CHAPTER 4. ESTIMATING THE VARIABILITY OF RECHARGE RATES AND ITS RELATIONSHIP TO GROUNDWATER NITRATE CONCENTRATIONS

4.1. INTRODUCTION

There is no evidence of geological sources of nitrate in the vicinity of the study area (Waterhouse 1977). Therefore the elevated nitrate concentrations observed in groundwater and discussed in detail in Chapter 3 are expected to be derived from natural or anthropogenic surface sources. An understanding of the source of the nitrate would be aided by determining the origin of the groundwater. This includes an understanding of the geographic origin (locally recharged or transported by lateral flow) as well as the temporal origin of the groundwater. An understanding of when the water entered the groundwater system assists in determining potential sources of nitrate, and also allows determination of whether the sources remain.

As the historical groundwater nitrate data described in Chapter 3 illustrates that high levels of nitrate concentrations in groundwater were present in the early 1980s an understanding of the recharge mechanisms to the unconfined aquifer during that period can provide a basis for consideration of the historical nitrate data.

The estimation of diffuse recharge to unconfined aquifers is usually undertaken through measurement of physical properties (e.g. field measurements of percolation through the unsaturated zone, measurement of responses in groundwater levels), environmental properties (e.g. from soil and landscape types) or chemical properties (including isotopic compositions) of the groundwater system. The different methods have different advantages and applications and have been used to varying degrees in the region. Reference texts describing these various recharge methods have been produced (Clark and Fritz 1997, Mazor 1997, Armstrong 1998, Bond 1998, Cook and Herczeg 1998, Mook 2004).

Colville and Holmes (1972) used the interpretation of hydrographs to estimate recharge under different land uses south of the study area. De Silva (1994) combined the interpretation of hydrographs with landuse and soil associations to estimate vertical recharge to the unconfined aquifer for part of the study area. Bradley and his colleagues (1995) used the same method for reviewing vertical recharge for the entire Border Agreement Area (refer *Groundwater (Border Agreement) Act 1985*).

A variety of other studies have used an assessment of hydrochemistry, often combined with isotopic methods, to estimate recharge to both the confined and unconfined aquifers in the South East region. These include the studies by Love, Armstrong and Stadter (1992, 1994), Love and others (Love et al. 1993, Love et al. 1994) and Leaney and Herczeg (1995). A considerable number of studies have also been undertaken throughout the South East region to demonstrate the applicability of tritium (a radioactive isotope of hydrogen) to estimate groundwater recharge (Allison and Hughes 1972, Allison and Holmes 1973, Allison and Hughes 1974, 1975, 1978).

Although other methods of estimating recharge have more recently become popular, such as $^3H/^3He$, chlorofluorocarbon and other radioactive isotopes (Clark and Fritz 1997, Cook and Böhlke 2000, Manning et al. 2005), tritium methods have the advantage that the isotope is incorporated into the water molecule and therefore travels with the recharging water.

Peter Airey (Australian Nuclear Science and Technology Organisation) provided for this research tritium results from groundwater samples collected within the study area in the late 1970s. This sampling was undertaken as part of the studies by MacKenzie and Stadter (1981) however the data was not reviewed or published. This tritium data provided an opportunity to estimate recharge mechanisms for the study area during the period when elevated nitrate concentrations in groundwater were being initially studied.

This chapter describes the application of tritium analysis to model recharge rates and mechanisms, and the implications of these for investigating the source(s) of nitrate contamination to the aquifer.

4.1.1 Tritium

Tritium, ^3H or T, is the only radioactive isotope of hydrogen (Eisenbud et al. 1978) with a half-life of 12.32 years (Lucas and Unterweger 2000). The other two isotopic forms are common hydrogen or protium, ^1H, and deuterium, ^2H or D. The relative abundance of these isotopes of hydrogen in the hydrosphere is dominated by common hydrogen (99.9844%), with smaller amounts of deuterium (0.0156%) and tritium (0.000005%) (Mazor 1997, Hoefs 2004).

