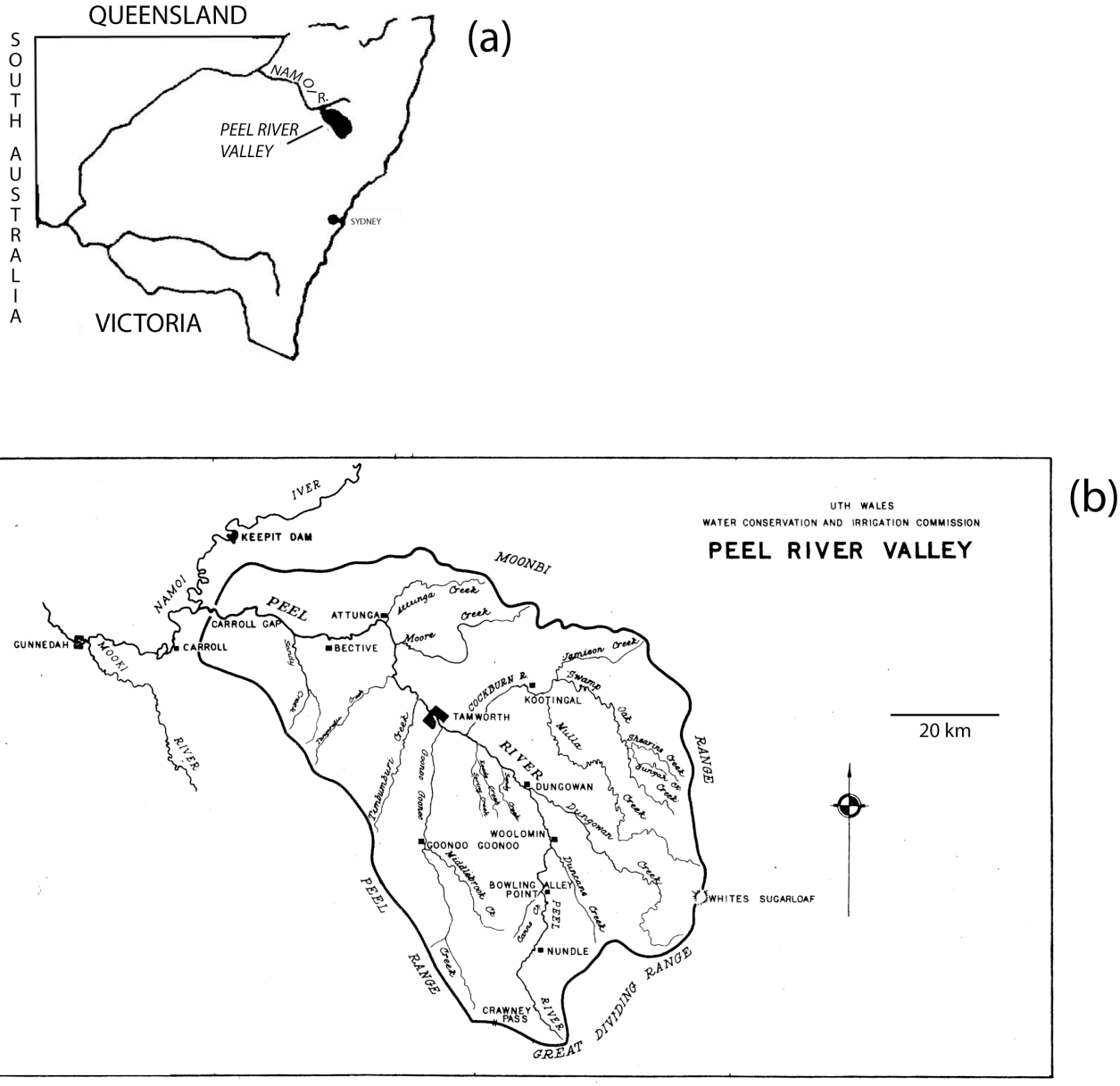

Figure 2-1 Figure (a) shows the location of the Peel Valley in New South Wales and (b) shows detail of the Peel Valley. Modified from WCIC, Figure 1 (1970)

Climate

Climate data are available for Tamworth Airport and for the Gunnedah Resource Centre (BOM 2010). Being both closer and upstream of the study area, the climate data from Tamworth are more pertinent to the project; however, evaporation data are only available from the Gunnedah site. Additionally, many of the rainfall samples discussed in this report (and the four samples actually analysed for this project) came from the Gunnedah site.

Mean rainfall for Tamworth is just over 660 mm per year based on the period 1878-2009 (data from Tamworth Airport and the superseding station Tamworth Airport AWS; weather stations 055054 and 055325, respectively). Precipitation is summer-dominated (December through February), as seen in Figure 2-2. Evaporation data from the closest available weather station, at Gunnedah, are presented in Figure 2-3.

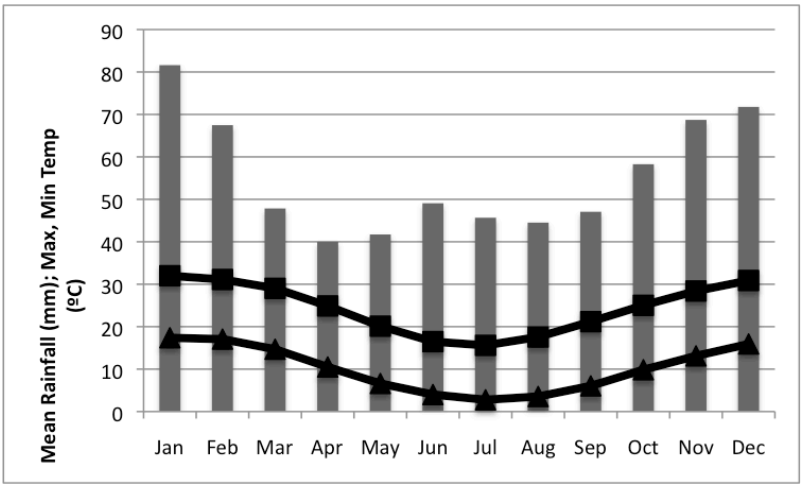

Figure 2-2 Mean monthly rainfall (columns) and mean maxima and minima temperatures (lines) at Tamworth Airport and Tamworth Airport AWS, Bureau of Meteorology sites 055054 and 055325. Temperature data are for the period 1907-2010 and rainfall data from 1876-2010 (BOM 2010).

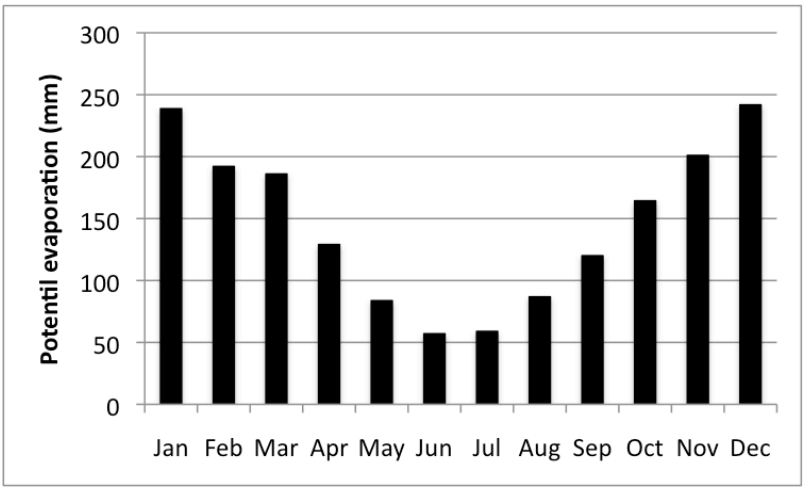

Figure 2-3 Potential evaporation at the Gunnedah Resource Centre, Bureau of Meteorology weather station 055024 for the complete dataset (1948-2010). Compiled from data from the Bureau of Meteorology (BOM 2010).

Flows in the Peel River at Carroll Gap and Tamworth rainfall correlate reasonably well, as can be seen in the residual mass plots of Peel River flow at Carroll Gap and Tamworth airport rainfall (Figure 2-4). Periods of missing streamflow record were replaced with flow records for dates with similar rainfall. 1941 was excluded from the rainfall chart as there was no rainfall data recorded for nine months of that year. The long-term trends in rainfall over the record period are broadly similar between Gunnedah, Tamworth, Narrabri and Walgett, although variation exists in the magnitude and duration of trends (Crapper *et al.*

1999). There is a marked wet period in the late 19th century and another between WWII and the mid-1950s. There were significant dry spells from *circa* WWI to WWII and from 1990 to the mid 2000s. These patterns are also mirrored in streamflow. Carroll Gap flow records also indicate that only 1 % of the time was no flow recorded in the river between 1923 and 2009. This indicates a significant capacity for groundwater discharge to maintain at least some flow in the river.

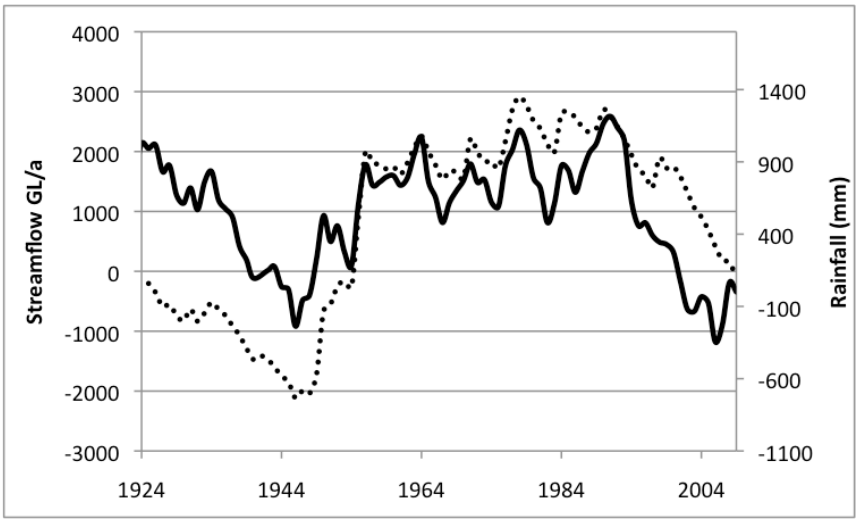

Figure 2-4 Carroll Gap flow (dotted line) and Tamworth Airport rainfall (solid line) residual mass plot. Flow data obtained from the NSW department Waterinfo. Rainfall data from the Bureau of Meteorology (BOM 2010).

Geological Context

The study area is located in the New England Fold Belt, the youngest of the Tasman Fold Belt systems (Scheibner 1996).

There is a major division of the Namoi Basin into Eastern and western parts, formed by the eastward-dipping Hunter-Mooki Thrust. The thrust, part of the Devonian-Carboniferous New England Fold Belt, runs NNW from the Great Dividing Range near Murrurundi in the South of the catchment to near Barraba in the Nandewar Range (1996, Ivković 2006, Kelly *et al.* 2007). The fault is near the junction of the Namoi and Peel Rivers (Land and Water 2000: 140). This part of the New England Fold Belt consists of an eroded mountain range, with bordering thrust fault systems on the south and west. The Fold Belt overthrusts the Gunnedah Basin to the west (Lavitt 1999). The central region of the Namoi Basin is Silurian to Permian, with deformation ranging from moderate in the west to high in the East (Kelly *et al.* 2007: 2; Zhang *et al.* 1999: 854). The thrust separates folded Upper Carboniferous-Lower Permian rocks of the north-east fold belt from the Permian and Triassic strata of the Gunnedah basin. These are largely overlain by Cainozoic alluvium (Ivković

2006). To the east of the thrust, uplift occurred approximately 5 million years ago (Department of Water Resources 1992: 4).

The local sediments were described in detail by White and Cotton (1964). The stratigraphy of sediments outcropping in and near the present study area are outlined below.

The Baldwin Formation, one of the dominant formations of the upper-bedrock in the study area, is an argillite that consists of greywackes, conglomerates, breccias and argillites (White & Cotton 1964). The formation's greywackes consists of less than half a percent quartz, approximately 15-30 % feldspar, with the remainder consisting of "rock fragments" and "matrix" (Voisey 1969). Morris (1988) more helpfully describes the Baldwin formation greywackes as having typical andesitic composition. Approximately one fifth of the Baldwin formation is described as feldspars, 55-75 % "lithic", and <10 % quartz, with ~2 % clinopyroxene (Cawood 1991). The Baldwin Formation flanks the Peel River for much of its length in the present study area (White & Cotton 1964, Brown *et al.* 1990).

Unconformably overlying the Baldwin Formation is the Keepit Conglomerate (White & Cotton 1964). The Keepit Conglomerate consists of greywacke clasts, in places with slabs of Baldwin Formation argillite.

The Keepit Formation is conformably overlain by the Mandowa Mudstone (White & Cotton 1964), dated to middle Famennian (Late Devonian) based on ammonoids (Roberts & James 2010). The Mandowa Mudstone consists of "interbedded mudstones and fine-grained feldspathic arenite bands" and contains less silty material than the Baldwin Formation (White & Cotton 1964, Voisey 1969). Interbedded between mudstone laminae, feldspathic arenite laminae are present (White & Cotton 1964). The Mandowa Mudstone is ~600 m thick near Somerton (the westernmost end of the present study area), narrowing westwards to 60 m thick near Keepit dam (Voisey 1969). The Mandowa Mudstone crops out in the area between this study's two bore transects (White & Cotton 1964).

Within the Mandowa Mudstone, the fine-grained Kiah Limestone is sometimes present as lenses, 6-30 m above the top of the Keepit Conglomerate (White & Cotton 1964).

Analysis of Goonoo Goonoo mudstones was carried out by Morris (1988). Based on lithology and bedding, it has been suggested that Goonoo Goonoo mudstones are in fact part of the same unit as the Mandowa mudstone (Morris 1988). Both the volcanic clasts in the mudstone and the matrix material are dominated by plagioclase, with some clinopyroxene. Some calcite patches occur in the matrix.

The Mandowa Mudstone is overlain by the Tangaratta Formation, which consists largely of interbedded mudstone and arenite. This formation was first described by White and Cotton (1964) and outcrops in Tangaratta Creek, an ephemeral tributary of the Peel in the present study area upstream of the Peel4 sampling site.

The plagioclase and feldspars reported in at least the Baldwin Formation may weather in part to produce Na-smectites, consistent with the reported "cracking" natures of the clays of the alluvium (Hird 1979).

The mineralogical composition of the area's soils has not been determined, but there is some literature on their characteristics. The Soil Conservation Service of NSW (Amos 1979, Hird 1979) reported that the soils of the alluvial floodplain consisting of juvenile soil, with "red brown earths" at the fringes of the alluvium. The red brown earths are reported as usually having an accumulation of carbonates in the B horizon and were formed in part from the Mandowa Mudstones, Keepit Conglomerate and Baldwin Formations (Amos 1979, Hird 1979).

There is approximately NW-SE faulting in the area (Figure 2-5). The most significant faults are the Appleby and Attunga Faults. The Appleby Fault cuts across the Peel River slightly to the west of the downstream bore transect. The Attunga Fault runs parallel to this, just to the northeast of the westward bend in the river, cutting underneath the alluvium of Attunga Creek, near its confluence with the Peel (White & Cotton 1964, Brown *et al.* 1990).

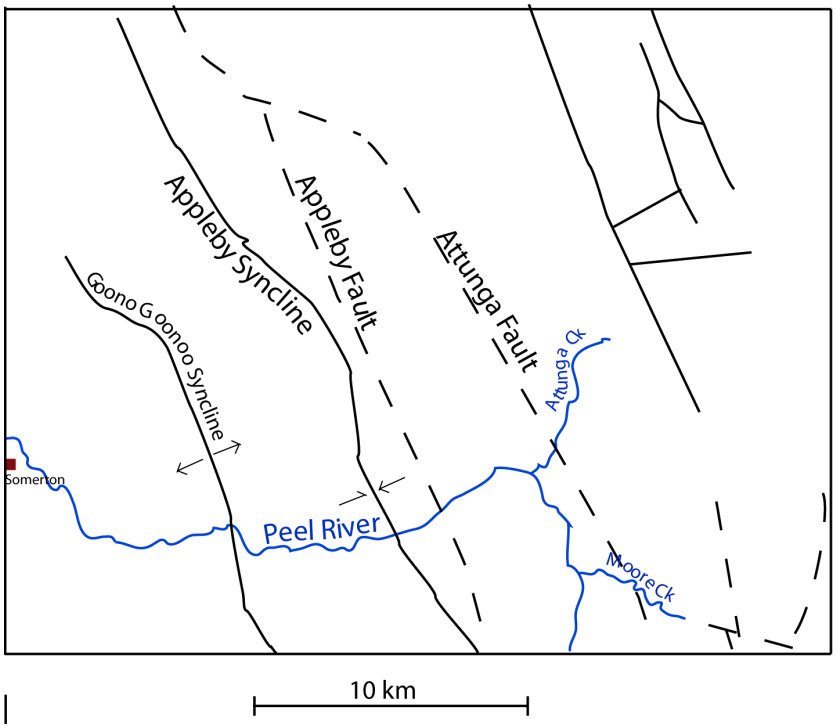

Figure 2-5 Map displaying major faults and synclines in the study area. Map derived from the Manilla geological map (Brown *et al.* 1990) and (White & Cotton 1964).

Hydrogeology

The Peel River valley's groundwater system has been relatively little-studied (Ivković 2006). The shallow river alluvium of the Peel and its main tributaries is the source of most groundwater in the region. Drillers' logs obtained from the NSW Office of Water in Gunnedah, from construction of piezometers, show that the alluvium is up to about 20 m in depth. It appears from these records to be thickest in the region of the bores sampled in this study, where the alluvium is also at its broadest (see Figure 2-6). At the lower end of the study area, the alluvium is only about 10 m thick. The alluvium's porosity has previously been quoted as 10 % (1989, Crean *et al.* 2000, Tomlinson & Boulton 2008). This porosity estimate is lower than that generally reported even for coarser sediments (Fetter 2001). This estimate of 10 % may more realistically correspond to "effective porosity" or specific yield than to porosity (*i.e.* water that may be extracted, rather than the total present). At an average thickness of 10 m, this gives extractable groundwater storage of 10 ML/ha. The hydraulic conductivity is estimated to be about 1-2 m/d (CSIRO 2007). This estimate of hydraulic conductivity is slightly over an order of magnitude lower than that of the upper (Narrabri) aquifer in the Namoi Basin (CSIRO 2007) and corresponds to the upper end of the range expected for fine sand (Fetter 2001). There is a high degree of connectivity between the river and the bores, which are generally located close to the river (Braaten & Gates 2003). The groundwater in the alluvium of the Peel's tributaries is noted to be quickly depleted during periods of extended drought, highlighting the high degree and short timescale of river-groundwater connection in this region (WCIC 1970).

The alluvium (Figure 2-6) consists of Carboniferous metasediments and extends in a relatively narrow channel associated with the river and covers an area of ~200 km^2 (NWC 2005, CSIRO 2007). The alluvium is deposited in a steep valley, in direct hydraulic connection with the river (CSIRO 2007). The following figure illustrates the extent of the alluvium in the Peel Valley and the extent of fractured bedrock in the region, from which groundwater is also extracted (CSIRO 2007, NOW 2009b).

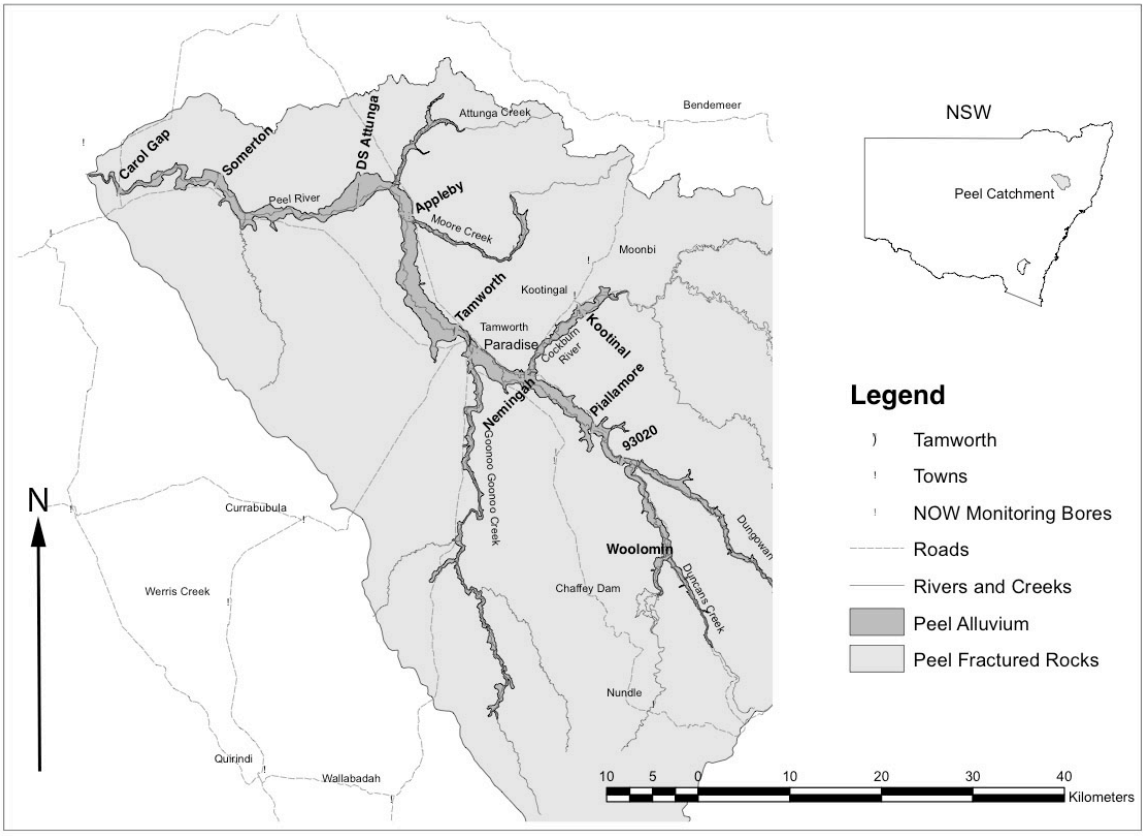

Figure 2-6 Alluvium of the Peel River and its tributaries. Modified after OOW (NOW 2009a)

Rainfall recharge is estimated by the CSIRO (2007) to be 145 mm per year or 29 GL/a, about double present extraction rates.

Drillers' logs from the construction of departmental monitoring bores (obtained from the NSW Office of Water, Gunnedah), indicate that underneath a layer of clay topsoil, the alluvium is patchily formed from sands and gravels with clay lenses; mixtures of these sediment types are also common. The bedrock is generally described as "slate". This "slate" is probably the "Noumea beds" unit mapped around this section of the Peel River on the 1990 Manilla 1:250 000 map (Brown *et al.* 1990).

Study Area

The Study area, depicted in Figure 2-7 below, is located north of Tamworth, encompassing a bend in the Peel River where the predominant direction changes from north to west. The most upstream sampling point was just upstream of the confluence of Tangaratta Creek with the Peel River, while the most downstream sample was taken from the Peel River at Somerton Bridge. The minor tributaries shown on the map are quite ephemeral, and were not flowing at the time of sampling.

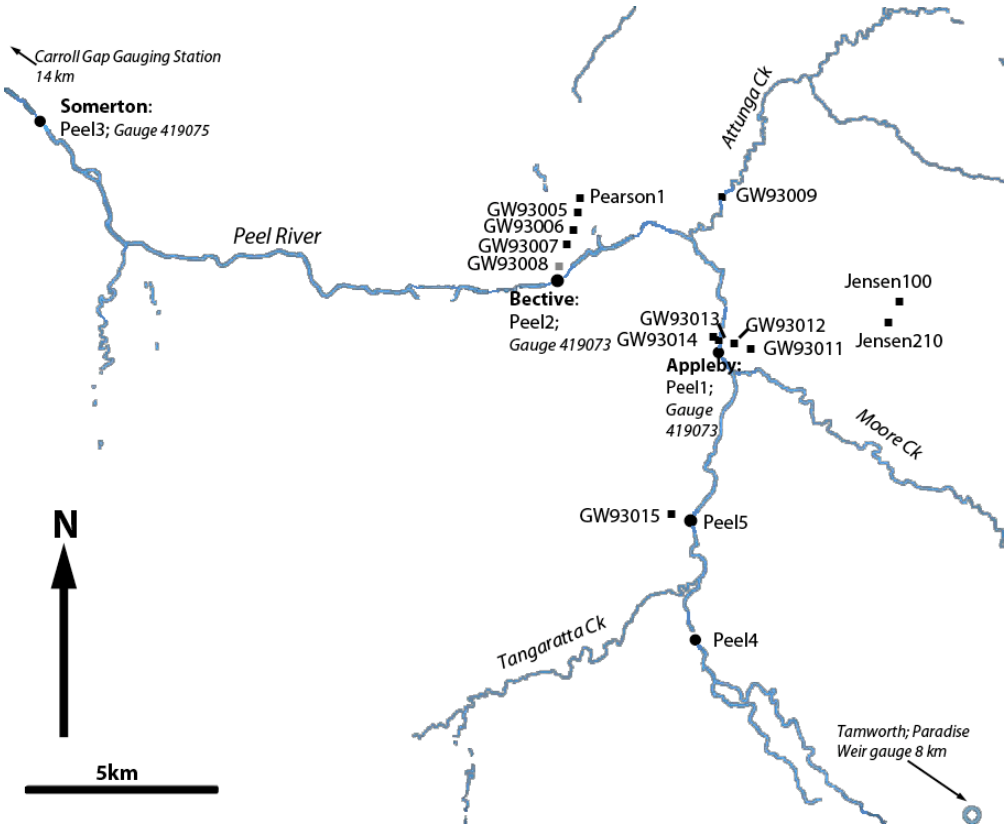

Figure 2-7 Map of sampling sites in the Lower Peel Valley. Bores are marked as squares and river samples (Peel1 to Peel5) as circles.

The local topography is dominated by hills to the east, and a shallow river valley. The valley floor falls from ~ 350 m near Moore Creek to ~ 310 m near Somerton. The eastern hills in Figure 2-8 are up to 500 m in height on th edge of the map, but rise to over 900 m about 5 km further east.

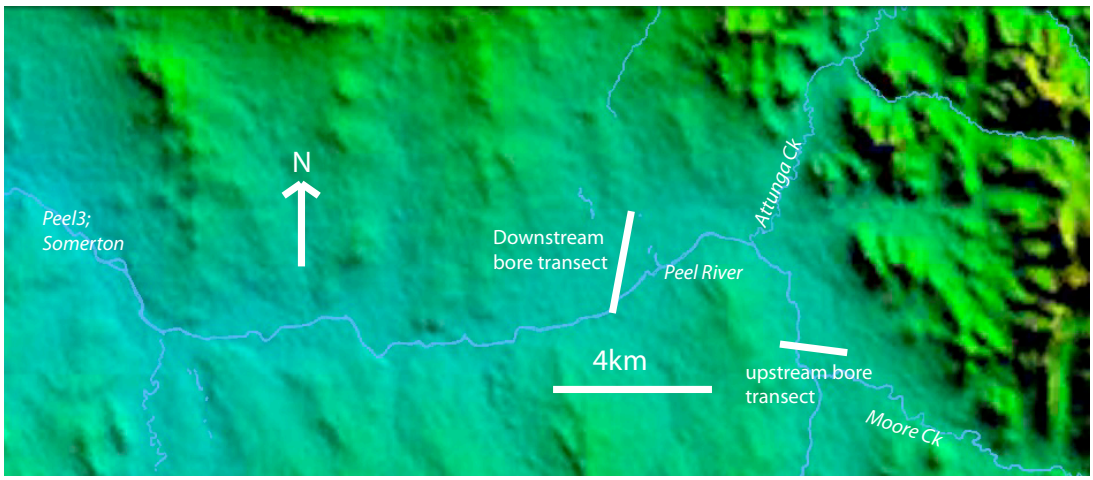

Figure 2-8 Local topography generated using Global Mapper (Global Mapper 2010) using data from the shuttle RADAR topography mission (USGS 2010).

Water use and Regulation

Irrigation in the Peel Valley is primarily of the alluvial soil adjacent to the Peel River and tributaries, with water sourced from both the river and the alluvial aquifer (NOW 2010d). Irrigation has increased markedly since the Second World War. In 1944, the Peel Valley contained just over 7 km^2 of irrigated farmland. This had increased to 15.5 km^2 by mid-1963 and 66 km^2 by the late 1990s (WCIC 1970, NOW 2009a).

Irrigation is primarily of pasture, with some irrigation of fodder and other crops. 48% of the Peel catchment's total irrigated land (6 640 ha) is in the Lower Peel, 36% in the Upper Peel, 10% in the Cockburn River, 5% in Goonoo Goonoo Ck and 1% at Chaffey Dam (NOW 2010d).

Extraction from the Peel River (called the "Peel Regulated River" in the Water Sharing Plan (WSP 2010)) averaged 16.2 GL/a over the period 1991-98, of which 7.6 GL was for irrigation and the remainder for town water supply (mainly Tamworth). Extraction from the alluvium averaged a little under 9.3 GL/a between 1997 and 2004 (WSP 2010). Extraction from the bedrock aquifer was 16.3 GL in 2004-05 (MDBC 2007). These figures compare with total surface water diversions for the Namoi Basin as a whole of 13 700 GL/a (MDBA 2010a).

In 1998, the Lower Peel river was classified as being under medium hydrological stress and this may be contributing to the high level of environmental stress in the area (DLWC 1998). Water use from the alluvial aquifer and the river is not allowed to increase from these values under the Water Sharing Plan (2010). Extraction from the fractured bedrock of the Peel Valley is capped at just over 71 Gl/a. Climate change modelling under three scenarios for 2030 (dry, medium and wet) suggested rainfall recharge in the Peel alluvial and bedrock aquifers would be little changed (within 5 % of present averages) except for the wet scenario, where recharge was predicted to increase by about a third (CSIRO 2007).

Modelling by the CSIRO (2007) indicates that present groundwater extraction from the alluvium results in approximately 6 GL/a of water loss from the Peel River, if the system is at equilibrium. The same report also states that the Peel River is a gaining river in its highland reaches and is losing in its lower reaches *i.e.* in this study area.

Most of the irrigation in the Peel is using spray irrigation systems. There is a small amount of flood irrigation, and there has been a recent uptake of subsurface drip irrigation systems. Water usage varies markedly with climatic fluctuations, with irrigators using from between 8 to 67 % of their allocated yearly entitlements between 1987-88 to 1998-99 (Baillie

et al. 2008). The main crop in the Peel Valley is lucerne (NOW 2010d). Lucerne accounts for the majority of irrigated crop area in the Valley. Other irrigated land includes (in descending order of irrigated area) pasture, oats, forage sorghum, summer cereal and wheat (Baillie *et al.* 2008).

Bedrock Aquifer

The aquifers in the bedrock of the Peel Valley, referred to as the "Peel fractured bedrock aquifer", is composed of sedimentary rocks, is calculated ultimately to receive approximately 32 % of its recharge from surface water flows, with the remainder derived from rainfall (CSIRO 2007). The NSW Office of Water suggests, conversely, that all recharge of the bedrock aquifer is from rainfall (NOW 2010d) The equilibration time, for changes to the system such as extraction or climate change, is longer than for the alluvial aquifer and estimated to be 10-50 years. Rainfall recharge is much higher than extraction (CSIRO 2007). The NNW-SSE faulting in the region (White & Cotton 1964) suggests that water flow within the bedrock may be along this line; if so, probably following topography SSE. The author has been unable to find any reports of the connectivity of the bedrock aquifers.

Chapter 3. Methods

Introduction

In this chapter, the sample collection strategy, including sampling locations, is presented, followed by the details of data collection and analytical methods are presented.

Sample Collection Strategy

The study area was selected for this study because of the co-location of a high density of NSW Office of Water piezometers with two streamgauges. This allows for the complementary use of streamflow data, chemical tracers and historical hydraulic head measurements from the piezometers. The selected bores include two lines of bores perpendicular to the river, referred to in this thesis as the upstream transect and downstream transect. These are depicted in Figure 3-1 and in small-scale maps in Figure 3-2.

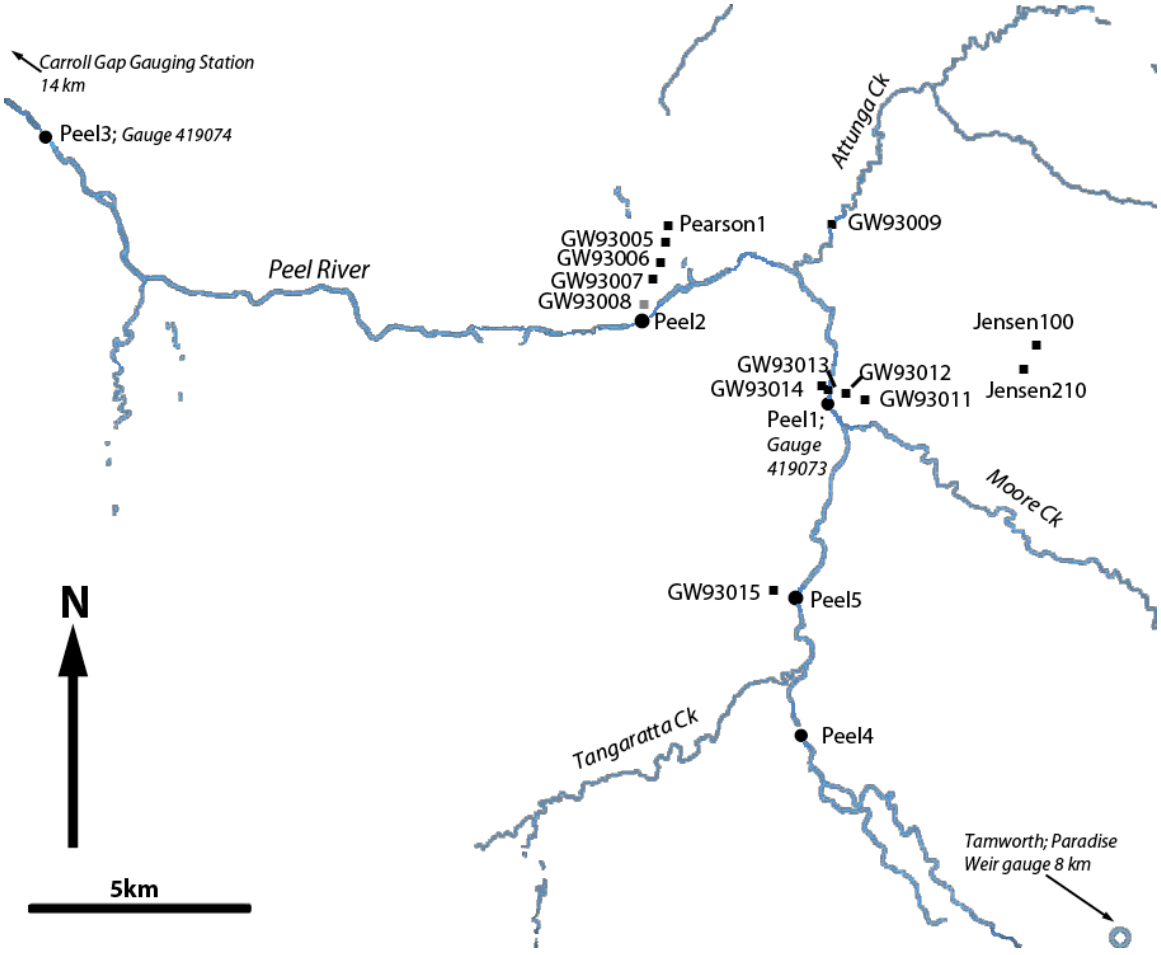

Figure 3-1 Sample collection points and streamgauges in the study area.

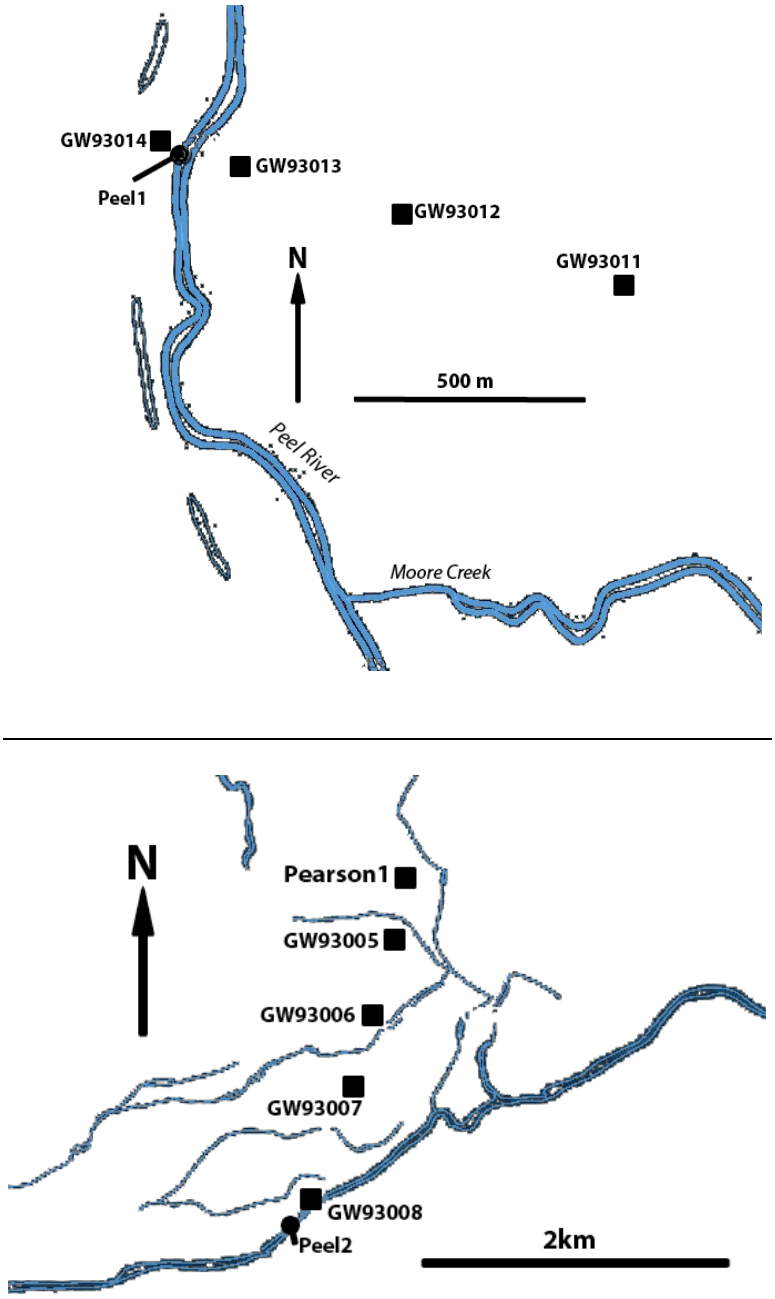

Figure 3-2 Enlarged sections of map showing the two bore transects, with river samples labelled as circles. The upper figure is of the upstream bore transect, and the lower figure is of the downstream transect. The tributary shown on the upper map is Moore Creek. The rivulets shown on the lower figure only carry water during periods of high rainfall. River overlays heavily modified after images obtained from Google Earth, September 2010.

The alluvium of Attunga Creek, an ephemeral creek that joins the Peel River between the two bore transects, was sampled by bore GW93009. It was planned to similarly sample groundwater from the alluvium Moore Creek, another ephemeral tributary, but the bore (GW93034) was dry.

The narrow band of alluvium on the south-western side of the river has very few monitoring bores installed. The upstream bore transect includes one bore on this side of the river, and one other sample was obtained on this side of the river, further upstream (GW93015). Two more private bores provided samples from the bedrock aquifer, in shale and limestone, as samples of a possible endmember for alluvial groundwater recharge.

River samples were collected near both the above bore transects. Additionally, a river sample was taken near Somerton Bridge (sample Peel3), the location of gauge 419075. Another river sample, Peel5 was collected near the most upstream bore sampled (GW93015), and a final sample (Peel5) was collected upstream of this, to provide a river sample upstream of all the bores sampled.

Later analysis of the hourly streamflow records showed that flow conditions had varied markedly between the collection of some of the river samples. Peel1, Peel2 and Peel3, however, were collected under very similar flow conditions. Peel1 and Peel2 are especially comparable, as flow at the time of each sample was taken deviate by less than 1 %. Additionally, samples Peel1 and Peel2 provide ideal endpoints for comparison of chemical and physical data, since the river is gauged very near these two sampling points (there are some problems with data reliability at the gauge near sample Peel3). It is therefore these three river samples that will be used for the calculations in this report.

Samples Peel4 and Peel5 were taken during a period when river flow was approximately twice that of when the other three samples were collected. Additionally, flow rates were somewhat variable at this time, making comparison of these samples with the others highly problematic and comparison of these two samples with each other somewhat difficult. Additionally there may have been small flows of water into the Peel River from Tangaratta Creek, an ephemeral tributary of the Peel with a confluence between the sampling points Peel4 and Peel5.

Sampling Procedure

Bore Sampling procedure

At each bore, the depth to water from the bore casing and the casing height were recorded, and a photo taken. A GPS reading was also recorded.

Where feasible, a flow-cell containing the probes listed above was connected to the pump outflow, and readings recorded approximately every 15 minutes. Bores were pumped

until the probes indicated constant chemistry, at least five bore volumes for bores pumped at a high flow-rate. It was necessary to bail one bore (GW93015), as the standing water column was too short for either pump. This was bailed for seven bore volumes prior to sampling. The three farmers' bores sampled were purged using the farmers' pumps, for a minimum of 6 bore volumes (and all had been recently used). One bore was sampled using a low-flow pump (150 mL/min), but this required considerable purging time until constant chemistry readings were obtained. All other bores were sampled with a high capacity pump (*c.* 10 L/min).

River Sampling Procedure

River samples were collected in a polyethylene bottle attached to a two-metre pole, upstream of bridge piers, pumps, and any other visible obstructions.

Logistical limitations meant the river samples could not all be collected on the same day. Analysis of streamflow at the two gauging stations in the area (upstream gauge 419073 and downstream gauge 419074) was used to check if flow conditions had changed between collection of the different river samples. As discussed in the Introduction, samples Peel1, Peel2 and Peel3 are considered to have been taken under comparable flow conditions; analyses from the other river samples is not as useful to this project.

Filtration

Sample water was collected in a plastic bucket thrice rinsed with the river or bore water.

All samples were filtered with 0.45µm filters with positive pressure. Most of the bore samples were filtered using cellulose nitrate filters (Whatman), which were handled with clean nitrile gloves. The most turbid samples were filtered through disposable high-capacity 0.45 µm filters (Waterra).

Table 3-1, were rinsed twice with filtered sample water prior to completely filling (no headspace). Samples for cation analysis were preserved with approximately 2mL of 50% nitric acid (~0.1M samples).

Table 3-1 Sampling Bottles.

Parameter	Bottle type
Cations	125 mL HDPE
Anions	125 mL HDPE
Halides	100 mL amber glass
$^{2}H/^{18}O$	2•50 mL HDPE
Reserve	1 L HDPE

All samples were placed in portable ice chests with frozen water containers to keep cool in the field. Subsequently samples were all kept refrigerated until analysis.

Quality Assurance

Two field blanks were taken to validate the collection procedure. This consisted of taking "samples" of ultra-pure water using the same sampling procedure as for river or bore samples (*i.e.* using the same containers, filtering procedure, bottles and acidification for the sample for cation analysis). In cases where one these "field blanks" were found to have a higher analyte concentration than the method detection limit, this concentration was taken instead to be the detection limit.

Additionally, duplicates of samples at two bores and one river collection site were taken. These samples were taken several minutes apart, so discrepancies very possibly reflect true differences in bore or river water. Reproducibility of ion concentration in these duplicates compared to the original samples has been used in estimation of combined analytical and methodological precision.

Field Analysis

All water samples were measured for the following parameters using Orion probes calibrated each day:

- Electrical conductivity (± 5 %)
- pH (± 0.05 units)

- dissolved oxygen (± 20 %, due to entrainment of air in the sample lines)
- reduction potential
- Temperature

Where possible, these probes were inserted into a flow cell connected to the outflow from the pump. Where this was not feasible, and with the river samples, the probes were placed in a thrice-rinsed polymethylpentene beaker of sample water.