Due to the small concentrations of tritium that usually exist in nature, tritium concentrations are expressed in Tritium Units (TU). One TU is the number of tritium atoms per 10^{18} protium atoms (Ingraham 1998).

The main natural source of tritium to the hydrosphere results from bombardment of nitrogen by cosmic radiation in the upper atmosphere (Clark and Fritz 1997). This process generates ^3H atoms which quickly oxidise to form water which then falls to earth in precipitation (Ingraham 1998). The continuous process of tritium production in the upper atmosphere, its subsequent radioactive decay ($^3H \rightarrow \beta^- + {}^3He$) and incorporation in the world's oceans results in the natural tritium concentration in rainfall being consistently around 5 TU (Mazor 1997).

The opportunity for using tritium as a hydrological tracer arises because once tritium is incorporated into the water molecule (e.g. $^1H^3HO$) and isolated from the atmosphere (such as after it infiltrates into soil), the concentration of tritium will reduce as the result of radioactive decay only, such that;

$$a_t\,{}^3\mathrm{H} = a_0\,{}^3\mathrm{H} \cdot e^{-\lambda t} \qquad \text{(Clark and Fritz 1997)}$$

Where $\alpha_0{}^3\mathrm{H}$ is the initial concentration of tritium (TU), $\alpha_t{}^3\mathrm{H}$ is the remaining concentration of tritium after time t (in years). The first order decay term λ is equal to ln2 divided by the half-life of tritium (half life = 12.32 years).

The naturally low levels of tritium in rainfall might have limited its application for groundwater dating but this changed with the beginning of atmospheric testing of thermonuclear devices in the 1950s.

The production of tritium through the atmospheric detonation of thermonuclear devices results from the large quantities of neutrons emitted at the end of the chain reaction (Clark and Fritz 1997). These neutrons react with atmospheric nitrogen in the same process that produces tritium naturally through cosmic radiation, although the quantities are significantly greater. In 1963, when the maximum in atmospheric tritium was observed, tritium concentrations in rainfall reached up to 10,000 TU in the United States (Mazor 1997) and more than 5,000 TU in Central Europe (Dinçer and Davis 1967). In the southern hemisphere the peak of tritium in rainfall was one to two orders of magnitude lower (Doney et al. 1992).

The dramatic increase in tritium released into the stratosphere between 1952 and 1962 ceased in 1963 with a Soviet-American treaty banning atmospheric testing of thermonuclear devices (Eisenbud, et al. 1978, Clark and Fritz 1997). Although smaller tests by China and France occurred up until the 1980 (Östlund and Masin 1985, Clark and Fritz 1997), the radioactive decay of tritium, and its incorporation into the world's oceans, has resulted in tritium concentrations in precipitation now returning to natural, cosmogenic levels (Mazor 1997, Solomon et al. 1998).

While high tritium concentrations were reported, it is estimated that the amount of tritium water injected into the atmosphere from the 1961-1963 thermonuclear detonations was only in the order of 300-500 kg (Östlund and Masin 1985), however this was substantially more than the pre-1954 quantities-estimated to be 900 g (Evans 1974). That this quantity of tritium became so widely spread throughout the world's water is remarkable.

Other ongoing anthropogenic sources continue to release tritium into the atmosphere. These sources include underground detonation of fusion devices (which release tritium gas as $^3H_2$, $^2H^3H$ or $^1H^3H$), release of tritiated water from nuclear power plants and nuclear fuel reprocessing operations (Solomon, et al. 1998) and the manufacture and disposal of sealed tritium light sources (Östlund and Masin 1985). It has also been identified that tritium may be produced in the subsurface as a result of the spontaneous fission of uranium and thorium (Clark and Fritz 1997). The tritium produced through these other mechanisms may enter the hydrological cycle either directly or through interaction in the stratosphere. These types of sources are not likely to affect the study area.