Alkalinity was measured twice for each sample by titrating a filtered water sample with ~0.1M HCl (precise concentration known) using a digital titrator and methyl orange indicator (pH range 3.2-4.4 (Weast & Astle 1981)). The pipette, titrator and hydrochloric acid were all calibrated for volume and concentration. The method used here for alkalinity determination, although traditionally widely used, is not the most accurate method for alkalinity determination (Neal 1988, Marchetto *et al.* 1997). In addition to the problems associated with using a single endpoint (rather than extrapolating a potentiometric endpoint), the methyl orange endpoint is somewhat subtle. A mixed indicator helps to sharpen the endpoint, reducing the error. Ideally, automated potentiometric titration would be used instead (Cooper 1941, Neal 1988, Marchetto *et al.* 1997). HCO_3^- was later calculated using PHREEQC (Parkhurstand & Appelo 2010).

Iron(II) and sulfide were measured in the field using a spectrophotometer (Hach DR 2800) and filtered sample water.

Laboratory Analysis Methods

Major cations: ICP-AES

Filtered acidified samples were used for cation analysis. The purpose of this acidification is to prevent precipitation of dissolved cations from solution. Prior to analysis, samples were diluted by a factor of between 1 (*i.e.* no dilution) and 5 with 0.3 M (2 %) nitric acid. This dilution, based on electrical conductivity of the samples, was to prevent exceeding the method's upper detection limit for sodium of 100 ppm (4.5 mM). Detection limits are based on periodic runs of low-concentration standards. Precision figures are based on the sum of differences in reproducibility of standard solutions and reproducibility of field duplicates, except where otherwise stated in the results table. The field duplicates were taken after several more minutes of field pumping compared to the original samples, so differences may

represent actual heterogeneity in groundwater as well as field-based, non-systematic contamination. Note that detection limits quoted are for the diluted samples – to obtain the detection limit for the sample, it is necessary to multiply it by the dilution factor. Uncertainty figures for analyses are presented with the results in the Chemical Tracers chapter.

Major anions: ion chromatography

Fluoride, chloride, nitrate, phosphate and sulfate were analysed by ion chorography, using a Dionex Series 4500i ion chromatograph and 0.8M sodium carbonate/0.1M sodium hydrogen carbonate as eluent, with a conductivity probe as detector.

Phosphate was mostly below detection limits of 0.1 (1 μM). Prior to analysis, samples were diluted with ultra-pure water by between a factor of 1 (no dilution) and 5. This dilution was based on electrical conductivity measurements, with the aim of diluting sufficiently to not exceed the method's maximum detection limit for chloride of 200 mg/L (5.6 mM). Conservative detection limits were based on low-concentration standards (run approximately 6-monthly on the instrument). Analysis of the calibration standards indicated that response was linear and consistent for all analytes except phosphorous at low concentrations, so a higher detection limit was used for phosphorous. Precision was calculated as for ICP-AES samples (see above). Uncertainty figures for analyses are presented with the results in the Chemical Tracers chapter.

Trace elements: inductively coupled plasma mass spectrometry

Trace elements were measured using a Varian 820 ICP mass spectrometer. Detection limits were taken as 3 standard deviations of analytical blanks, except for analytes where higher concentrations were recorded in one of the two field blanks, in which case the field blank concentration was used.

Iodide: ion-specific electrode

Iodide analysis was attempted using an iodide-specific electrode (Orion Thermo 9653BN). The filtered water samples used for iodide analysis were stored in amber glass bottles with no headspace, kept refrigerated at 4ºC. The samples were analysed six weeks after collection. A calibration line was calculated using 76 μM and 0.76 mM iodide solutions (as KI) with

$NaNO_3$ solution added to bring the solution to solution to *c.* 0.1M $NaNO_3$. 50 mL samples were then analysed by similarly adjusting ionic strength of the solution, then using addition of 0.50 mL of 100ppm iodide solution.

The detection limit for such probes is quoted as being 10^{-6} to10^{-5} M, depending on the individual electrode (Kontoyannakos *et al.* 1976). Kuleshova *et al.* (2006) report a similar figure of *c.* $5•10^{-6}$ M, although the manufacturer is more optimistic, quoting a detection limit of $5•10^{-8}$ M (Thermo 2008). Only the four of the samples with highest chloride concentrations were analysed, since all but one of these were substantially below 10^{-7} M. At low concentrations of iodide, the linear relationship between log[I^-] and electrical potential, on which the analysis is based, breaks down; at very low concentrations, potential is almost constant with changes in concentration (Kontoyannakos *et al.* 1976). The calculated concentration of a 0.05ppm ($4.3•10^{-7}$ M) standard from the response of the electrode was 9% higher than its true value. This demonstrates that this deviation was occurring with the meter used, and in the direction expected.

Major Ions – NSW Office of Water data

A dataset of river water analysis at Paradise Weir, at the upstream end of Tamworth, was obtained from the NSW Office of Water. Data availability is described online (NOW 2010b) while the data are available by request from the Office. The dataset comprised 62 sets of analyses between 2002 and 2007. Analytes were: Ca^{2+}, HCO_3^-, Cl^-, Mg^{2+}, SO_4^{2-}, K^+, Na^+, PO_4^{3-}, B^{3+}, SiO_2 and CO_3^{2-}. Analytical details are unknown, but charge balance calculations imply a high degree of reliability.

Charge Balance

A charge balance was calculated for each of the samples using PHREEQC (Parkhurstand & Appelo 2010). The charge balance is defined as the sum of cation charges valences multiplied by concentrations divided by:

$\frac{\sum zM_c - \sum zM_a}{\sum zM_c + \sum zM_a}$, where z is the charge on the ion, M_c is the molarity of cations and M_a is the molarity of anions. The figure is expressed as a percentage and is a common way of analysing total analytical error (Freeze & Cherry 1979). Charge balance errors of up to 10 % are considered acceptable for natural waters (Timms & Acworth 2002, McLean 2003). A study

into analytical procedures for freshwater at a over 70 scientific laboratories for Ca, Mg, Na, NH_4, SO_4, Cl and NO_3 found that alkalinity measurements produced the greatest errors (Marchetto *et al.* 1997). Given that the alkalinity measurements were not ideal, as discussed above, it is reasonable to ascribe most of the charge balance error to alkalinity measurement here. Only two of the samples have a charge balance error of greater than 10 %. The generally positive charge balance error may be the result of systematically judging the alkalinity titration endpoint to be too soon, or dissolving cations from particles finer than the filter (0.45 μm) in the samples preserved with acid for cation analysis.

The charge balance for the data supplied by the NSW Office of Water varied between +6 % and -5 %, with a median value of 0.9 %. This implies that the data are of good accuracy and precision.

^{18}O and ^{2}H (external lab)

Deuterium and ^{2}H were analysed by GNS Science in New Zealand. Analysis was undertaken using a GVI Isoprime isotope ratio mass spectrometer. For ^{18}O analysis this was coupled with AquaPrep and for ^{2}H analysis this was coupled with PyrOH. Analyses are reported in delta notation relative to the standard VSMOW (see *e.g.* Clark & Fritz 1997). Precision for $\partial^{18}O$ is ± 0.1 ‰ and for $\partial^{2}H$, ± 1.0 ‰ (1 σ intervals based on duplicate analysis).

Chapter 4. Physical Hydrogeology

Foreword

As discussed in the Introduction, it is important to make use of multiple lines of evidence to understand the interaction of surface and groundwater. In this chapter, the results of application of different physical methods are presented and discussed.

Analysis of the difference in flow between two streamgauges in the Lower Peel provides a starting point for estimating the groundwater discharge in this river reach. Baseflow analysis at the two gauges provides an estimate of groundwater discharge over this reach that excludes surface flow, and is therefore preferred. To enable comparison between these results and the results of chemical tracer analysis in Chapter 5, the baseflow analysis is first performed for the same period as the collection of water samples. The same technique is extended to an examination of a decade's records, to estimate average and average seasonal groundwater discharge.

While streamflow analysis provides a useful way of understanding the net groundwater discharge over the reach between the gauges, it does not provide any information on the spatial variation in groundwater/surface water interaction. Bore hydrographs provide information on groundwater flow patterns along two bore transects in the deepest part of the Peel's alluvium. They additionally provide an indication of the recharge dynamics of the aquifer.

Stream Hydrographs

Context: River Variability and Regulation

The Peel River has a large range of flow rates, due in part to the absence of extensive control of river inflows. The river's flow characteristics can be seen Figure 4-1, a flow duration curve at Carroll Gap the first gauge upstream of Keepit Dam. This gauge is used due to the long record available. Periods of no-flow were recorded on 2% of days and have not been plotted on the chart due to the limitations of the logarithmic scale. The infrequency of no-flow periods suggests groundwater discharge maintains river flow most of the time.

The variability of flow rate (Figure 4-1) implies that the upstream Chaffey Dam, ~ 50 km upstream of Tamworth, does not have a large effect on the pattern of streamflow. Releases

from the dam are equivalent to 19 % of flows at Carroll Gap (in total, over the period 1972-2009). Extractions and transmission losses in the intervening river stretch mean that this figure of 19 % regulation is an extreme upper figure for the fraction of flow regulated in the Lower Peel, *i.e.* the downstream of Tamworth.

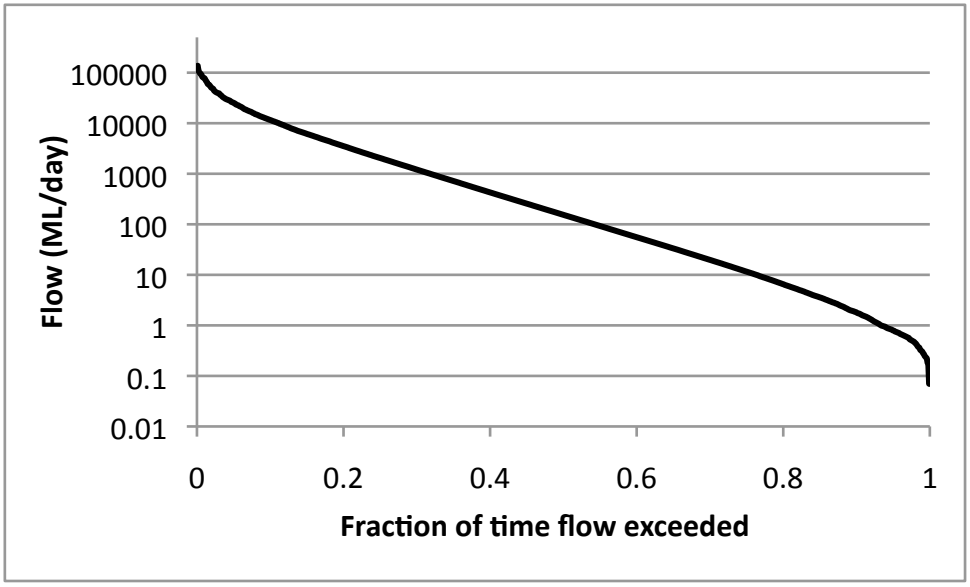

Figure 4-1 Flow Duration Curve for Carroll Gap, based on data obtained for 1923-2010 from the NSW Office of Water (NOW 2010a). The horizontal axis shows the fraction of days on which flow was greater than the figure on the vertical axis

Average discharges from Tamworth's two sewage treatment plants total 4 278 ML/a (Nancarrow 1998). This is equivalent to only 2 % of Chaffey Dam discharge (*cf.* NOW 2010a), but could significantly affect river water chemistry. The river is therefore only slightly regulated in the lower reaches.

Stream-Aquifer Interaction

Direct streamflow measurement

Interaction of surface and groundwater was first estimated by comparison of discharge records at three gauges. The two upstream gauges, Bective (gauge number 419073) and Appleby (419074) are located approximately 10 km apart, with the upstream gauge, Bective, located approximately 21 km downstream from Tamworth. The third gauge, at Somerton (419075) is a further ~20 km downstream of Appleby. Daily flow data for all three gauges and hourly flow data for the two upstream gauges were obtained from the NSW Office of Water (NOW 2010a). Hourly data was unavailable for Somerton (419075). Kazmann (1972) reports the errors associated with the ratings tables used to determine flow from these measurements have errors of less than 10 %, and with careful procedures less than 5 % in

alluvial rivers, in the absence of weirs. New rating tables were produced within days of sampling, so the lower error bound is deemed appropriate here. Water levels at the two gauges were almost a metre, and water level measurements are expected to have an error of no worse than ±10 mm (Mosley & McKerchar 1993), giving an error of less than 2 %. The sum of the independent errors at each gauge is thus taken to be: $\sqrt{0.05^2 + 0.02^2} = 5.4\%$

As the errors at each gauge are also presumed to be independent, the error for the difference between them is:

$$\sqrt{0.054^2 + 0.054^2} = 7.6\%$$

The primary concern here is the interaction of surface and groundwater at the time samples were taken, so that results are comparable with results from chemical tracers (the focus of the following chapter). Making an allowance, from the hourly flow data, of the time it took water to flow between the two upstream gauges:

Flow at 419073: 64.27 ML/d ± 5.4%

Flow at 419074: 78.75 ML/d ± 5.4 %

$$\sqrt{[0.054 \bullet 64.27]^2 + [0.054 \bullet 78.75]^2} = 5.49 \text{ ML/d,}$$

The error is taken as the sum of the squares of the errors at each gauge (*i.e.* assuming the errors to be independent)

Expressed as a fractional increase in flow, this is 22.5 ± 8.5 %.

As hourly data was not available for the downstream gauge, at Somerton (419075), it is not included here, as without this data, it is not possible to distinguish any change in flow between the gauges from variation in flow with time (mirrored at both points on the river).

Some of this increase in flow between the gauges was probably due to surface runoff, as there was some rain at the time of sampling: 19 mm was recorded at Tamworth over this period (BOM 2010). The surface runoff cannot be quantified, however the baseflow calculations in the next section overcome this problem. Nevertheless, it provides a useful maximum estimate of net groundwater discharge over this river reach.

Baseflow Calculations

While the total increase in flow between the gauges is a useful starting point for examining groundwater discharge, surface flow is likely a confounding factor in this instance. Baseflow

calculations avoid this issue. Basesflow fractions have traditionally been calculated graphically, but these are time-consuming to apply to long time-series (Chapman 1999). There are numerous numerical algorithms which are suitable for this purpose (*e.g.* Chapman 1999, Halford & Mayer 2000) and numerical approaches generally give similar results to traditional graphical approaches (Halford & Mayer 2000).

Since the nature of the baseflow in the Peel River is not well-known, and the groundwater system appears to be quite dynamic, a simple baseflow filter that does not rely on a detailed physical understanding of the system is employed. The filter employed here is that developed by Croke *et al.* (2001). This filter, called a minimum filter, takes a running minimum of width 2n+1 timesteps (here days) and then smooths this by taking a running mean of the running minimum, also of width 2n+1. A width of 5 (*i.e.* n = 2) is employed here as a starting point, as this filter width has previously been found suitable using this filter (Croke *et al.* 2001, Ivković 2006).

Automated baseflow recession techniques have met with some criticism (Halford & Mayer 2000), particularly in areas where bank storage, discharge from wetlands or unsaturated zone flow contribute to baseflow. Halford and Mayer (2000) cite a number of recent studies where the authors have wrongly attributed all of baseflow to groundwater discharge. In the present study, the combined use of chemical tracers (Chapter 5) helps to critically evaluate the performance of the automated filter used. There are small areas marked as wetlands on some maps covering the Lower Peel catchment, just below the downstream bore transect (Brown *et al.* 1990, AUSLIG 2001), but from field reconnaissance these are presently recognisable only by topographic lows and an abundance of trees, so are considered insignificant to surface runoff (and evaporation). Additionally, as the riverbanks are in the same hydrological unit as the groundwater system, they are likely to be continuous with the alluvial groundwater system, so can be considered part of the aquifer. Except where otherwise stated, "groundwater" is taken therefore to include bank storage within this document.

Baseflow Increase at sampling time

In order to compare results from baseflow calculation with chemical tracer analysis (Chapter 5), baseflow calculation at the time of sampling is of primary concern.

Using the filter described in the "Baseflow Calculations" section, with a filter width of five (days), the increase in baseflow between the two upstream gauges (Appleby and Bective, 419073 and 419074), was equivalent to 11.2 % of streamflow at the upper gauge; *i.e.* an

increase of 11.2 % between the gauges was attributable to baseflow. Baseflow volume at the most downstream gauge, Somerton (419075) was 2 % lower than at gauge 419074.

Sensitivity analysis was undertaken by comparing filter windows of widths 3 and 7 (the minimum increment wider and narrower) with the value calculated above. This resulted in baseflow increase of 14.5 % for the window width of 3 and 11.4 % for a window width of 7.

Given that time for water to flow between the two gauges is almost a day (see above), a window width of three (considering the days either side of the sampling day) is conceptually unlikely to exclude surface flow. The difference of less than 0.5 percentage points between the widths of 5 and 7 implies that a width of five is sufficient to separate surface runoff from baseflow, under the prevailing conditions in the area.

The error in this measurement is largely due to errors in flow measurement at each gauge. Measurement uncertainty is present for each gauge and therefore the baseflow calculated at each gauge (5.4 % at each, as in the above section). Additionally, the increase in baseflow was expressed relative to the total flow at the upstream gauge at the hour of sampling – flows in the hour before and after were only different by 1 %.

Adding in the < 1 % error associated with the baseflow filter, at each gauge, the error is estimated as:

$$\sqrt{0.054^2 + 0.01^2 + 0.01^2} = 5.6\%$$

The baseflow at Appleby (gauge 419073) was 47.4 ML/d ± 5.6 %

Baseflow at Bective (419074) was 58.1 ML/d ± 5.6 %

The difference between these is $10.7 \pm \sqrt{[0.056 \bullet 47.4]^2 + [0.056 \bullet 58.1]^2} = 4.2$ ML/d

Expressing this increase in baseflow as a fraction of total upstream flow, the increase is 11.2 ± 6.5 %.

The baseflow at Somerton was 56.8 ML/d ± 5.6 %

Similarly, this is a decrease in baseflow from Bective to Somerton of 2 ± 6.5 %. That is, there was approximately no change in baseflow over this river stretch at this time.

Over the whole river stretch between Appleby and Somerton, baseflow increase was 10 ±6.5 %.

The likelihood of bank storage being a significant contributing factor at this time is low, since river flow and height were higher at this time (28-29 May) than at any time in the preceding two months, as seen in Figure 4-2.

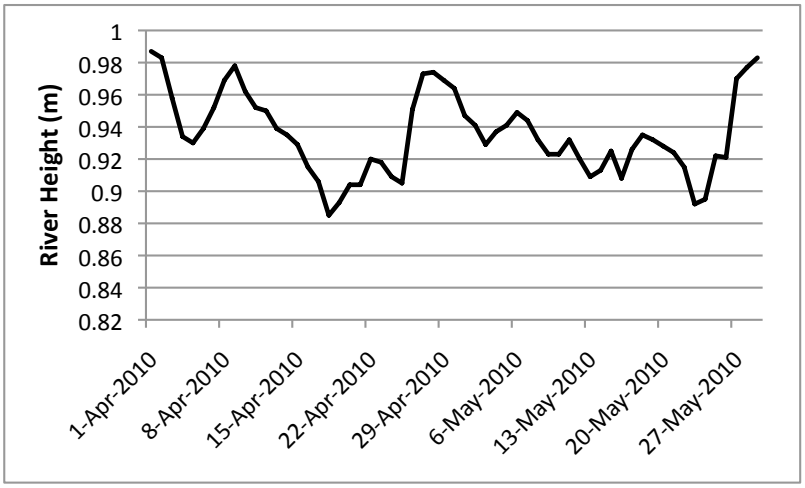

Figure 4-2 River height at streamgauge 419074. The last day shown on the graph, 29 May, is the day considered in the calculations in this chapter.

The increase in baseflow between the two upstream gauges, at Bective and Appleby, may be interpreted as the net increase in the river flow due to groundwater discharge (including bank storage) between the two gauges. This figure is substantially lower than the increase in total flow between the gauges, though within the combined error margins. This difference is attributed to runoff.

Baseflow Increase: long-term analysis

The period 1 August 1998 to 1 August 2010 was compared for both upstream gauges. Over the whole period, there was an increase of 3.9 % in the river between the gauges attributable to baseflow (calculated as above, but with a filter width of 7). Comparison was also made with the downstream gauge, 419075 at Somerton, but this indicated an almost doubling of total flow volumes relative to the two upstream gauges. In the absence of any major tributaries in the intervening river reach, this was considered highly implausible, and therefore the data were considered to be unreliable.

Sensitivity analysis was performed by widening the width of the baseflow filter. Using a window width of 7, baseflow was calculated to be 15 % lower than with a window of width 5. Increasing the filter width again (to 9) produced a figure only 7 % lower again. The result from the filter width of 7 is considered appropriate here, since further increase in the width produces an estimate of baseflow that is only slightly lower. The use of a wider filter than in

the above section is conceptually justifiable on the grounds that at lower flow velocities (lower flow rates) surface flow would take longer to pass through the system.

Over this same period of 1/8/1998 to 1/8/2010 and using the same filter, the total baseflow contribution at the upper gauge was 37±4 % and at the lower gauge 41±5 %, with errors only taking into account sensitivity analysis of the filters. By taking the aggregate of a long time-series, random measurement errors in each gauge should cancel, although systematic bias is plausible, particularly at low flow rates. Periods of very low flow are only a minor contributor to total baseflow, however. An indication of the distribution of flow is given by the fact that baseflow is responsible for more than half of total flow on 80±4 % of days at each gauge (based on a window of 7 and error calculated from sensitivity analysis of the window-width).

Additional errors are likely to be associated with flow during periods of low-flow. Ratings tables are unlikely to be accurate for low flows, due to small heterogeneities in the riverbed, resulting in potentially large errors. These could impact measurement reliability by causing the measured cross-section shape to differ substantially from the rating tables. Additionally, (ungauged) localised sub-surface flow may become significant during low-flow periods. These periods may introduce a systematic bias into low-flow periods. To a large extent, it is thought that during most periods ratings curve errors are likely to be random, and so to cancel by examining several years of data, as here.

Some preliminary hydrograph analysis has been done previously for the Peel River (as part of larger projects). Both Braaten and Gates (2002) and Ivković (2006) classified the lower Peel River as a losing river (*i.e.* one that is losing water to the groundwater system). The results of the present study indicate that this stretch of river would be more accurately described as variably gaining-losing, a classification used by Ivković (2006) for some other river-stretches, including the Mooki River (also in the Namoi Basin). On average, it seems that the reach of the Peel River between Appleby and Bective is gaining water from groundwater discharge.

Seasonality

The long-term patterns of baseflow can be further illuminated by examination of seasonal patterns. As seen in Figure 4-3, there is very little baseflow increase (groundwater discharge) between the streamgauges over the summer months. For comparison, seasonal rainfall is given in Figure 4-4. Groundwater extraction is not high enough to produce a consistent

seasonal drop in bore levels, as evidenced by a lack of seasonal trends in monitoring bore hydraulic heads. The lower baseflow contribution calculated for summer may be the result of river extractions to supply the summer-dominated irrigation in the area (NOW 2010d); unfortunately, seasonal extraction data are not available. If irrigation extractions from the river are approximately constant, extractions have the effect of cancelling baseflow in the baseflow filter, meaning that actual groundwater discharge is likely to be higher than estimated by this method in summer. Total increases in baseflow are gradually higher through autumn, winter and spring, positively correlated with streamflow; correrlation with Tamworth rainfall is less clear. This may suggest that a component of groundwater discharge is relatively short-term in nature, possibly due to bank storage.

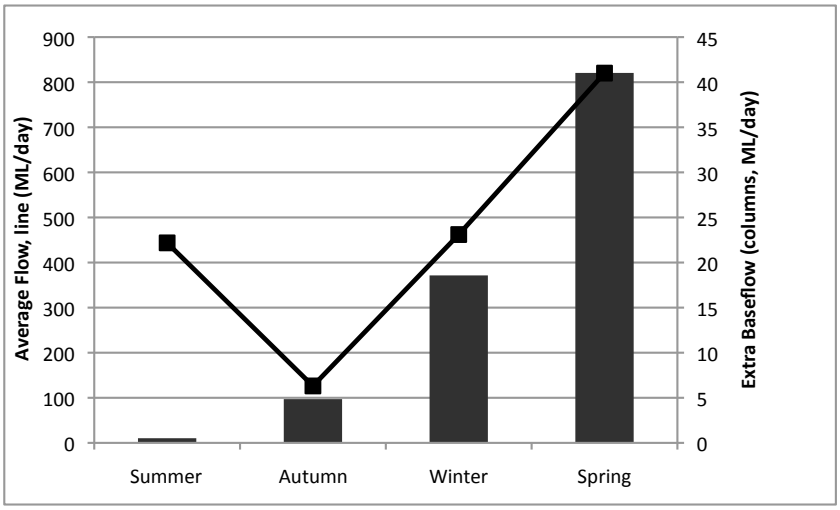

Figure 4-3 Increase in Baseflow between Streamgauges 419073 and 419074 over the period August 1998- August 2010 (columns). The points on the line represent average flow and the columns average increase in baseflow between streamgauges 419073 and 419074 (sites of samples Peel1 and Peel2, respectively).

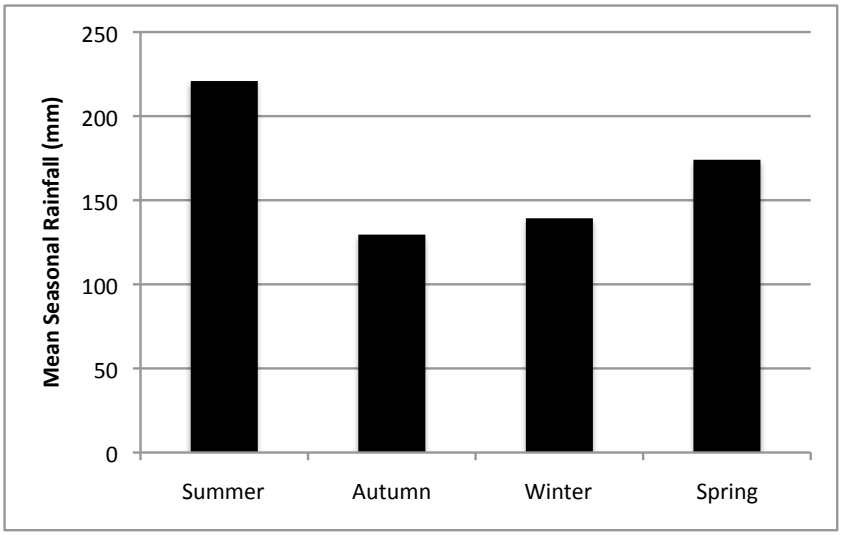

Figure 4-4 Mean seasonal rainfall at Tamworth Airport 1876-2009. Based on Bureau of Meteorology weather station 55054 and its replacement 55325 (BOM 2010)

Darcy's Law Calculations

Another physical method for investigating the interaction of surface and groundwater is based on application of Darcy's Law. The results are consistent with the other methods employed, although the error is large, demonstrating the need for an integrated approach.

The hydraulic conductivity of the sediment of the alluvial aquifer is estimated at 1.5 m/day (CSIRO 2007). The hydraulic gradient is taken as that between the two bores in the downstream transect closest to the river, approximately 1/500 (see Figure 4-6). The cross sectional area is estimated to be approximately 1 m (the depth of the river at the gauging stations) by the half the length of river between Bective Appleby, since some of this stretch is known to be losing, as discussed in the next section. The other side of the river is ignored, since the extent of the alluvium on the other side is much smaller, as seen in Chapter 2. This yields the following calculation

$$Q = KA\frac{dh}{dl} = 1.5m/d \bullet (1m \bullet 500m)\frac{1m}{500m} = 1.5 \bullet 10^{1}$$ ML/d, equivalent to an increase in river flow of ~22 % (Q = total discharge, K = hydraulic conductivity, A = cross-sectional area, h = hydraulic head, l = distance) .

This value is within a factor of two of that calculated using the baseflow increase (see above). Uncertainty in hydraulic conductivity in a single sediment type (*e.g.* gravel) is generally about 3 orders of magnitude (Fetter 2001), and the aquifer here is heterogeneous, so ± 100-fold is a reasonable uncertainty estimate. The uncertainty in the length of aquifer with a hydraulic gradient towards the river could be ±2-fold, as could the height of river bank below the water table. The simplified extrapolation of a single hydraulic gradient to the whole river could also easily be in error by a factor of 2, given the variability observed in hydraulic gradient. An uncertainty range of 3 orders of magnitude in each direction is therefore possible, *i.e.* 15 kL/d to 15 GL/d This range is so large that an upper bound in groundwater discharge would actually be 100 % of river flow, at the time of sampling 80 ML/d.

The agreement of this calculated groundwater discharge with other (much better-constrained) estimates implies that the average hydraulic conductivity may be within about one order of magnitude of the value used here, which is well constrained for hydraulic conductivity, as mentioned above.

Recent work has tended to use Darcy's Law calculations in conjunction with other constraints. Hannula *et al.* (2003) used groundwater flux calculated by baseflow recession combined with Darcy's Law to constrain aquifer properties for use in further calculations for

different flow conditions. Dawes *et al.* (2000) constrained hydraulic conductivity of an aquifer by comparing the behaviour of a model based on Darcy's Law to known long-term behaviour of the aquifers they were considering and a known water budget. The present example serves to illustrate the importance of such integrated approaches and the danger of using Darcy's Law on its own. If a more accurate river survey were available, the constraints imposed on hydraulic conductivity by the other methods for calculating groundwater discharge presented in this thesis may allow development of a Darcy's Law-based flow model of the region.

Bore Hydrographs

The above analyses of the interaction of surface and groundwater have provided insight into the phenomenon over a river stretch of ~ 10 kilometres. Analysis of bore hydrographs allows the interaction to be investigated on a much smaller spatial scale. The NSW Office of Water maintains a network of piezometers in the Peel's alluvium, in which hydraulic head has been measured approximately monthly over the past decade. These give an important indication of the direction of groundwater flow. Hydrographs for the two bore transects considered in this study are shown in Figure 4-5 and Figure 4-6 with both mean water level heights and water level heights at the time of sampling.

The survey heights obtained by differential GPS were provided by the Office of Water and are considered accurate to ± 1 cm. Height of the bore casings (against which the depth to water is measured) and the depth to water are each considered accurate to ± 0.5 cm. The total uncertainty is given by the root of the sum of the squares of these independent errors and is 1.2 cm.

The most immediate point to be made from the hydrograph is the direction of the hydraulic gradient – the upstream transect (Figure 4-5) shows a hydraulic gradient away from the river, but also a gradient from the far edge of the alluvium closer to the middle of the transect. It should be noted that the hydraulic gradient is unlikely to correspond exactly to the line of bores; it is probably at some angle to the transect. The exact river height at the time of sampling is not known, but the level of the bores very close to the river is considered a good proxy, as the river is almost certainly connected to the aquifer, given the shallow nature of the alluvial sediment.

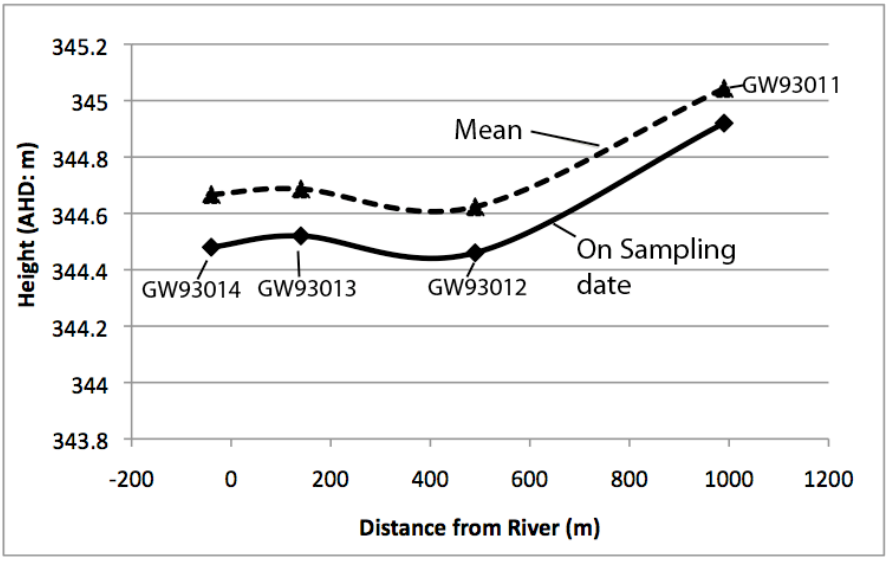

Figure 4-5: Hydraulic Head in the upstream bore transect: GW093014 (leftmost point), 93013, 93012, 93011. Note that the river level is considered to be similar to the hydraulic head in the leftmost-plotted bore above. Height error bars of ± $\sqrt{3}$ cm are within the symbols.

The hydraulic head measurements in the upstream transect (Figure 4-5) are interpreted as indicating recharge of the alluvium in this area both from the river and the edge of the alluvium, with groundwater following the topographic gradient parallel to the river, before flowing towards the river upstream of the confluence with Attunga Creek. Discharge is likely in this region as the topography of the alluvium again slopes towards the Peel River in this area.

The hydrograph of the downstream transect, Figure 4-6, appears to show a simpler pattern of flow towards the river, with the low hydraulic head in GW93005 explained by local topographic variation.

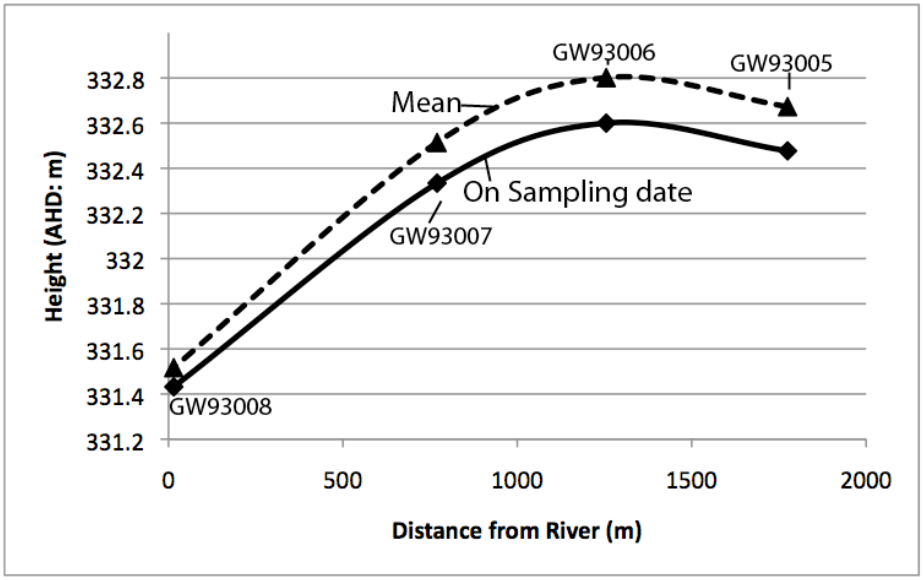

Figure 4-6 Hydraulic Head in the downstream bore transect: GW093008 (leftmost point above) to GW093005. The two lines represent mean head, compiled from 150 measurements between 2000 and 2010. The hydraulic head on the date water samples were taken is also shown (see next chapter for chemical analysis). Note that the river level is presumed to be similar to the bore closest to the river, the leftmost point above. Height error bars of ± $\sqrt{3}$ cm are within the symbols (derived from 1 cm errors each for surveyed height, casing height and water depth measured from the bore casing)

In fact, local topography and rivulets suggest that the pattern of groundwater flow may be slightly more complicated. The rivulets indicated in Figure 4-7 correrspond to depressions in the landscape and seldom receive flow, as evidenced by the lack of flow at the time of sampling, despite rainfall at that time. Groundwater flow may in fact follow the rivulets, rather than flow directly along the transect.

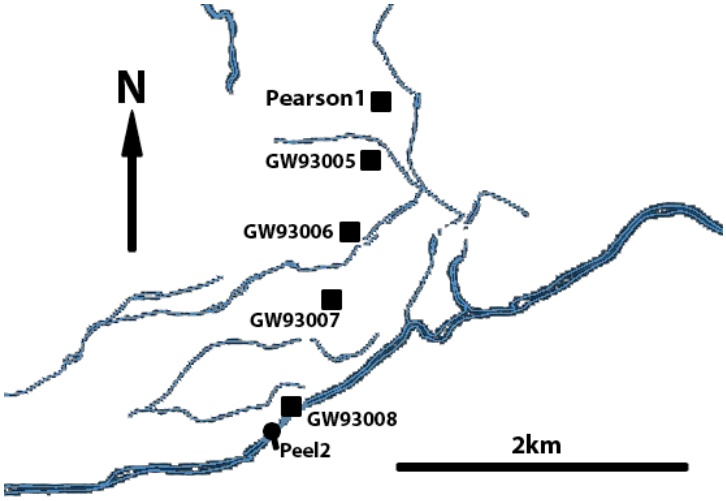

Figure 4-7 Locations of bores in the downstream transect, and location of river sample Peel2. Small lines indicate very ephemeral rivulets.

Long-term patterns

Hydrographs for the bores in the two main transects over the last decade are shown in Figure 4-8. For comparison, gauged river height at Appleby (gauge 419074) is shown together with a 90-day running mean of rainfall at Tamworth AWS.

The 10-year record of hydraulic head in most of the bores in the alluvium allows the behaviour of the groundwater system to be examined on a longer timescale, providing important evidence for the importance of flooding to recharging the alluvial aquifer.

At a broad-scale level, there is clearly a pattern of major recharge associated with very high river flow (flooding) (Figure 4-6). After flood events, bore levels decrease gradually over a period of years. In both transects, the bores closest to the river show greatest variation in hydraulic head, including in flood events. They also seem to show a faster rate of decrease

in hydraulic head following recharge. The fast rate of hydraulic head decline suggests that bank storage is significant here. To some extent, the decline in hydraulic head of these bores is probably also due to the generation of a groundwater "mound" (an area with high hydraulic head), which then disperses into the aquifer. This behaviour would be expected to be more gradual than discharge to the river. Higher frequency (preferably automated semi-continuous) monitoring would help to discriminate between these two possibilities.

From analysis of Appleby flow records, it appears there was significant flooding in July 1998, November 2000 and November 2008. The effects of the 1998 flooding are still apparent in the beginning of the records for the bores in the two bore transects, which start in June 2000. This influence is seen in the gradual decline in hydraulic head between ~2000 and 2004. A similar pattern is observed after flood recharge in early 2004 and late 2009.

In Figure 4-1 (a), the water level in GW093014, the closest bore in that transect to the river, exhibits much greater variation in water level than do the other bores in that transect. The bore closest to the river, GW93008, exhibits similar behaviour, though the effect is less dramatic. This is because the effects of recharge from the river decrease with distance from the river. When the river level drops, the water level in the bores adjacent to the river quickly drops. Greater temporal resolution of hydraulic head data would reasonably be expected to show more extreme variation and may help to distinguish between dissipation of the groundwater mound into the aquifer and back into the river.

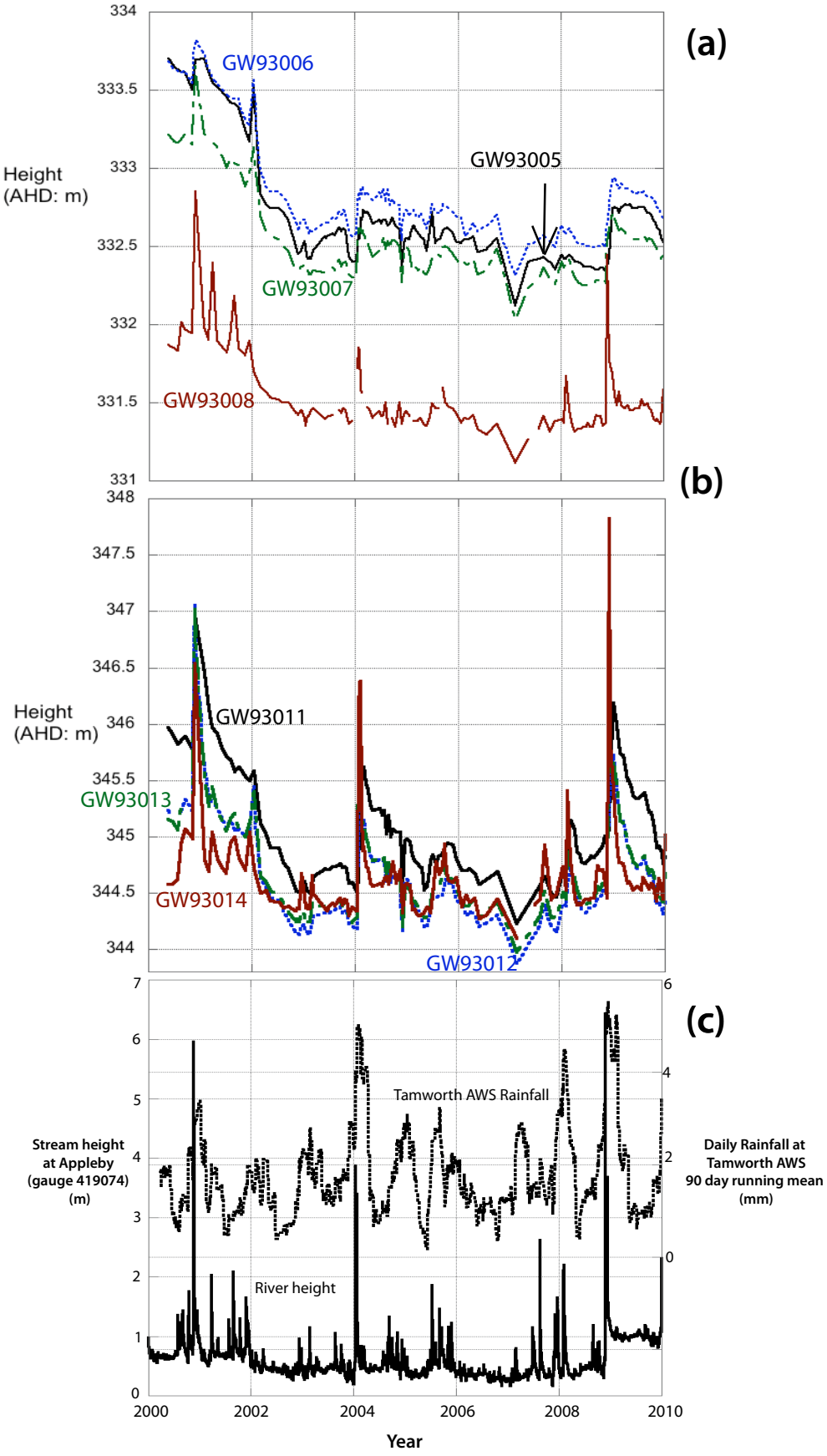

Figure 4-8 Hydraulic Head at the upstream (uppermost figure) and downstream (middle figure) bore transects with river height at gauge 419074 (Bective). The response to high flow events is apparent. Also note that the gradient between the bores is relatively constant. Bore levels are estimated to be ± cm. River height is ± 1 cm. Actual datapoints omitted for clarity; the river height is based on daily data and the bore levels on approximately bi-monthly readings.

This pattern of flood recharge is also evident in the longer-term hydrograph in Figure 4-9, where the hydrograph of GW930136 displays high-flow periods accompanied by recharge resulting in approximately a metre's increase in water-table height. This bore is located only about 10 m from the river (near Tamworth) – this explains the relatively quick response of hydraulic head in this bore.