4.1.2 The Use of Tritium as a Tracer in hydrology

Tritium was recognised as being useful for hydrogeology studies as early as the 1950s (Östlund and Masin 1985) and was used extensively until the 1980s for the aging of modern water (Clark and Fritz 1997). The key reasons why tritium was a valued tracer for hydrological studies through this period include;

1. The tritium atom is part of the water molecule (eg $^{3}H^{1}HO$) and not a dissolved tracer (such as, for example sulphur hexafluoride, chloride ion, ^{14}C or chlorofluorocarbons). This means tritium is not subject to the chemical or physical exchanges that need to be considered in some tracer applications. Tritium displays the same diffusion characteristics as water except for an insignificant difference in vapour pressure (Eisenbud, et al. 1978).

2. There are readily available data for tritium concentrations in precipitation throughout the world with many locations having monthly records back to 1960.

3. The injection of large quantities of tritium into the atmosphere occurred over a discrete period (1952-1963) and resulted in significant increases in tritium concentrations in precipitation. This meant that while natural (pre-1953) tritium concentrations in precipitation are difficult to detect in mixed groundwater samples (modern water and

older water), the elevated tritium concentrations of the younger recharge water can still be detected if mixed with very old water: having no detectable tritium.

4. Once tritium is no longer in contact with the atmosphere it is only lost by radioactive decay with the predicable half-life of 12.32 years.

A variety of methods have been adopted to make use of tritium to estimate recharge and to describe groundwater flow behaviour. Within the South East region, a number of studies have estimated recharge from tritium profiles in the unsaturated zone (Allison and Hughes 1972, Allison and Holmes 1973, Allison and Hughes 1974, 1975, 1978, Allison et al. 1985, Allison 1988). Tritium analysis has also been used in the region to estimate groundwater discharge as a means of understanding groundwater flow behaviour (Allison et al. 1975).

Allison, Holmes and Hughes (1973) sampled boreholes for tritium throughout the Northern Adelaide Plains (South Australia) to estimate recharge to an aquifer predominately recharged through infiltration from watercourses. This was undertaken by measuring the time taken for water to flow from the watercourses to a series of boreholes. A similar approach was used to determine groundwater flow and recharge contributions in an aquifer in Queensland where recharge was due to artificial and nature sources (Airey et al. 1974).

In the Padthaway area to the north of the study area, Allison and Hughes (1975) used groundwater tritium concentrations to develop a one-dimensional mixing cell model for an unconfined aquifer which was then able to predict the contribution of vertical recharge across the Padthaway area.

In studies where the intention is to estimate the quantity of recharge reaching the water table, measurement of tritium in groundwater may be more reliable than methods analysing tritium in soil moisture to estimate recharge. The latter may not be a reliable estimate of water actually reaching the water table (Dinçer et al. 1974).

Today, the use of tritium for quantifying groundwater flows may be limited due to the low concentrations of tritium in precipitation, and the time elapsed since the peak tritium in precipitation of the early 1960s. However, the availability of tritium data for groundwater within the study area during the late 1970s provided the opportunity to assess its recharge rates.

4.2. METHODS

4.2.1 Groundwater Isotope Data

Between 1975 and 1977 water samples were taken from 36 wells within the study area by staff of the (then) South Australian Department of Mines (Figure 4.1). The methodology included bore resampling at different stages within the year; with six discrete sampling events occurring throughout the three years. The sampling program has not been substantially documented and it was not possible to locate any field records. Available documentation indicated however that all samples were collected through the use of a suction pump, and that all wells were purged for at least thirty minutes (at a rate of 6,800 to 9,000 L/hr).

Departmental correspondence reported that the groundwater samples were collected from as close to the phreatic surface as possible, however samples taken in 1975 may have not have been from the top of the aquifer. Given the pumping technique of purging, and that the majority of the bores were open hole (only surface casing), the samples are likely to be composite across the depth of the aquifer that is penetrated.

All samples were analysed at the Australian Atomic Energy Commission (now the Australian Nuclear Science and Technology Organisation) for tritium concentrations (Table 4.1). The construction and water depth details for each of the bores listed in Table 4.1 is provided in Appendix 4.

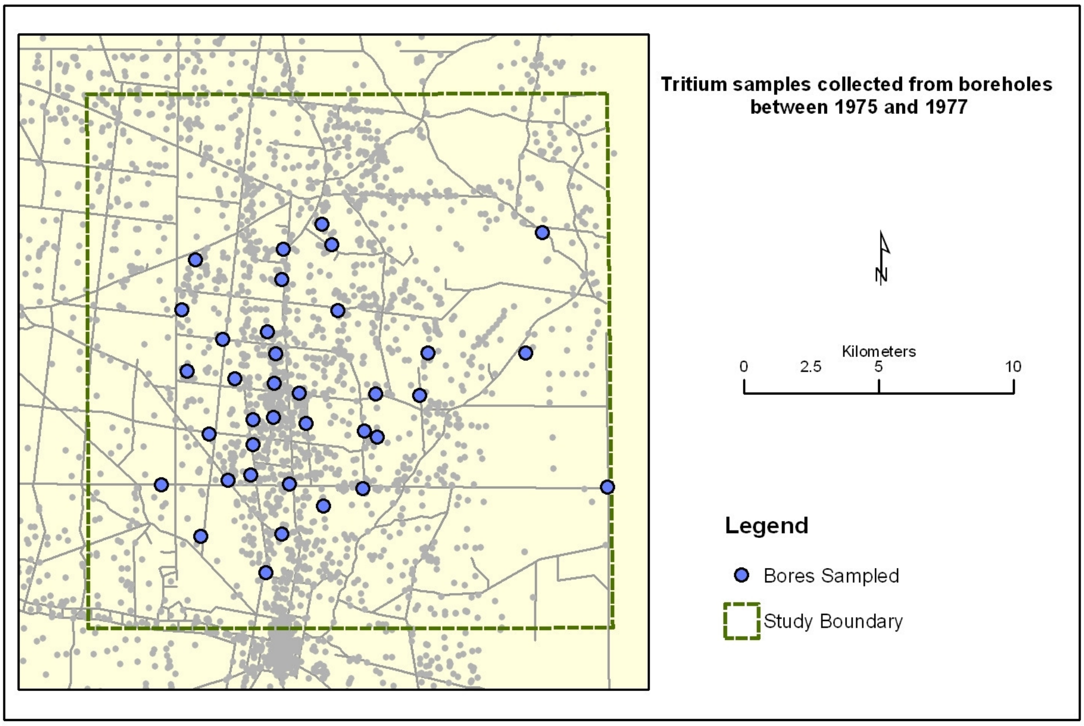


Figure 4.1: **The bore locations of tritium sampling in study area with all known bore locations plotted (grey)**

4.2.2 Tritium Input Function

In order to determine the tritium input into the unconfined aquifer it is necessary to construct a time-based input function; a Tritium Input Function (TIF). For the purposes of groundwater recharge studies, an annual tritium concentration, weighted according to precipitation is required (Allison et al. 1971). It is not valid to use the mean concentration in precipitation as the tritium concentration in recharge water because the former has pronounced seasonal variation. Coupled with this is the reality that recharge to an aquifer will only occur when the soil moisture is replenished and downward percolation occurs. Therefore the TIF was constructed to include the estimated tritium concentration, weighted against precipitation, for those months of the year where infiltration is assumed to occur (during winter and spring).

A TIF was constructed for the study area primarily based upon the tritium precipitation data available from the International Atomic Energy Agency

Table 4.1: Recorded tritium concentrations in groundwater with analytical precision in brackets