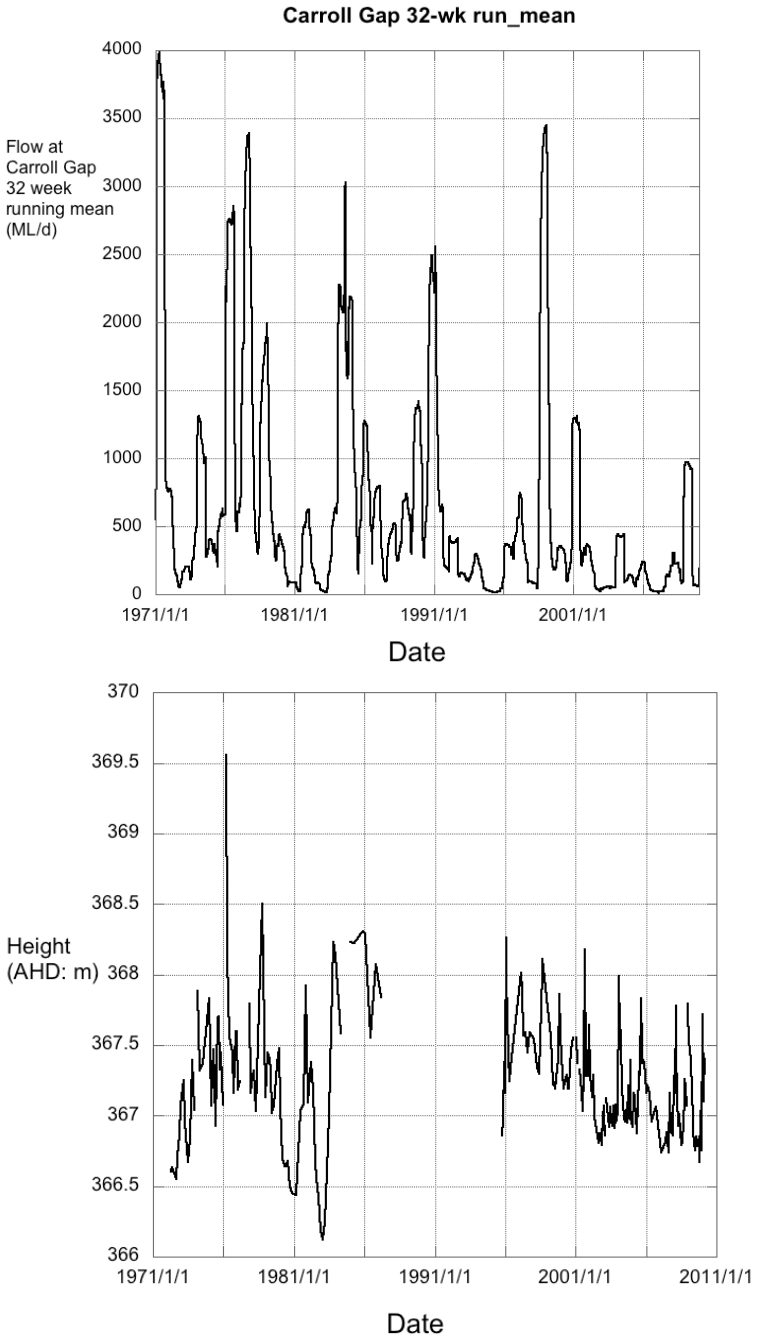

Figure 4-9 The (discontinuous) 40-year record of hydraulic head at bore GW0930136 coupled with streamflow records at Carroll Gap, show the relationship between high-flow events and significant recharge. The break in the record unfortunately corresponds to an unusually wet period, as seen in the flow records at Carroll Gap. The influence of this period of higher flows is visible in the average decline in hydraulic head from the time the record again starts. Bore level is based on approximately bi-monthly readings and is accurate to ± $\sqrt{3}$ cm.

Chapter discussion

River hydrograph analysis indicates that the Peel River is gaining 11.2 ± 6.5 % between the gauges at Appleby and Bective due to an increase in baseflow at the time of sampling. There appeared to be no change in baseflow between Bective and Somerton. A long-term analysis of records at Appleby and Bective indicates that the stretch is gaining on average, but that the reach is variably gaining-losing. The gain appears to be correlated seasonally with streamflow, except during summer, due to river water extraction. The long-term data for the gauge at Somerton appears to be unreliable.

Bore hydrograph analysis has demonstrated that there is groundwater recharge from the river in the vicinity of the upstream bore transect. Groundwater is hypothesised to flow in the alluvium parallel to the river for some kilometres downstream of this point. There is groundwater discharge in the vicinity of the downstream bore transect. Comparison of the bore hydrographs with river height data points to the importance of periodic flooding in recharging the groundwater system.

Chapter 5 Chemical Tracers: Results and Discussion

Introduction

In the previous chapter, baseflow analysis suggested that an increase in the river flow of 11.2 ± 6.5 % between the streamgauges at Appleby and Bective could be attributed to groundwater discharge at the time river samples were collected. In this chapter, chemical tracers provide an independent means of calculating groundwater discharge, providing an important check on the reliability of different methods.

An examination of several different chemical tracers provides not only an independent estimate of groundwater discharge, but also insight into the nature of the interaction between the groundwater and river systems. Finally, there are some clues that some interaction may be taking place between the alluvial and bedrock aquifers.

Water compositions for the Lower Peel Catchment

The waters of the Peel Valley are all close to neutral pH, with a range in groundwater samples of 6.8 to 7.3, and in river samples from 7.2 to 8.2. Electrical conductivity is generally high, but quite variable, ranging from 472 to 2259 μS/cm in the groundwater samples and 654 to 1022 in the river water samples. Water samples contained high concentrations of Ca and Mg, with up to 4.5 mM of Ca and 3.0 mM of Mg in groundwater samples.

The water composition of groundwater and surface water samples collected in the Lower Peel Valley are given in the following tables

Table 5-1 Field Chemistry data and sample locations

Sample ID	Sampling date and time	Longditude (GPS) (ºE)	Northing (GPS) ºN	Ground Elevation m	Casing height m (from to of casing)	Depth to water m	Water Table Height GDA, m	Temp ºC	Water Collection Depth m	pH	EC µS/cm	DO mg/L	Eh RmV	Fe2+ mg/L	Bore Depth m	Alkalinity mEq/L -
[GW93010]	30/05/10 15:40	150.8483	-30.93113	353.63	1.29	6.785	348.14		-							-
[GW93034]	30/05/10 16:40	150.9016	-30.98842	377.01	0.88	>4.4			-							
GW93005	27/05/10 11:40	150.8061	-30.93876	339.98	1.32	7.843	333.46	22.0	20	7.0	900	3.1	101	0.02	22	6.77
GW93006	27/05/10 14:13	150.80524	-30.94337	338.53	1.01	6.95	332.59	20.4	17	**6.9**	832	3.7	113	0.02	24	5.34
GW93006B	27/05/10 14:40	150.80524	-30.94337	338.53	1.01	6.95	332.59	20.4	17	7.1	835	3.7	116	-	24	[5.34]
GW93007	27/05/10 16:55	150.80439	-30.94771	338.15	1.32	7.136	332.33	20.0	18	**6.8**	802	4.1	148	-	21.5	4.74
GW93008	29/05/10 10:32	150.80279	-30.95457	338.15	1.51	8.568	331.09	19.7	14	**6.9**	866	5.0	394	-	16	5.13
GW93009	30/05/10 15:40	150.84785	-30.93012	356.98	1.23	7.08	351.13	18.7	11	**6.9**	897	0.1	327	0.08	13.5	6.17
GW93011	28/05/10 16:50	150.86297	-30.96734	350.79	1.51	7.623	344.68	20.4	8	6.7	472	1.3	281	0.09	17.5	3.07
GW93012	28/05/10 15:03	150.85777	-30.96659	349.61	1.264	6.645	344.23	20.9	9	6.8	859	4.7	367	-	13.5	4.89
GW93013	28/05/10 9:50	150.85401	-30.96609	349.75	1.439	6.773	344.42	21.0	8	**6.8**	694	2.9	447	-	8.5	4.47
GW93014	29/05/10 15:10	150.85213	-30.96583	349.84	1.44	6.84	344.44	20.1	8	**6.9**	896	2.0	432	-	9.5	6.20
GW93015	30/05/10 10:10	150.84644	-31.01244	359.29	1.62	7.027	353.88	17.3	8	**7.3**	1836	3.8	518	-	9	11.54
Jensen100	31/05/10 10:55	150.90197	-30.95606	461	n/a	12.2	449	19.5	26	**6.9**	2259	3.5	451	-	30	12.51
Jensen210	31/05/10 12:28	150.90437	-30.95052	459	n/a	12.5	447	20.3	59	**7.3**	2066	6.4	437	-	64	11.43
Pearson1	31/05/10 15:45	150.80625	-30.93516	347	n/a	~7	340	19.1	9	**7.2**	1022	7.1	439	-	11	6.12
Peel1	28/05/10 12:17	150.85262	-30.96602	350	n/a	n/a		15.9	0.15	**8.2**	739	10.1	739	-	n/a	3.98
Peel2	29/05/10 10:50	150.80143	-30.95616	338	n/a	0.15		15.1	0.15	**8.2**	1019	8.5	524	-	n/a	4.25
Peel3	29/05/10 12:35	150.64311	-30.9348	313	n/a	0.15		14.6	0.15	**8.7**	898	9.9	406	-	n/a	4.53
Peel4	30/05/10 8:40	150.85768	-31.0437		n/a			13.0	0.1	**7.8**	792	6.8	496	-	n/a	3.23
Peel5	30/05/10 11:45	150.85205	-31.01307	358	n/a	n/a		14.1	0.4	**8.2**	654	8.5	630	-	n/a	3.03
Detection Limit														0.02		0.2
Precision (± %)					5 mm	5 mm			5	.1 unit	5	20	5	10	5	10

- Indicats sample below stated detection limit

n/a not applicable

NB Elevation figures to the nearest metre from the Shuttle RADAR Topography Mission (SRTM 2010)

Elevation data to the nearest centimetre provided by the NSW Office of Water and obtained by differential GPS.

Table 5-2 River and Groundwater analytical results. For samples with dilution factors greater than 1, multiply the method detection limit by the sample's dilution factor to obtain the detection limit for a particular combination of sample and analyte. For example, the detection limit for sample GW93005 for Al is 8 µM.

Analytical Method		ICP Atomic Emission Spectrometry														Ion Chromatography					Calculated	ICP Mass Spectrometry								MS	
Sample ID	Dilution Factor	Al µM	B mM	Ba µM	Ca mM	Cu µM	Fe µM	K mM	Mg mM	Mn µM	Na mM	Ni µM	Si mM	Sr µM	Zn µM	F µM	Cl mM	Br µM	NO_3 mM	SO_4 mM	HCO_3^- mM	As nM	Rb nM	Sc nM	U nM	V nM	Cr nM	Y nM	Charge Balance (%)	$\partial^{18}O$ ‰	$\partial^{2}H$ ‰
Blank1	1	-	-	-	0.004	-	-	-	0.002	-	0.01	-	-	-	-	-	-	-	0.001	-		-	-	-	-	-	-	-	n/a	n/a	n/a
Blank2	1	-	-	0.001	0.009	-	-	-	0.001	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	n/a	n/a	n/a
GW93005	2	-	-	0.26	2.72	-	-	0.030	1.1	-	1.43	-	0.56	7.4	5.8	7.1	1.58	3.3	0.10	0.45	6.50	6.6	1.9	24.3	7.5	26.1	-	1.5	4.4	-6.04	-38.5
GW93006	2	-	-	0.32	2.01	-	0.66	0.055	1.6	0.54	2.65	-	0.53	6.7	11	7.6	1.73	3.7	0.26	0.73	5.18	9.3	-	22.8	8.5	29.6	4.4	1.3	15.7	-5.17	-32.7
GW93006B	2	-	-	0.43	2.02	-	0.41	0.027	1.5	0.46	1.46	0.89	0.53	6.5	10	7.7	1.76	3.5	0.26	0.74	n/a	9.1	-	21.8	8.2	28.9	4.7	-	7.8	n/a	n/a
GW93007	2	-	-	0.19	1.92	-	-	0.037	1.2	-	1.53	-	0.51	7.0	5.0	3.1	2.00	3.7	0.27	0.69	4.62	5.1	1.5	22.2	6.0	17.2	-	-	6.6	-5.83	-36.4
GW93008	2	-	-	0.20	1.91	-	0.45	0.042	1.5	0.20	1.66	-	0.51	8.9	4.9	3.7	1.99	3.6	0.23	0.95	4.99	6.0	-	21.1	10.6	23.0	-	1.2	7.7	-5.36	-32.9
GW93009	2	-	-	0.62	1.91	-	1.53	0.031	1.6	10.7	2.17	-	0.57	5.9	5.1	8.3	1.63	3.7	0.0040	1.55	6.00	24.2	1.7	24.4	31.3	25.8	-	1.6	6.1	-5.35	-32.9
GW93011	1	-	-	0.10	0.89	-	1.40	0.061	0.74	1.01	1.22	-	0.67	3.9	0.2	6.7	1.03	2.5	0.03	0.24	3.03	4.5	-	28.2	2.2	16.1	-	-	4.5	-6.01	-37.4
GW93012	2	-	-	0.53	1.48	-	-	0.100	1.3	-	2.55	-	0.57	6.0	4.9	11.8	2.56	5.6	0.13	0.57	4.77	31.8	-	25.8	87.7	135	-	-	4.3	-5.42	-33.8
GW93013	2	-	-	0.21	1.23	-	-	0.035	1.1	-	2.09	-	0.47	5.5	5.0	9.8	1.28	2.5	0.06	0.77	4.38	8.6	-	19.8	15.1	44.7	-	-	7.3	-3.83	-23.0
GW93014	2	-	-	0.16	1.80	-	-	0.042	1.6	-	2.31	-	0.42	8.1	4.9	7.3	1.78	3.4	0.15	0.87	6.03	12.7	2.6	18.7	20.1	40.1	-	1.2	5.3	-4.41	-28.2
GW93014B	2	-	-	0.18	1.78	-	-	0.041	1.5	-	2.29	-	0.42	8.0	5.2	7.1	1.80	3.3	0.15	0.88	n/a	13.4	2.8	18.2	19.8	37.9	-	1.3	4.7	n/a	n/a
GW93015	5	-	41	0.84	2.66	-	-	0.021	3.0	-	6.94	2.21	0.46	21.5	27	22.1	4.05	10.1	0.73	2.48	11.04	15.8	5.3	22.8	17.4	55.4	10.7	4.9	6.7	-5.16	-33.8
Jensen100	5	10.6	-	4.29	4.49	5.6	1.47	0.023	3.0	-	6.34	21.0	0.52	13.9	200	22.0	8.60	13.1	0.52	0.85	11.76	120	3.0	27.8	6.6	38.8	8.1	5.2	-1.4	-5.75	-36.4
Jensen210	5	-	-	0.38	3.97	-	-	0.026	2.8	-	6.98	1.94	0.53	13.7	25	12.5	6.86	11.5	0.19	2.87	11.06	22.8	5.7	28.4	6.8	19.0	-	6.5	-13.9	-5.66	-36.8
Pearson1	2	-	-	0.62	3.11	-	-	0.024	1.2	-	1.36	-	0.52	7.8	7.0	8.6	2.59	4.4	0.15	0.92	5.91	8.4	4.7	26.2	4.4	26.4	-	4.0	5.4	-5.35	-34.3
Pearson1B	2	-	-	0.60	3.11	-	-	0.023	1.2	-	1.36	-	0.51	7.8	5.9	7.9	2.59	4.5	0.15	0.92	n/a	8.6	4.7	25.8	4.4	26.6	-	4.0	5.3	n/a	n/a
Peel1	2	-	-	0.31	1.08	-	-	0.167	1.1	0.13	2.53	-	0.21	4.7	4.8	8.9	1.98	2.7	0.14	0.88	3.78	18.1	33.9	9.3	5.4	60.2	-	1.5	7.0	-2.51	-15.9
Peel2	2	-	-	0.41	1.15	-	-	0.146	1.2	0.20	2.70	-	0.17	5.2	7.8	9.1	2.22	3.4	0.084	0.97	4.02	19.9	24.1	8.1	7.2	54.9	-	4.2	5.9	-2.66	-16.3
Peel3	2	-	-	0.36	1.26	-	-	0.098	1.4	0.27	2.72	-	0.13	6.9	5.8	9.0	2.54	4.3	0.014	1.21	4.02	21.2	5.9	5.5	8.6	51.2	-	1.4	5.5	-2.92	-18.4
Peel4	2	-	-	0.47	0.83	-	-	0.222	0.82	0.17	2.11	1.04	0.23	3.2	11	8.8	1.62	1.9	0.24	0.66	3.14	13.9	74.1	10.2	3.1	48.9	-	1.2	6.0	-3.09	-16.0
Peel5	5	-	-	0.61	0.88	-	-	0.126	0.86	-	1.85	2.33	0.20	3.6	28	7.4	1.22	2.0	0.14	0.58	2.90	17.9	39.9	10.6	3.2	57.5	-	4.0	-3.6	-3.71	-20.9
Detection Limit		4	9	0.01	0.009	0.2	0.2	0.003	0.002	0.04	0.006	0.3	0.02	0.06	0.2	1	0.03	0.3	0.001	0.005	0.2	4	1	4.4	0.1	2	4	1	Precision	0.1	1
Precision (± %)		-	-	11	2.5	-	2*	7	8	2*	1	2*	3	1	8	3	1	4	5	1	10	5	8	5	3	5	0.2	2	± ∂-units		

- Indicates sample concentration less than indicated detection limit

* precision estimate based only on standard reproducability due to lack of field duplicates above DL

n/a not analysed

Table 5-3 Analysis of four rainfall samples collected at the Gunnedah Resource Centre (BOM weather station 55024)

	Method	ICP Mass Spectrometry														Ion Chromotography					MS	
Sample Date	Rainfall mm	Ba µM	Ca mM	Co nM	Cr µM	Cu µM	K mM	Mg mM	Mn µM	Na mM	Ni µM	Pb µM	Rb nM	Sr µM	V µM	Zn mM	F µM	Cl mM	NO_3 mM	PO_4 mM	SO_4 mM	$\partial^{18}O$ ‰	$\partial^{2}H$ ‰
25-May	1.6	0.02	0.015	9.3	0.018	0.29	0.117	0.019	0.85	0.057	0.03	0.0028	23.6	0.056	0.006	0.12	2.4	0.06	0.033	0.011	0.055	-3.50	-9.7
26-May	15.2	-	-	1.1	-	0.092	0.006	-	0.088	-	-	0.0030	1.5	0.009	-	0.019	-	0.01	0.009	0.004	0.005	-7.71	-42.3
29-May	8.4	-	-	2.2	-	0.076	0.006	0.0024	0.158	0.023	-	0.0032	1.5	0.011	-	0.047	0.6	0.03	0.011	0.004	0.014	-3.29	-5.8
30-May	7.6	-	-	1.7	-	0.050	0.003	-	0.112	-	0.02	0.0022	0.9	0.006	-	0.032	-	-	0.004	0.003	0.007	-6.02	-29.7
Detection Limit		0.01	0.002	0.8	0.010	0.0008	0.003	0.0004	0.009	0.004	0.02	0.0005	0.6	0.001	0.001	0.0002	0.5	0.01	0.001	0.001	0.002	0.1	1

Water type and broad trends

The river and groundwater samples are predominately bicarbonate-type and range from Na + Mg to Ca type (Figure 5-1). There is a slight trend to more chloride-dominated water between the three directly comparable river samples, Peel1, Peel2 and Peel3 (from upstream to downstream). Additionally, there is a slight shift to more Ca-Mg dominated water between the same samples.

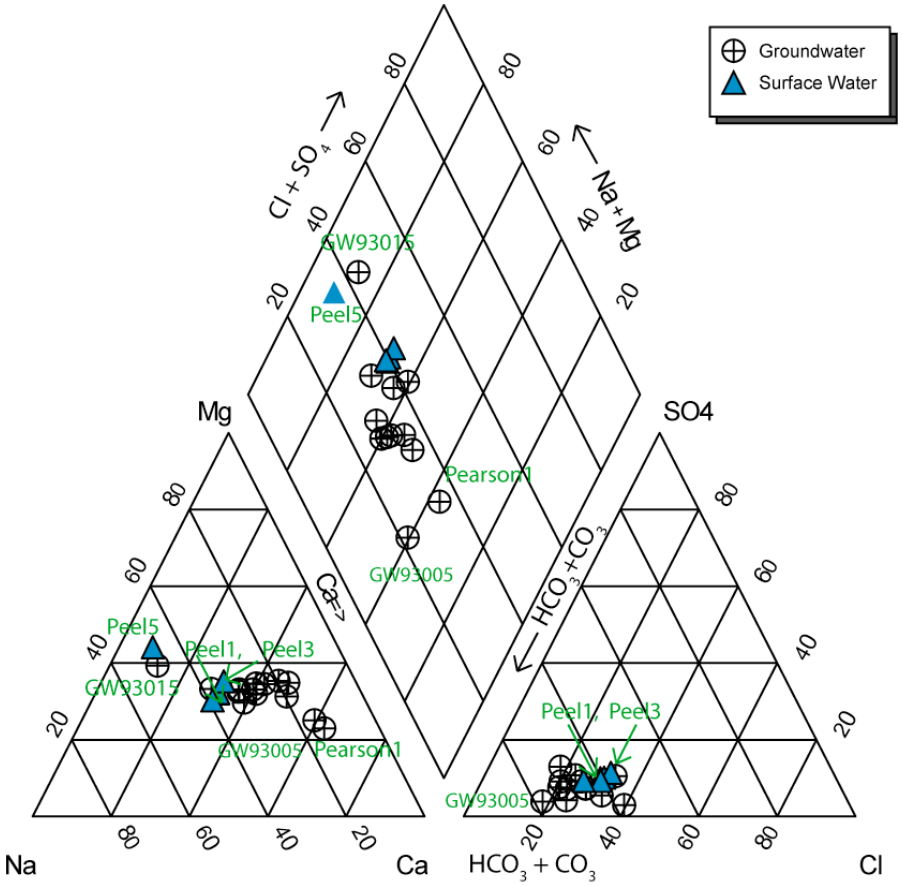

Figure 5-1 Piper plot of all groundwater and river samples (Peel4, Peel5, Peel1, Peel2, Peel3 from upstream to downstream).

More clearly, Figure 5-1 shows that samples Pearson1 and GW93005, which are situated close to the edge of the alluvium in the downstream bore transect, are of substantially different composition to the other samples. This may reflect interaction with a bedrock aquifer, or may be the result of differences of the ground surfaces over which localised surface flow occurs. The dominant NNW-SSE faulting associated with the Peel Fault may provide a conduit for water flow in the bedrock. There is certainly some groundwater movement within faults in the bedrock, with groundwater extraction occurring in the Valley from faulted rock (WCIC 1970, NOW 2010d). River sample Peel5 (upstream of Peel1) is

different to all other river samples, probably reflecting different flow conditions at the time this sample was collected.

Flowing from the sampling sites of Peel1 to Peel2 to Peel3, the water increases in overall solute concentrations, as shown in Figure 5-2. As discussed in Chapter 3, these three river samples are considered to be directly comparable, as river flow was similar at the time each sample was taken. For this reason will be used for most river comparisons in this chapter. Peel1 and Peel2 were taken under especially similar flow. Interestingly, Na concentrations increase very little, although Cl^- increases notably. This is discussed in more detail in the "Chloride and Bromide" and "Sodium and Potassium" sections of this chapter.

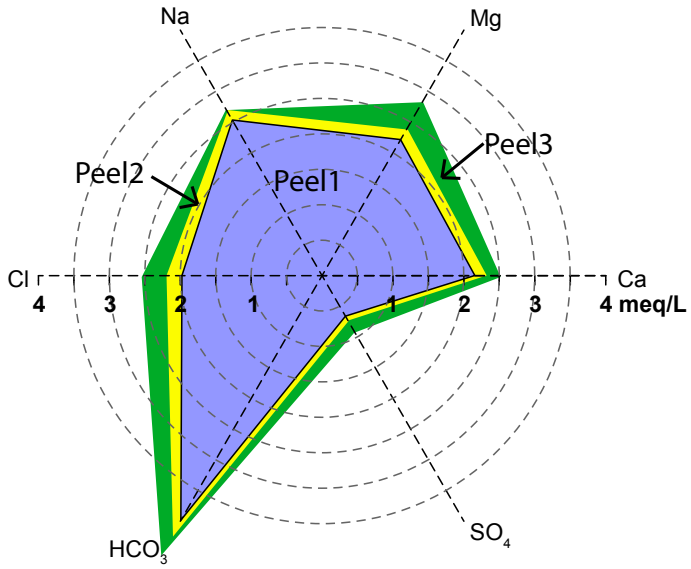

Figure 5-2 Radial diagram of major ion concentrations in the three river samples Peel1, Peel2 and Peel3.

Chloride and Bromide

Chloride and bromide potentially provide conservative tracers for calculating mixing of different water bodies. Chloride behaves conservatively in natural water systems, provided that halite dissolution/precipitation does not occur (Herczeg *et al.* 1993, Herczeg *et al.* 2001, Cartwright *et al.* 2007a). Bromide behaves less conservatively than chloride, but is still often taken to be a conservative element (Herczeg *et al.* 1993, Herczeg *et al.* 2001, Cartwright *et al.* 2007a). As a result, variation in (molar) Cl^-/Br^- ratios and absolute concentrations can thus be used as a conservative tracer to distinguish between different endmembers and to elucidate mixing between them (Davis *et al.* 1998).

Both Cl^- and Br^- increase in concentration down the river; concentrations are similar in the river and groundwater samples (Figure 5-3). Peel5 deviates from this trend, but was taken

under substantially higher flow conditions, so may be influenced by contributing water sources, such as overland flow. As noted elsewhere, only Peel1 and Peel3 were taken under very similar flow conditions.

Figure 5-3 The increasing trend in the river samples, Peel4, 5, 1, 2, 3 (in order from upstream to downstream) riverine Cl^- and Br^- concentrations (triangles). Note that the two bores in bedrock, Jensen100 and Jensen210, have not been plotted, the higher concentrations in these bores would compress the axes of the chart, obscuring the visible trends. Errors of ±1 % for Cl^- and ±4 % for Br^- are within the size of the symbols.

The Cl^-/Br^- ratio is fairly constant for all water samples (shown by the straight line through zero on the Cl^- and Br^- graph, Figure 5-3). Four of the river samples plot in a straight line on the Cl^-/Br^- graph. This implies mixing with another water body with a similar Cl^-/Br^- ratio, but at higher concentration. The slight deviation observed from the riverine Cl^-/Br^- ratio is likely the result of uptake and release by plants, as discussed below. The river sample that deviates from the straight line, Peel5, was collected under different flow conditions to the other samples. As mentioned previously, Peel1, Peel2 and Peel3 are the only directly comparable river samples, as they were collected under similar flow conditions.

On average, rainfall Cl^-/Br^- ratios reflect the oceanic value of 288 (Gerritse & George 1988). However, there is a tendency for higher values inland, since there is a tendency for NaCl to be removed from a mass of humid air in early precipitation (Cartwright *et al.* 2004). Large deviations from this ratio imply halite dissolution or precipitations, since Br is excluded from the halite structure (Herczeg *et al.* 1993, Herczeg *et al.* 2001, Cartwright *et al.* 2007a), with Cl^-/Br^- ratios of ~10^4 observed elsewhere (Cartwright *et al.* 2004). The Cl^-/Br^- ratios here of up to 870, with most 400-600 may indicate some halite dissolution; Cartwright *et al.* (2010) interpreted ratios of 700-900 in the Murray Basin as indicative of minor halite

dissolution. The consistency of the Cl^-/Br^- ratio (Figure 5-3) is evidence that if halite precipitation is occurring, it is of small significance.

The small deviations from a straight line on the chloride/bromide plot (Figure 5-3) may be the result of interactions with organic matter, or localised slight contamination. Plants take up Br, and subsequent depredation of organic matter releases Br (Gerritse & George 1988). Degradation and growth of organic matter could thus explain what deviations there are from a straight line through 0 on the Cl^-/Br^- figure (Figure 5-3) Bromide contamination can be significant in some areas, since 1,2-dibromoethane was routinely added to leaded petrol and brominated pesticides were once also widespread (Davis *et al.* 1998, Cartwright *et al.* 2006), though there is little evidence of anomalously high bromide in any water sample in this area.

The similarity in chloride and bromide concentrations in river and groundwater samples means that ~100 % of the river flow at downstream points would need to be derived from groundwater to account for the increase in their river concentrations. Alternatively, the river could be undergoing substantial evaporation. The only groundwater sample with substantially higher concentrations of chloride and bromide than the river (GW93015) was taken well upstream of Peel1, so cannot itself be contributing to the increase in chloride between Peel1, Peel2 and Peel3. There are two possibilities. The river itself may be undergoing substantial evaporation between the sampling points, or groundwater with substantially higher chloride and bromide concentrations than that sampled is contributing to the river over this reach.

Cl^- and Br^- in the Upstream bore transect

The patterns of chloride and bromide concentration in the upstream bore transect (perpendicular to the Peel River, upstream of Attunga Creek; maps and discussion of the locations are found in Chapter 3) indicate a pattern of groundwater flow parallel to the river in this region. They also indicate that evapotranspiration may increase solute concentrations in the groundwater between the sampling points and its area of discharge to the river. The two bores close to the river (Figure 5-4) show Cl^- and Br^- concentrations and ratios similar to those in the river, as expected given that these bores are known from an analysis of their hydrographs (Chapter 4) to receive recharge from the river.

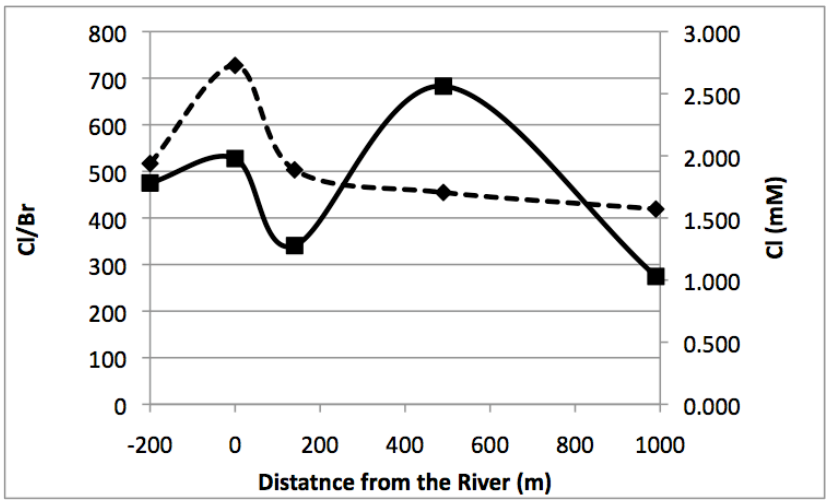

Figure 5-4 Cl^-/Br^- ratios (dashed line) and Cl^- concentration (solid line) in the upstream bore transect from east to west (reading left to right): GW93014, the river (Peel1, at 0 m), piezometers GW93013, GW93012, GW93011. Errors are ±1 % for the chloride measurements and ±3 % for the ratios. Error bars and are within the symbols.

Based on bore hydrograph analysis (Chapter 4), GW93012 has the lowest hydraulic head in this bore transect. The increase in chloride in GW93012 is probably due to transpiration as water moves to this region of the alluvium from both the river and the eastern edge (discussed in more detail below). The variation in Cl^-/Br^- ratios would be explained if the local rainfall has a lower Cl^-/Br^- ratio than the river water, as a result of rainout of NaCl as water vapour passes over the higher areas of the catchment. The rain-fed recharge (and conceivably some bedrock aquifer interaction) of the non-river edge of the alluvium would then have a lower Cl^-/Br^- ratio than the river flow derived from upstream rainfall. Cl^-/Br^- ratios in local rainfall are not known; Blackburn and McLeod's (1983) study did not analyse for Br^-, and the Br^- concentrations in the four rainwater samples analysed in the present study were below the Br^- detection limit. Some or all of the variation may also be explained by decay of organic matter enriching the alluvium further from the river with Br^- (eastern side; right side of Figure 5-4).

A diagram of a conceptual model, explaining the increase in chloride concentration in the middle of the bore transect and in the river is presented in Figure 5-5. At the bottom of the diagram, corresponding to the vicinity of the upstream bore transect, water flows into the middle of the alluvium from the river and from the far edge. The far edge of the alluvium is likely fed to some extent by overland flow, due to topographic relief. This edge of the alluvium may also be fed by a bedrock aquifer. The other side of the alluvium is likely to behave similarly, although the much smaller extent of the alluvium on this side of the river, combined with the lesser relief make this side of the river (left in Figure 5-5, south-west in the valley) are likely to make this less important. As groundwater flows towards the middle of the

alluvium and from there down-gradient parallel to the river, it undergoes transpiration, before flowing into the river.

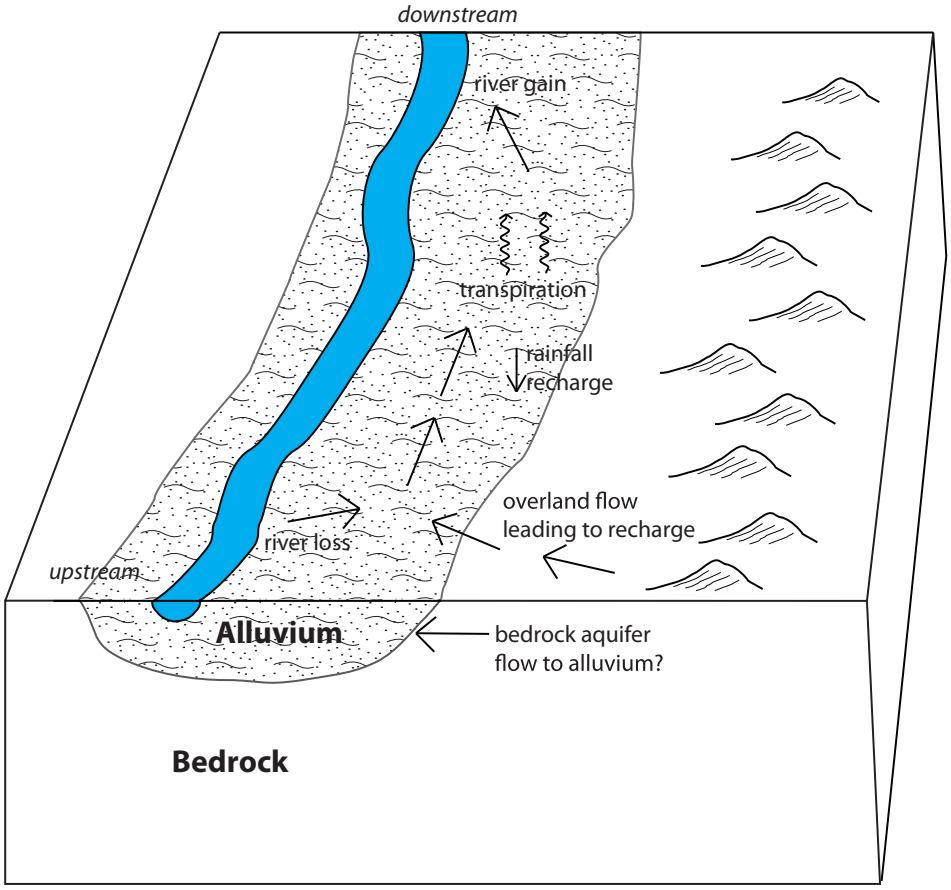

Figure 5-5 Conceptual Model of flow in the alluvium in the vicinity of the upstream bore transect. Water flows from the river to the alluvium near the bores (front of figure). Water then flows parallel to the stream in the alluvium and flows back into the river further downstream after undergoing transpiration (back edge of figure). Surface flow (derived from rainfall) and possibly a bedrock aquifer also recharge the alluvium.

This model of constricted alluvial groundwater flow resulting in considerable transpiration is reminiscent of the model for alluvial groundwater systems in the Liverpool Plains (also a part of the Namoi Basin) developed by Stauffacher *et al.* (1997). In their model, they proposed that bedrock highs constricting groundwater movement, combined with artificially high water tables as a result of land clearing, have led to high levels of evapotranspiration. Parts of the Lower Peel are similar, except that in the Peel, bedrock does not prevent groundwater flowing out of the area and the water table remains low enough that salt concentration is increased only by transpiration, without evaporation (see "Stable Water Isotopes" section below). Also in contrast to the Liverpool Plains, there is little evidence for historical storage of salt in the alluvium subsequently being remobilised by the modified system, as evidenced by the Cl^-/Br^- ratios of the water samples.

Chloride and bromide concentrations and ratios in the downstream bore transect (downstream of Attunga Creek; see maps and discussion of locations in Chapter 3) do not

provide such a clear trend in variation, in part because the transect is thought not to correspond well to a flow-path, as discussed in Chapter 4.

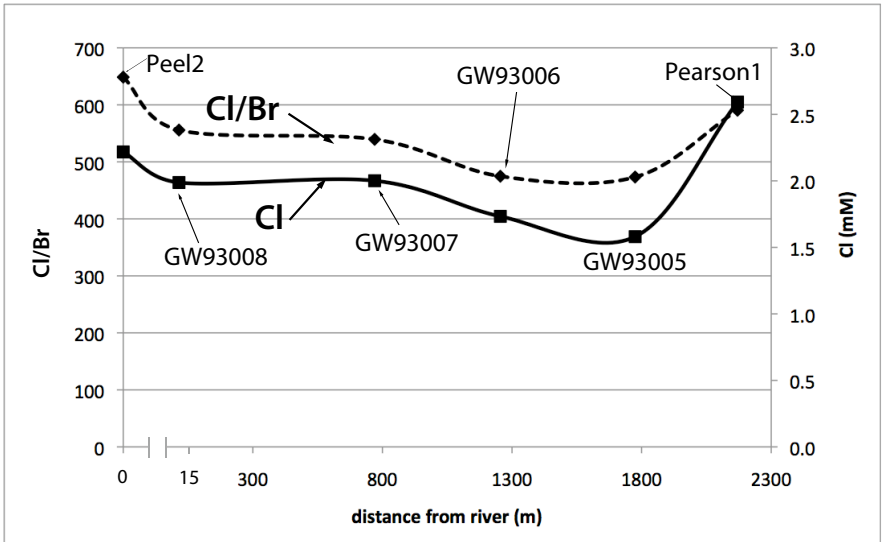

Figure 5-6 Cl^- concentrations (solid line) and Cl^-/Br^- concentration ratios (dashed line) in the downstream bore transect. Transect runs from south to north (left to right). Lines shown only for clarity and are unlikely to accurately represent the variation between points. Note the discontinuous distance scale. Errors are ±1 % for the chloride measurements and ±3 % for the ratios; error bars are within the symbols.

Pearson1, the furthest bore from the river in this transect, is higher in chloride and has a higher Cl^-/Br^- ratio than the two adjacent bores, indicating a different input, possibly input from a bedrock aquifer. If overland flow prior to recharge is significant, recharge from a slightly different sub-catchment may be sufficient explanation – topography indicates that Perason1 and the two adjacent bores are probably sampling groundwater recharged by drainage from slightly different areas.

Calcium and Magnesium

Concentrations and concentration ratios of Cl^- and Br^- suggest there may be some interaction between a bedrock aquifer and the edges of the alluvium. Such interaction is most likely in the vicinity of the downstream bore transect, downstream of Attunga Creek, since the dominant NNW-SSE faulting in this region is perpendicular to the river and alluvium and follows the topographic gradient.

All water samples were of high alkalinity: 4.5 to 6.8 mEq/L in the alluvial bores; 4.0 and 4.5 mEq/L in Peel1 and Peel3, respectively. The water samples also all had (molar) Ca:Mg ratios of around 1:1, implying Mg as well as Ca dissolution is taking place. Dissolved Ca and Mg are charge balanced by HCO_3^-. Both Ca and Mg increase in concentration between Peel1 and Peel3, but the Ca:Mg ratio decreases from 1.1 to 0.9. The Peel Valley contains a number of limestone deposits, at least one of which is magnesite-rich as testified by the

existence of the (former) Attunga magnesite quarry (Oskierski 2010). That magnesium is reasonably widespread in the region's limestones may further be indicated by analysis of the sample with the highest calcium concentration. This bore, Jensen100 is drilled into "limestone", according to the property owner, and has a Ca:Mg ratio of 1.5, indicating that at least the limestone in that area probably does contain significant magnesium.

Surface- and ground-water in contact with Mg-bearing limestone may come to have a low Ca:Mg ratio because of solubility constraints. The log of the solubility product (log K_{sp}) at 25ºC for calcite is -8.480, whereas the log K_{sp} value for magnesite at 25ºC is -8.029 (a factor of 2.8 difference in their saturated concentrations, for constant pH and in the absence of common-ion effects). A number of the bore samples were supersaturated for calcite at the temperature measured, when calculated using PHREEQC (Parkhurstand & Appelo 2010).

Furthermore, the Peel Fault is reported as containing a 15 cm thick layer of chlorite and magnesite, separating schistose serpentinite from sandstones (Glen & Butt 1981). Magnesite and chlorite associated with the Fault are therefore also potential sources of magnesium.

Dissolution of limestone does not readily explain the Ca:Mg ratio in the groundwater samples. The alluvial soils (*i.e.* the infiltration zone) is described as containing carbonate (Hird 1979), which may include $MgCO_3$. However, the same solubility constraints, whereby Ca saturation is reached before Mg saturation, would tend to deplete the soil of Mg. The ~1:1 Ca:Mg ratios are evidence for a combination of river recharge of the alluvium, with precipitation of calcite reducing Ca:Mg ratios, and possibly overland flow to recharge and possible interaction with a bedrock aquifer. The argument for interaction with a bedrock aquifer is weakened somewhat by the high Ca:Mg ratios in the two groundwater samples obtained from a bedrock, albeit several kilometres away, so not necessarily representative. The Ca/Mg ratios in these bores were 1.4 and 1.5.

In the downstream transect (Figure 5-7), the two bores furthest from the river are clearly different to the other bores, with much higher calcium concentrations and Ca/Mg ratios. As this bore is sunk on the edge of the alluvium, influx from a bedrock aquifer could also explain the trend.

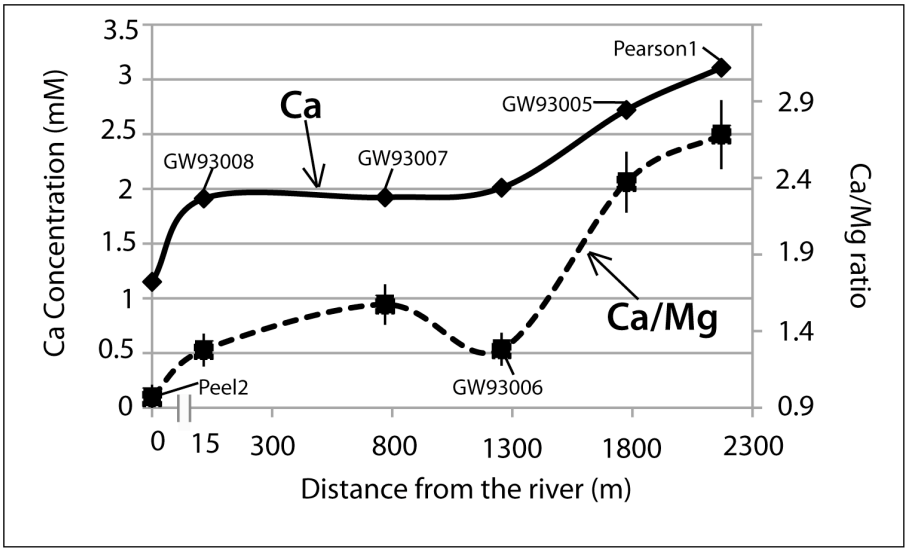

Figure 5-7 Calcium concentration and Ca/Mg ratio in the downstream bore transect, with a river sample. Note the discontinuous distance scale. Ca error bars are within the symbols.

From this examination of Ca concentrations and Ca/Mg ratios, overland flow prior to recharge and/or interaction with a bedrock aquifer is likely.

The trend in Ca concentration in the upstream bore transect supports the conceptual model based on the Cl^- and Br^- results of this study. Ca/Mg ratios are not significantly different in the samples in this transect. A trend along the upstream bore transect is clearly visible on Figure 5-8. The Ca concentration ratio in all groundwater samples is higher than in the river. The highest concentration on the eastern side of the river is in the middle of the transect (GW93012), supporting the notion advanced in the "Chloride and Bromide" section of this chapter that groundwater in this part of the transect has undergone more transpiration. The sample from the other (western) side of the river is also high in calcium.

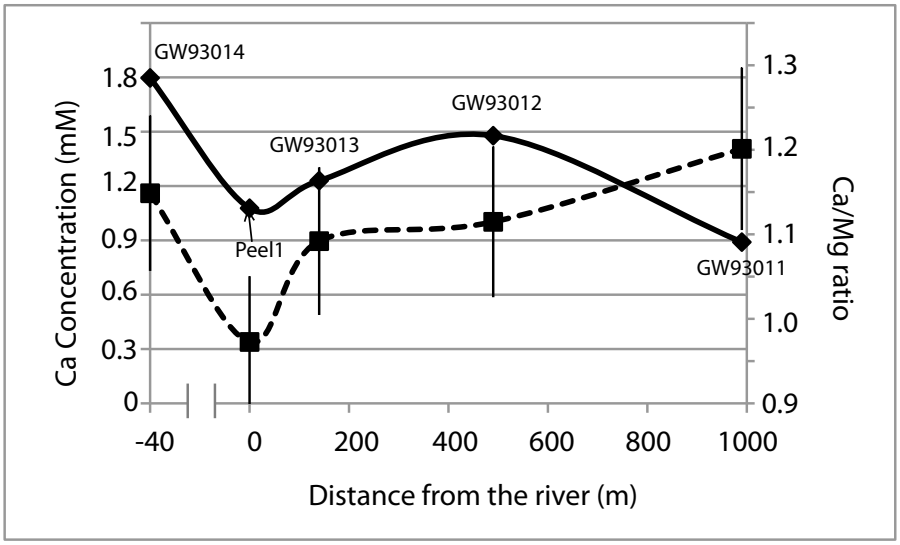

Figure 5-8 Calcium concentration and in the upstream bore transect including a river sample (at 0 m). Note the discontinuous distance scale. Ca error bars are inside the symbols.

Nitrate

The increase in chloride and bromide concentrations observed in the river could be a result of groundwater discharge, if groundwater increases in solute concentration between the points of sampling and the areas of discharge to the river, as discussed above. An analysis of nitrate concentrations in the river and groundwater samples adds weight to this argument, since it is shown that significant groundwater discharge in the stretch of river between where the groundwater samples were collected and the lowermost river sampling site is unlikely. This means that the increase in river salinity (in the absence of evaporation) probably is attributable to groundwater discharge near where groundwater samples were taken. This is consistent with the hydrograph analysis that found that all of the increase in baseflow between Appleby (site of sample Peel1) and Somerton (site of sample Peel3) could be attributed to the reach of river between Appleby and Bective (site of sample Peel2).

The decrease in nitrate concentration is so great (from 140 at Peel1, 84 μM at Peel2 and 14 μM at Peel3) that denitrification must be the cause of the decrease; dilution would require a much greater influx of low-nitrate water than is plausible. In experiments conducted on sediment from a creek near Toronto, as much as about 19 $mM/m^2/d$ of nitrate was reduced (Hill 1979). Richardson *et al*. (2004) give a range of figures for potential enzyme activity extending as high as 380 $mM/m^2/d$. Richardson *et al.* (2004). and Mitchell and Baldwin (1999) both noted that rates of denitrification vary widely between different sediment samples. Sorption and conversion of nitrate to ammonia can contribute as much to nitrate loss as denitrification (Richardson *et al.* 2004). Given water depth of just under a metre recorded at the gauging stations at the time of sampling (NOW 2010a) and ~24 h for water to flow between the gauges, a high denitrification rate of ~ 100 $mM/m^2/d$ would be required to account for the decrease in nitrate concentration.

Additionally, nitrate concentrations in groundwater samples ranged from 60 to 730 μM, with the highest concentration observed in the most saline bore. Conceptually, nitrate concentrations should increase along groundwater flowpaths, where these are underneath nitrate-fertilized crops. The nitrate concentrations in groundwater in the areas of discharge to the river are probably higher than that recorded in many of the bores sampled. These high nitrate concentrations imply that groundwater discharge to the river must carry with it a significant flux of nitrate. Since even to diminish the nitrate concentrations in the river without an additional input of nitrate requires a high rate of denitrification, it seems unlikely that there is a substantial flux of nitrate-rich groundwater into the river for several kilometres upstream of the most downstream sampling point, where no groundwater samples were

obtained. This gives greater confidence that the samples collected are representative of the groundwater that is interacting with the river over the river stretch considered in this study.

Stable Water Isotopes: ^{18}O and ^{2}H

The chloride and bromide concentrations in river and groundwater samples suggest that evapotranspiration increases solute concentrations between the sampling points and the areas of discharge to the river. Stable water isotope data support this hypothesis and are also shown to be a suitable tracer for calculating groundwater discharge flux in this area. The calculation based on this corresponds well with the results of hydrograph separation in Chapter 4.

In Figure 5-9, the river and groundwater samples are seen to plot on a reasonably straight line, slightly offset from the global meteoric water line (GMWL). Between Peel1 and Peel3, the river water becomes more depleted in heavy isotopes; the opposite of a trend attributable to evaporation (*cf.* Clark & Fritz 1997). Under less than 100% relative humidity, non-equilibrium evaporation results in differential partitioning of ^{18}O and ^{2}H such that they plot on a line with a shallower gradient than the GMWL. The trend for river samples to become more similar to groundwater samples in their stable water isotope composition is exactly as would be expected from groundwater discharge to the river. This lack of an evaporation signature in the groundwater samples does not negate the hypothesis formed in the "Chloride and Bromide" section that evapotranspiration is important in the groundwater system, since transpiration, unlike evaporation, does not fractionate water isotopes (Turner *et al.* 1987, Clark & Fritz 1997). The absence of evaporation also makes calculation of groundwater discharge to the river more robust, since changes in isotopic composition can be attributed solely to water mixing.

The heaver isotopic signature of the river samples may support the interpretation of the hydrographs (Chapter 4) of flood recharge being significant for this aquifer. In high rainfall events, the rainwater is more depleted in heavy isotopes than it is during events of low rainfall, due to factors including raindrop size and the isotopic changes in atmospheric water vapour during a storm (Lee & Fung 2008). Groundwater recharged during either flood events (resulting from high rainfall) or directly from high rainfall events would be isotopically lighter than are average precipitation or river water.

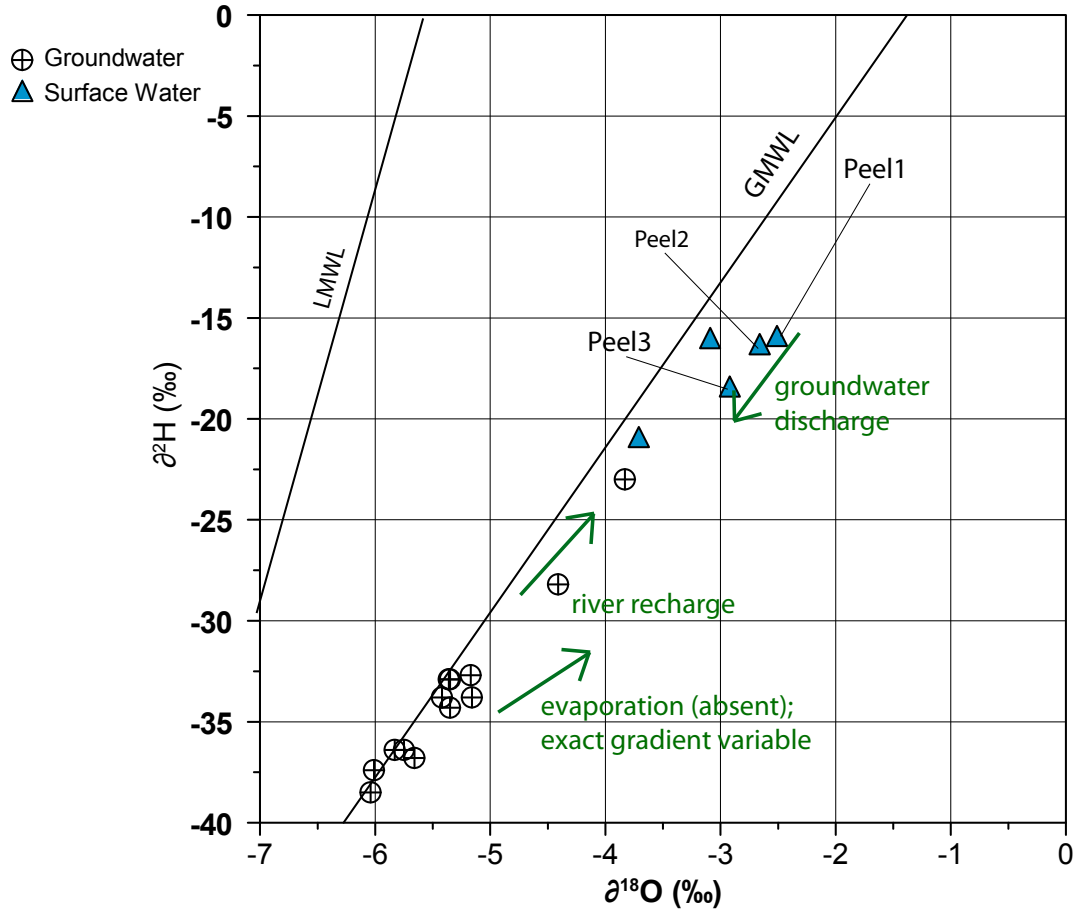

Figure 5-9 Stable Water isotopes with the Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL): equation from Rozanski *et al.* (1993). River samples are represented by blue triangles; groundwater samples by crossed circles.

Since precipitation is the ultimate starting composition of river water and groundwater (prior to any evaporation), knowing its local composition is a valuable reference when attempting to understand subsequent processes. A local meteoric water line (LMWL) is plotted with the data for river and groundwater samples in Figure 5-9. The LMWL has been constructed by taking the amount-weighted average of 19 water samples, mostly taken from the Gunnedah Resource Centre (BOM weather station No. 055024). The author is indebted to the Office of Water the Water Resources Lab and ANSTO for many of the datapoints. The equation of the line is $\delta^2H = 5.2 \times \delta^{18}O + 29.6$. For comparison, a LMWL constructed for the same area had an equation of $\delta^2H = 8.17 \times \delta^{18}O + 11.3$ (Andersen *et al.* 2008). The scatter of the isotopic signatures of rainfall samples encompass all of the water samples collected (see Appendix for rainwater data). The wide scatter of the data suggest that the line may not be representative of the long-term average at Gunnedah. A LMWL for Gunnedah would, however, be expected to have a shallower gradient than the GMWL, due to evaporation of falling raindrops in the arid climate.

The lack of deviation from the GMWL is interpreted not only as evidence that the rainfall in the present study area's catchment undergoes less evaporation during precipitation

than rainfall at Gunnedah, but as evidence that little evaporation occurs within the groundwater system. This is despite the evidence for substantial evapotranspiration along groundwater flow-paths outlined in the "Chloride and Bromide" section above. Increases in solute concentrations are therefore presumed be largely the result of transpiration – this is despite the possibility of substantial cycling of groundwater through extraction, irrigation, and loss from the fields to the water table. The plausibility of transpiration being responsible for the observed increase in solute concentrations in the groundwater system is explored in the "Capillary Fringe" section later in this chapter.

Water Isotopes: Groundwater Discharge Calculation

It has now been established, due to transpiration, that a simple mixing calculation between the groundwater samples and river water based on solutes cannot be used to calculate groundwater discharge. It was also seen in the previous section that neither groundwater nor the river appears to be subject to substantial evaporation, meaning that the stable isotope signature can be considered conservative. The late Autumn sampling time was probably helpful in this regard. Further, the change in the isotopic signature of river water is consistent with groundwater discharge to the river. In the "Nitrate" section, it was argued that groundwater discharge in the area where no samples were obtained is likely to be insignificant. River hydrograph analysis also indicates that little of the groundwater discharge is taking place over this part of the river (between Bective and Somerton). Groundwater discharge flux may now be estimated with some confidence based on the stable water isotope composition of the groundwater samples collected.

Water isotopes fractionate during evaporation and precipitation. Lighter isotopes preferentially evaporate, while heavier isotopes preferentially precipitate from water vapour. There are fewer complicating factors than for dissolved tracers (Kendall & Caldwell 1998). If distinct mixing endmembers can be characterised in this way, stable water isotopes can therefore be used to elucidate mixing. Discrimination of different water endmembers by stable water isotope analysis has become common (*e.g.* Katz 1998, Burns *et al.* 2001, Cartwright *et al.* 2006, Cartwright *et al.* 2007b). Occasionally, for example in the work of Katz (1998), such characterisation has been used to quantify the mixing of endmembers.

Between the three comparable river samples, Peel1, Peel2 and Peel3, the stable water composition of the river becomes more depleted in the heavy isotopes. This is consistent with the river gaining groundwater over this river reach. The groundwater samples are all more depleted than are the river samples and they plot on a line parallel to the local meteoric water

line. The alluvial groundwater has rather variable isotopic composition, making the choice of an appropriate endmember for mixing calculations difficult.

Excluding the two bores in an area of the alluvium that receive direct river recharge even during low flows (GW93014 and GW93013: adjacent to the river in the upstream bore transect, between Moore Creek and Attunga Creek), the two extremes are represented by GW93006 and GW93005. Taking GW093006, the groundwater sample least depleted in ^{2}H and ^{18}O (with the above exceptions), mixing of 15.4% of this with 85% of Peel1 would give Peel3 $\partial^{18}O$ composition. Performing the equivalent calculation using $\partial^{2}H$ values gives a groundwater contribution of 14.9 %. Taking GW93005, the most depleted groundwater sample, mixing 11.6 % of this groundwater with 88.4 % of Peel1 would give Peel3 $\partial^{18}O$ composition; making the calculation using $\partial^{2}H$ values gives 11.1 %.

After accounting for analytical errors, there is a groundwater contribution of between 8 and 21 % to the Lower Peel River is implied. This assumes that the mean discharging groundwater isotopic composition is not outside the extremes of the water sampled (excluding samples influenced by bank storage). Since neither of the above samples are affected by bank recharge, their isotopic signatures are not diluted by recent direct river recharge. In the actual river system, with stretches balanced between gaining and losing, bank storage is likely to occur, so this range of values should be considered a groundwater contribution *sensu stricto*. In contrast, the estimates of groundwater contribution based on the flow data would include any bank storage contribution. However, the bank storage contribution is likely to have been small at the time of sampling, since the streamflow at this time was greater than at any time during the previous month (see Chapter 4).

This range of 8 to 21 % is very similar to the figures computed from baseflow calculations (10.0 ± 6.5 %, see Chapter 4), although the baseflow calculation indicate that all of this increase is occurring between the sites of samples Peel1 and Peel2, with no approximately no change between Peel2 and Peel3 (Bective and Somerton). It is hypothesised that there is significant groundwater discharge just upstream of the sampling site Peel2, resulting in incomplete mixing. The river sampling procedure, sampling only a point near one edge of the river, could easily produce a non-representative sample. This is especially true as the river's shallow gradient results in non-turbulent flow, meaning mixing of the river water will be slow. There does not seem to be significant groundwater discharge flux downstream of this area (as supported by evidence in the Nitrate section of this chapter), so the sample obtained at Peel3 probably represents the stable isotope composition of water at site Peel2, but fully mixed.

The close agreement of these two independent methods implies that the baseflow separation technique employed in the previous chapter is appropriate and that the streamgauges were as reliable as estimated. The methods' close agreement also implies that the sampling of a limited number of groundwater bores does give a reasonable representation of the isotopic signature of the water discharging to the stream. It also demonstrates that no other water inputs, such as input from a bedrock aquifer, are required to account for the change in isotopic composition of the river water.

This level of groundwater discharge, increasing flow by ~ 10 %, is higher than seems to be average for this area (~ 4 % from hydrograph analysis). This may indicate that groundwater discharge is high after periods of rain, even when the stream level is higher than average.

Transpiration

The hypothesis that evapotranspiration substantially increased solute concentrations in groundwater along flow-paths between the points where samples were collected and the areas of discharge to the river was first raised in the "Chloride and Bromide" section of this chapter. The stable water isotopes indicate that evaporation is not significant in the groundwater system, or the river. The plausibility of the hypothesis that transpiration is responsible for the concentration of solutes in groundwater is now investigated in detail.

Blackburn and McLeod (1983) reported major ion composition for rainwater samples collected across the Murray-Darling Basin in 1974-75, including at Gunnedah. They reported that average chloride concentration was 31 μM. Pearson1, the groundwater sample between river sample sites Peel1 and Peel3 most concentrated in chloride, is 57 times more concentrated in chloride than this. At least some recharge from the river is likely and some may be from a bedrock aquifer, so the increase in chloride is actually from a concentration higher than that of rainwater. However, the parts of the alluvium furthest from the river (which also have hydraulic gradients towards the river) do not receive river recharge, except during floods, when river water would be expected to be relatively fresh.

The edges of the alluvium may be recharged from an abutting bedrock aquifer; all the alluvium receives river recharge during flooding. If all recharge came from the river, transpiration of groundwater must still be concentrated by a factor of at least 4 along the flow-path before discharging to the river (based conservatively on the Cl^- concentration of river water at Peel1 and a groundwater contribution calculated from physical data and stable water

isotopes of ~15 % at the time of sampling). The implication is that the cropping regime allows at least this rate of transpiration.

Transpiration clearly does achieve this degree of recharge in the area, as demonstrated by the chloride concentrations in a near-by alluvial bore. GW93015, a bore upstream of Peel1, and unlikely to be on a groundwater flow-path discharging downstream of Peel1, does have chloride concentration high enough to account for the increase in salinity in the river, if it were discharging at this point.

Lucerne, the most deep-rooted crop grown in the area, may have roots as deep as 4.5m, although its root system is generally confined to shallower depths if irrigated (McCallum *et al.* 2001). The greatest depth to the water table recorded at the sampling time was *c.* 5.5 m. Therefore, large-scale transpiration could only occur either in the capillary fringe (during either natural recharge or irrigation), or when the water table is elevated. Cycling of groundwater through irrigation may play a role, providing multiple occasions for the 'same' water to undergo evapotranspiration in the unsaturated zone. However, the reader is reminded that this cycling does not result in an observable evaporation signature in the groundwater, as evidenced by the stable water isotope data.

Capillary Fringe Water Use

Since the water table is not within the root zone, water use from the capillary fringe must explain the increase in solute concentration. This is plausible based on the existing knowledge of the soil and alluvium and from studies in other areas.

In a study of a sandy/sandstone aquifer in Israel, the capillary fringe was found to extend to a maximum of just over 2 m above the water table, although with spatial variation of approximately 1 m in capillary fringe height over a few metres horizontally (Ronen *et al.* 1997). The same authors undertook modelling which suggested that this degree of variation is possible even in macroscopically homogenous sediments. Later work on the same aquifer by the same researchers found that the capillary fringe was more variable after a wet period. Lack of homogenous behaviour in the capillary fringe was explained by both micro-scale grain size variation and by hypothesised variation in packing (Ronen *et al.* 2000).

The top 1-4 m of the Peel Valley alluvium is clay-rich (NOW 2010d). Below this, an examination of drillers' logs from the construction of piezometers (available from the NSW Office of Water) indicate layers of clays, sands and gravels, often with clay incorporated into

other layers (*e.g.* "sandy clay" or "gravelly clay"). The height of capillary rise is related inversely to the width of the capillary by the following relation (Atkins & de Paula 2006):

$h = \frac{2\gamma}{\rho g r}$, where: h = height of capillary rise,

γ = surface tension, ρ = density of the liquid,

g = acceleration due to gravity,

r = capillary radius.

In a soil profile, the "throat size", the size of the opening between grains, is equivalent to the capillary diameter. Smaller grain sizes thus allow for greater capillary rise. In real soil systems, water content in the capillary fringe does not drop suddenly at a definite height above the water table. Due to the random geometry of real sediments, especially heterogeneous ones, the water content may vary gradually in the capillary fringe. The same factors can result in small-scale (metres) horizontal variation in capillary fringe thickness (Ronen *et al.* 1997). Given that a capillary fringe of up to two metres thickness is reported for a relatively homogenous sandy aquifer, the capillary fringe in the Peel alluvium is likely to be higher than this in at least the clayey patches in the alluvium. To allow significant water to be available for transpiration does not necessarily require that water is everywhere available for transpiration. It is quite reasonable to assume that the capillary fringe is within the root zone of crops over significant parts of the alluvium.

Using a value of 2 μm for pore throat diameter and γ from Tschapek & Falasca (1986), a capillary rise of approximately 7 m would result:

$$h = \frac{2\gamma}{\rho g r} = \frac{2 \bullet 0.072 Nm^{-1}}{1000 kgm^{-3} \bullet 9.81 ms^{-2} \bullet 2 \bullet 10^{-6} m} = 7.3m$$

2 μm is the maximum value obtained on a study of clay-rich marine sediments by mercury porosimetry (Bolton *et al.* 2000). This value is considered a reasonable point for the Peel Alluvium's sandy clays (which may have relatively large pore throats due to the presence of sands). The above figure for capillary rise is uncertain, since the above calculation makes the false assumption of homogeneity and the actual pore throat diameters are not known. Nevertheless, the *ab inito* method (with crude assumptions) and with values reported elsewhere both demonstrate the plausibility of a capillary fringe thick enough to allow substantial transpiration by crops.

Indeed, the former Soil Conservation Service of NSW reported that sufficient soil moisture is available to plants for much of the year in the Tamworth area (Amos 1979). This

may be due to some extent by slow transport of water to the saturated zone, in which case it still provides a mechanism for rainwater to become somewhat concentrated. Even if this is the case, it does not preclude significant patches of capillary fringe water close to the surface, as discussed in the above paragraphs. It is therefore entirely plausible that the capillary fringe allows crops to access groundwater, resulting in substantial transpiration of the groundwater and accounting for the observed increases in chloride and bromide concentrations.

Environmental Implications

The Lower Peel River's salinity, as measured by electrical conductivity (EC), has been considered to be of concern. The Lower Peel was reported to have higher EC than any other monitored site in the Namoi Basin in the late 1990s (Nancarrow 1998). Although EC is usually considered a proxy for sodium and chloride concentrations, in this river system the high levels of calcium, magnesium and bicarbonate (see "Calcium and Magnesium" section in this chapter) contribute substantially to EC; chloride and sodium concentrations are lower than might be inferred solely from EC measurements

Whether salinity has increased as a result of human activities in the area is not clear. The change in the evapotranspiration system after the development of agriculture and later development of the groundwater resource is difficult to quantify in the absence data prior to clearing and irrigation. Lucerne, one of the area's dominant crops, is thought to produce greater transpiration than most crops. Native vegetation produces greater transpiration than other types of land-use (Dawes *et al.* 2004). The lesser transpiration potential of annual and perennial crops compared to native vegetation is partly counterbalanced by the effect of cycling groundwater via irrigation. It is therefore unclear whether the salinity of the river, described as an environmental problem (Nancarrow 1998), is actually higher than prior to human disturbance.

Sodium and Potassium

In the first part of this chapter, it was observed that between Peel1 and Peel3, Cl, HCO_3, Ca and Mg all increased, consistent with influx of groundwater of broadly similar composition, but at higher concentration. However, the Na concentration increased only slightly. The Na/Cl ratio decreases in the river from 1.3 to 0.53 between Peel1 and Peel3. A simple influx of groundwater of the compositions measured cannot explain this change: the lowest Na/Cl ratio

measured in a groundwater sample was 0.53. Similarly, the K/Cl ratio in the river decreases from 0.14 to 0.009. This change actually reflects a reduction in K concentration from 0.17 mM to 0.10 mM over the same river reach. It is demonstrated below that this behaviour does not detract from the likelihood of the proposed model for groundwater flow and influx into the river as proposed in the preceding sections of this chapter. Rather, this behaviour is likely the result of cation exchange.

Calculations performed with PHREEQC (Parkhurstand & Appelo 2010) indicated that no K- or Na-containing minerals are close to saturation in any water samples. The highest saturation index for the sample most concentrated in Na was -3.62 for nahcolite in GW93015; indices for K-minerals were even lower. Since precipitation cannot explain the behaviour of Na and K, the possibilities for cation exchange were investigated.

The region's feldspars (see chapter 2) may weather in part to produce Na smectites, consistent with the reported "cracking" natures of the clays of the alluvium (Hird 1979). Smectites have a high cation exchange capacity of 800-1500 meq/kg. The region's mudstones are known to be much richer in Na than K (Morris 1988), so it is reasonable to postulate the clays formed as weathering products do too. Potassium is held more strongly than sodium (Deer *et al.* 1992), so replacement of Na by K in smectites (or other clays) in the region is plausible. Clays in the riverbed thus could explain the diminishing K concentrations in the river.

A similar process is almost certainly also occurring within the alluvium, with water interacting along the flowpaths, potentially changing in composition between the points of sampling and areas of discharge to the river. The K/Cl ratios in the groundwater samples as well as river samples are lower than that reported for the local rainfall. K/Cl ratios were as low as 0.009 in groundwater samples and only as high as 0.14 in a river sample (Peel1). Local rainfall ratios are about 0.16 (Blackburn & McLeod 1983).

While not as favoured as exchange resulting in K in the interlayer, the lack of increase in Na in the river water (despite increasing Cl and the presence of Na in the groundwater samples) implies that Na is also exchanging with other cations (Ca or Mg). This may also be occurring both in the clays of the alluvium and along the riverbed.

Further investigation of these exchange phenomena would require mineralogical investigations of the clays of the riverbed and alluvium. For the present study, it is sufficient to observe that the trends in Na and K concentration in the river do not contradict the pattern of groundwater discharge discussed in this work.

Temporal Variations

The river and groundwater samples collected for this study represent only a single point in time. A NSW Office of Water chemistry monitoring study from July 2002 to November 2007, comprising data at Paradise Weir from 62 dates provides some understanding of long-term variation and chemical associations in river water. Paradise weir is located in Tamworth, ~ 19 km upstream of sampling site Peel1. A cross-correlation table is presented in Table 5-4 in order to show the consistency of water chemistry, independent of gross concentration.

Table 5-4 Cross-correlation (r) values for analyses from Paradise Weir between 2002 and 2007. From data provided by the NSW Office of Water, Tamworth.

	Ca	HCO_3	Cl	Mg	SO_4	K	Na
Ca	1.00	0.88	0.91	0.93	0.38	-0.26	0.93
HCO_3	0.88	1.00	0.74	0.93	0.02	-0.07	0.75
Cl	0.91	0.74	1.00	0.81	0.54	-0.43	0.92
Mg	0.93	0.93	0.81	1.00	0.24	-0.12	0.85
SO_4	0.38	0.02	0.54	0.24	1.00	-0.44	0.58
K	-0.26	-0.07	-0.43	-0.12	-0.44	1.00	-0.35
Na	0.93	0.75	0.92	0.85	0.58	-0.35	1.00

The generally high correlations between chloride, bicarbonate, magnesium and sodium imply that flow conditions do not impact greatly on river chemistry, other than by dilution/concentration. This may further imply that the river's water sources do not vary greatly with flow, or simply that the different water sources are chemically similar (with the limited range of analytes available in this dataset).

Of particularly interest are the weakly negative correlation coefficients for K. This supports the hypothesis of cation exchange of K for Na clays, even though there is not a strong inverse correlation between K and Na. This is because Na's much higher concentration relative to (~ 7 times in local rainfall (Blackburn & McLeod 1983)) K would make this only a relatively minor source of Na. Generally, most other ions are correlated with each other, implying that they are controlled by a common set of processes.

The temporal variation in electrical conductivity at three sites on the river is presented in Figure 5-10. Electrical conductivity (EC) is roughly inversely correlated with river flow, although the pattern is more complex. The time series also shows there is consistently higher salt concentration in the lower part of the catchment (Carroll Gap) than further upstream (Paradise Weir, near Tamworth). Interestingly, much of this increase occurs between Paradise Weir and Appleby Lane (also the sampling point for this study's Peel1). This implies that a

similar salt-concentrating process to the one in the present study-area is operating in this stretch of the river.

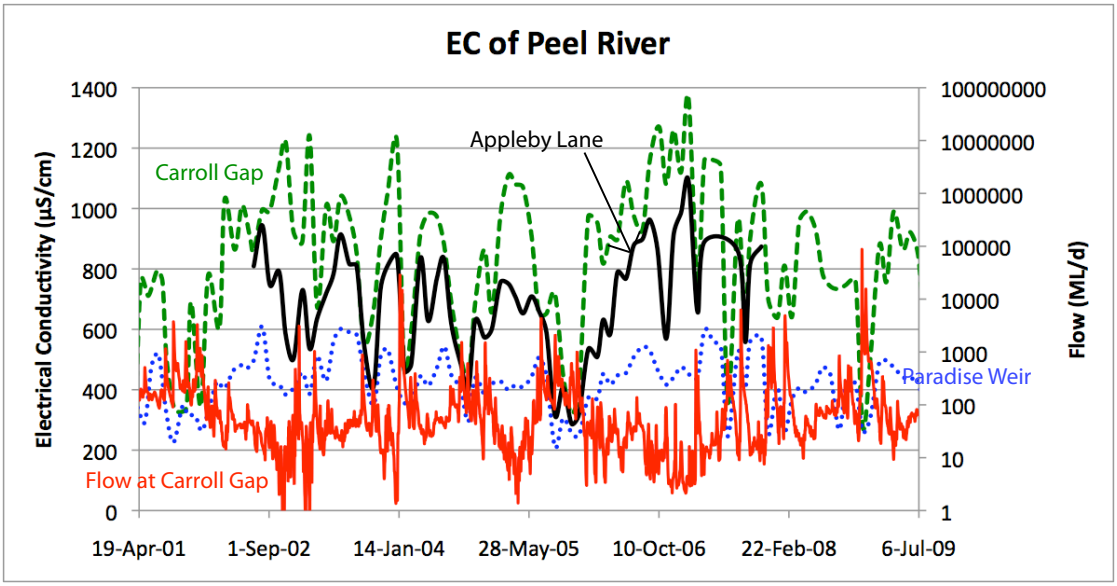

Figure 5-10 Figure displaying electrical conductivity at Carroll Gap (downstream of study area); Paradise Weir (upstream of study area, downstream of Tamworth); and Appleby Lane (site of stream gauge 419073 and sample Peel1). Streamflow at Carroll Gap is shown in red for comparison.

Chapter Discussion

The results presented here highlight the importance of collating multiple lines of evidence for understanding the interaction of surface and groundwater, particularly combining of physical hydrogeological data with tracer results.

The importance of investigating a suite of chemical tracers in conjunction has been highlighted as valuable. Only by the combination of stable water isotope analysis with chloride and bromide analysis was it possible to elucidate the importance of transpiration the groundwater system.

Using this combined approach, it has been possible to confidently estimate groundwater discharge and to propose a conceptual model for the behaviour of the hydrological system. Transpiration has a major impact on the salinity of the groundwater, and through groundwater discharge, on the river. There is some evidence that interaction with a bedrock aquifer may be occurring, but it is ambiguous, and warrants further investigation.

It has been demonstrated that chemical tracers can be a robust methodology for elucidating the interaction of surface and groundwater. The approaches outlined in this work could be replicated in ungaguged rivers, providing estimates of the interaction of surface and

groundwater even in the absence of physical data. Where river hydrograph data are available, the approach used here could help to quantify the uncertainties of the hydrograph separation approach.

An important environmental implication of this study is that salinity levels in the river are not obviously increased by human activity. Measures to reduce the salt loading in the Namoi Basin should probably focus on other areas, for example, where halite dissolution has been induced by human activities.

The high degree of interaction between the river and alluvial groundwater system demonstrated in the Lower Peel suggests that water managers should consider the units together in this system. Although the connectedness of the river and groundwater systems is acknowledged (NOW 2010d), the present separate allocation of water in systems as highly connected as the Lower Peel should be reconsidered. Studies in other areas with highly connected shallow groundwater systems could use similar methodology to that used in this present work to establish the extent to which this area is comparable with other upper tributaries of Australia's major river system. This is particularly important at present, when ways of increasing river flow in the Murray Darling Basin are being investigated (MDBA 2010b).

Chapter 6. Conclusions

This work has successfully demonstrated that combined use of physical hydrogeology and chemical tracers can provide much more detailed understanding of a hydrogeological system than a single methodology would do. This unified approach has allowed for two independent quantifications, with agreement well within the error margins for the different methods, of the interaction between a river and associated groundwater system, giving confidence in the findings. The important implication of this work is that chemical tracers could be used to assess quantitatively the interaction of surface and groundwater in ungauged rivers and to provide greater confidence in estimates of interaction in gauged rivers.

Making combined use of physical hydrogeology and the first concerted chemical study of the Lower Peel catchment, a conceptual model of the flow was developed, in which transpiration is central to the chemical evolution of the groundwater. Discharge of groundwater with high levels of dissolved solids due to transpiration, was found to be responsible for the increase in dissolved solids in the downstream reach of the Peel River. Further conclusions relating to the Lower Peel River include that:

- The Lower Peel between Appleby and Bective (site of gauges 419073 and 419074) is a temporally variably gaining-losing reach, which on average appears to be gaining ~ 4 % due to groundwater discharge. There is small-scale spatial heterogeneity, with some parts of the reach usually losing, and others gaining.
- The seasonal variation in baseflow and hydrographs of bores near to the river imply that bank storage may be a significant part of groundwater discharge.
- The river stretch upstream of Attunga Creek and downstream of Moore Creek is losing close to Moore Creek and gaining near Attunga Creek, with groundwater flowing in the alluvium parallel to the creek along this stretch.
- Combined analysis of chemistry and of river hydrographs suggests that approximately all of the groundwater discharge between Appleby and Somerton at the time of this study was between Appleby and Bective; and that
- Flooding plays an important role in aquifer recharge.

Further Work

The methodology established in this work could be applied to other similar river reaches. Where hydrograph information is not available, it has been demonstrated that a

hydrochemical approach can be successful. Greater information on the dynamics of highly connected reaches of river systems would help water managers to make more informed decisions. This is particularly important in Australia at present, as water reform with long-term implications is being contemplated (MDBA 2010b). The present work demonstrates that a hydrochemical approach makes a useful adjunct to physical measurements, or in their absence, can be a reliable method for assessing the interaction of surface and groundwater on its own.

It is hoped that the understanding of the Lower Peel's hydrogeology gleaned from this work will be used to help refine modelling in this part of the Namoi Basin, including in the models of the Centre of Integrated Catchment Management's model of the Namoi Basin in the Lower Pee Valley.

Within the Lower Peel Valley, understanding of the hydrological system could be substantially improved, building on the results from the present study. To establish the exact locations of high-salinity groundwater discharge to the Peel River, a continuous electrical conductivity transect could be made of the river by boat. This would define the areas and degree of heterogeneity in groundwater discharge and help to focus further groundwater sampling work.

Isotopic strontium analyses could help to identify contribution of water from the fractured bedrock aquifer to the Peel River. Water from the bedrock aquifer is reasonably likely to have passed through carbonate rocks, which should have a distinct isotopic strontium signature.

Automated monitoring of groundwater levels in some or all of the bores in this study would much better constrain the response times of the system. The four bores GW93011, GW93012, GW93013 and GW93014 would be particularly valuable in this regard. With high temporal resolution, a pulse of recharging groundwater from the river moving gradually away from the river could be discriminated from diffuse recharge, affecting water levels in all the bores approximately simultaneously. Additionally, bank storage phenomena in the two of these bores adjacent to the river could be investigated in this way.

Detailed understanding of the chemical evolution of the groundwater would be facilitated by a mineralogical study of the soils, particularly clays. As discussed, cation exchange is thought to play an important role, but this hypothesis would be much strengthened if the chemical mineralogical of the unsaturated zone and river-bed were known.

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Appendices

Table 0-1 Rainfall samples used in construction of the Local meteric water line. All the datapoints excepting the May 2010 samples, which were analysed as part of the present study, were provided by the NSW Office of Water, Gunnedah, with the cooperation of the Australian Nuclear Science and Technology Organisation.

Date	$\partial^{18}O$ (‰)	$\partial^{2}H$ (‰)	Place	Rainfall (mm)
23-Oct-99	-4.16	-11.9	GRC*	3.6
9-Nov-99	-2.97	-3.8	GRC	16
28-Jan-00	-4.22	-14.1	GRC	3.6
9-Mar-00	-8.28	-60.9	GRC	38.4
4-May-00	-2.66	-11.8	GRC	8
1999 Tank	-2.81	-10.5	GRC rainwater tank	**
2-Nov-00	-3.77	-15.55	Emerald Hill	15
15-Nov-00	-4.54	-20.3	Emerald Hill	26.8
16-Nov-00	-4.72	-22.9	Emerald Hill	12
21/22-Nov-00	-3.28	-18.8	Emerald Hill	12
31-Oct-00	-4.58	-30.4	Emerald Hill	3.4
30-Oct-00	-4.58	-30.4	Bryson Park (property near Gunnedah)	1.4
27-Feb-01	-0.93	-11.1	Narromine	1.8
12-Mar-01	-10.19	-73.1	Narromine	55.6
3-Apr-01	-2.96	-9.8	Narromine	15
25-May-10	-3.50	-9.7	GRC	1.6
26-May-10	-7.71	-42.3	GRC	15.2
29-May-10	-3.29	-5.8	GRC	8.4
30-May-10	-6.02	-29.7	GRC	7.6

* GRC denotes the Gunnedah Resource Centre, BOM weather station 55024
** Actual rainfall unknown; 100 mm was used for construction of the LMWL

Table 0-2 Analytes below method detection limits.

Analyte	Detection limit (µM)	AnalyticalMethod
Co	0.3	ICP-MS
Cr	0.2	ICP-MS
Li	14	ICP-MS
V	0.1	ICP-MS
PO4	160	Ion Chromatopgraphy

Table 0-3 Water Chemistry data for Paradise Weir, streamgauge 419024. Data supplied by the NSW Office of Water, Tamworth.

Date	Time	Soluble Ca	Alkalinity as HCO_3	Cl	Mg	SO_4	K	Na	PO_4	Charge balance
		mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	µmol/L	
5-Jul-06	11:30	1.00	4.10	0.73	1.03	0.29	0.03	1.57	1.00	0.02
7-Aug-06	10:20	1.15	4.59	1.04	1.15	0.41	0.04	1.78	1.12	0.00
5-Sep-06	12:30	0.85	3.77	0.56	0.91	0.22	0.04	1.22	0.92	0.00
11-Oct-06	13:00	0.80	3.61	0.45	0.82	0.19	0.04	1.09	0.88	-0.01
5-Nov-06	15:14	0.75	3.44	0.37	0.82	0.17	0.05	1.00	0.84	0.01
5-Dec-06	10:40	0.80	3.61	0.48	0.82	0.18	0.04	1.09	0.88	-0.01
9-Jan-07	12:15	0.85	3.77	0.65	0.86	0.23	0.04	1.17	0.92	-0.03
6-Feb-07	9:30	0.77	3.61	0.37	0.82	0.16	0.04	0.91	0.88	-0.02
5-Mar-07	12:45	1.02	3.77	0.65	0.99	0.48	0.05	1.44	0.92	0.01
9-Apr-07	10:15	0.87	3.93	0.56	0.86	0.20	0.04	1.09	0.96	-0.03
8-May-07	14:40	1.25	4.42	1.04	1.23	0.41	0.04	1.78	1.08	0.04
4-Jun-07	15:50	1.25	4.42	1.07	1.15	0.42	0.04	1.65	1.08	0.01
9-Jul-07	8:30	1.20	4.75	1.13	1.19	0.45	0.04	1.96	1.16	0.00
6-Aug-07	8:05	1.02	3.93	0.93	1.07	0.69	0.03	1.91	0.96	-0.01
3-Sep-07	13:10	0.87	2.95	0.54	0.82	0.59	0.04	1.39	0.72	0.02
9-Oct-07	7:50	0.62	2.46	0.37	0.58	0.37	0.04	1.00	0.60	-0.02
2-Dec-07	14:20	0.97	4.10	0.76	0.99	0.36	0.04	1.48	1.00	-0.01
6-Jan-08	13:50	0.82	3.77	0.37	0.91	0.17	0.05	1.13	0.92	0.02
4-Feb-08	15:10	0.72	2.79	0.45	0.66	0.28	0.06	1.04	0.68	0.01
2-Mar-08	9:20	0.65	2.79	0.45	0.62	0.24	0.05	1.00	0.68	-0.02
7-Apr-08	16:10	0.87	3.44	0.62	0.82	0.25	0.03	1.26	0.84	0.01
9-Jun-08	13:05	0.85	3.77	0.73	0.82	0.27	0.03	1.22	0.92	-0.05
7-Jul-08	12:00	1.10	3.93	0.99	1.07	0.37	0.03	1.61	0.96	0.03
3-Aug-08	8:40	0.85	2.95	0.65	0.82	0.52	0.04	1.35	0.72	0.01
8-Sep-08	10:00	0.72	2.79	0.45	0.78	0.50	0.04	1.22	0.68	0.00
7-Oct-08	14:20	0.55	2.13	0.31	0.53	0.25	0.04	0.87	0.52	0.02
3-Nov-08	8:30	0.90	3.44	0.45	0.62	0.21	0.03	1.44	0.84	0.02
9-Dec-08	12:30	0.77	3.28	0.45	0.82	0.18	0.04	1.13	0.80	0.03
6-Jan-09	9:00	0.80	3.28	0.59	0.74	0.26	0.04	1.22	0.80	-0.01
8-Feb-09	17:00	0.85	3.44	0.42	0.91	0.17	0.05	1.17	0.84	0.06
11-Mar-09	15:50	0.80	3.61	0.42	0.86	0.19	0.05	1.13	0.88	0.01
6-May-09	16:20	0.77	3.61	0.37	0.91	0.17	0.05	1.04	0.88	0.02
8-Jun-09	11:40	0.72	3.93	0.48	0.95	0.20	0.04	1.13	0.96	-0.03
7-Jul-09	15:20	0.87	3.93	0.73	0.91	0.26	0.04	1.30	0.96	-0.03
4-Aug-09	14:00	0.70	2.62	0.56	0.70	0.41	0.03	1.13	0.64	-0.01
6-Sep-09	11:50	0.37	1.23	0.18	0.35	0.31	0.05	0.61	0.30	0.02
7-Oct-09	15:45	0.62	2.46	0.42	0.62	0.28	0.03	0.96	0.60	0.00
9-Nov-09	15:35	0.50	2.13	0.17	0.49	0.21	0.04	0.83	0.52	0.02
7-Dec-09	14:40	0.50	2.13	0.22	0.45	0.22	0.04	0.78	0.52	-0.01
12-Jan-10	17:00	0.77	3.44	0.34	0.86	0.16	0.05	1.04	0.84	0.03
16-Feb-10	9:00	0.75	3.61	0.34	0.82	0.15	0.05	1.00	0.88	0.00
10-Mar-10	15:30	0.92	3.93	0.62	0.99	0.22	0.05	1.26	0.96	0.01
7-Apr-10	15:00	0.82	3.77	0.48	0.91	0.19	0.04	1.09	0.92	0.00
4-May-10	15:30	0.85	3.93	0.59	0.91	0.21	0.04	1.17	0.96	-0.02
6-Jun-10	16:45	0.92	4.10	0.62	0.99	0.22	0.04	1.26	1.00	0.00
6-Jul-10	9:40	1.00	4.26	0.93	0.99	0.31	0.04	1.35	1.04	-0.04
9-Aug-10	9:40	1.12	4.26	0.99	1.11	0.35	0.03	1.61	1.04	0.01
6-Sep-10	10:00	1.05	4.26	0.82	1.07	0.29	0.03	1.57	1.04	0.01
5-Oct-10	13:45	0.92	4.10	0.56	0.95	0.23	0.04	1.22	1.00	-0.01
8-Nov-10	13:00	0.82	3.77	0.45	0.95	0.17	0.05	1.26	0.92	0.03
7-Dec-10	13:00	0.82	4.10	0.42	0.91	0.15	0.05	1.13	1.00	-0.02
5-Jan-11	13:50	0.87	3.93	0.51	0.99	0.19	0.04	1.26	0.96	0.02
2-Feb-11	12:30	0.80	3.77	0.51	1.03	0.16	0.05	1.39	0.92	0.05
8-Mar-11	11:30	0.87	3.77	0.54	0.86	0.15	0.07	1.22	0.92	0.02
4-Apr-11	9:15	1.10	4.59	0.93	1.03	0.43	0.05	1.70	1.12	-0.03
8-May-11	14:15	1.07	4.42	0.90	1.11	0.28	0.04	1.61	1.08	0.01
7-Jun-11	11:15	1.05	4.42	0.85	1.11	0.27	0.04	1.57	1.08	0.01
3-Jul-11	10:45	0.42	1.59	0.23	0.41	0.29	0.04	0.74	0.39	0.01
11-Aug-11	16:00	1.05	3.61	0.85	1.03	0.48	0.03	1.61	0.88	0.03
7-Sep-11	12:30	0.75	2.62	0.51	0.78	0.43	0.03	1.17	0.64	0.03
27-Sep-11	10:20	1.05	3.93	0.82	1.07	0.49	0.04	1.65	0.96	0.02
9-Nov-11	13:20	1.07	4.10	0.99	1.07	0.34	0.04	1.65	1.00	0.02