	Tritium Concentrations (TU) for Each Sample Date					
Borehole	**September 1975**	**February 1976**	**July 1976**	**October 1976**	**March 1977**	**September 1977**
702300028			5 (0.3)	7.1 (0.4)	5.5 (0.4)	
702300133				1.6 (0.3)	2 (0.4)	
702300310				5.1 (0.4)	3.2 (0.3)	
702300374					1.1 (0.3)	
702300504					0 (0.3)	
702300631	3.7 (0.3)	2.4 (0.4)	3.8 (0.3)	4.5 (0.4)	2.5 (0.3)	
702300636				8.1 (0.4)	5.1 (0.4)	
702300752			0.6 (0.4)	0.9 (0.3)	0.6 (0.4)	
702300903		5.9 (0.4)	6.8 (0.3)	6.8 (0.4)		4.1 (0.4)
702301464				2.8 (0.3)	2.3 (0.3)	
702301472			1.4 (0.3)	1.9 (0.4)	1.3 (0.4)	1.2 (0.4)
702301484				2.4 (0.3)		
702301490			1.5 (0.3)	1.5 (0.3)	2.2 (0.4)	
702301573					0.6 (0.3)	
702302605			4.8 (0.3)	5.3 (0.4)	4.8 (0.3)	
702302611		3.9 (0.4)	4.2 (0.4)	4.2 (0.4)	4.1 (0.4)	
702302624	0.5 (0.3)	4.4 (0.4)	0.7 (0.4)	1.2 (0.3)	1 (0.4)	
702302642		4.5 (0.4)	5.5 (0.4)	5.6 (0.4)	5 (0.4)	
702302653	3.9 (0.4)	5.8 (0.4)	3.9 (0.4)	4.6 (0.4)	3.9 (0.3)	3.8 (0.4)
702302702				5.6 (0.4)	5.3 (0.3)	
702302708			5.5 (0.3)	5.8 (0.4)	5.2 (0.4)	
702302723			2.4 (0.3)	3 (0.3)	3.6 (0.3)	
702302750				2.1 (0.3)	1.5 (0.3)	
702302831				0.8 (0.3)	0.8 (0.4)	
702302835				6.1 (0.4)	3.2 (0.4)	
702302846			5.6 (0.3)	4.8 (0.4)	5.3 (0.3)	
702302854		5 (0.4)	4.8 (0.4)	6 (0.4)	4.1 (0.3)	
702302861		3 (0.4)	3.3 (0.4)	4.1 (0.4)	4 (0.3)	
702302897				8.5 (0.4)		
702302957		2 (0.3)	3.2 (0.4)	1.6 (0.4)	1.9 (0.4)	
702302964	6 (0.4)	6.9 (0.4)	6 (0.4)	6.6 (0.4)	7 (0.4)	
702302974	1 (0.4)	1.5 (0.3)	2.8 (0.3)	2.3 (0.3)	2.5 (0.4)	
702302991				8.8 (0.4)	6.2 (0.4)	
702302992	0.4 (0.3)	1 (0.3)	1.1 (0.4)	1.5 (0.4)	1.3 (0.4)	
702302993				1.9 (0.3)		
702302999					0.7 (0.3)	

(IAEA) Global Network of Isotopes in Precipitation (IAEA/WMO 2004) and the daily rainfall data available for the Mount Gambier airport (50 km south of the study area; Clewett et al. 2003).

4.2.3 Determining Monthly Tritium Concentrations in Rainfall

The closest monitoring stations included in the Global Network of Isotopes in Precipitation (GNIP) were Adelaide and Melbourne. From the beginning of 1960 to the end of 1977, this dataset was generally complete, with 148 months having both Adelaide and Melbourne records, and 48 months having a record from at least one of the stations. Only 20 months of the 216 during this period had no records for either Adelaide or Melbourne (most of these being during 1960-1962).

The GNIP dataset did not contain results prior to 1960, and this reflects a general absence throughout the world of tritium rainfall data before this period (Dinçer, et al. 1974, Doney, et al. 1992). In recognition that groundwater recharge studies in the southern hemisphere are sensitive to tritium loading prior to 1960, Allison and Hughes (1977) estimated tritium in precipitation prior to 1960 from bottled wine grown near Adelaide. This provided average annual estimated tritium in precipitation for the years 1954 to 1960 that were also included in the rainfall input model. Since their study, the decay rate for tritium has been refined (λ = 0.0563/yr) (Lucas and Unterweger 2000) whereas Allison and Hughes (1977) used the then accepted decay rate (λ = 0.0565/yr).

An assessment of the impact of this altered decay rate showed that for the years 1953-1962, the updated decay rate predicted the mean tritium concentration to within 1% of that predicted by Allison and Hughes (1977). This is well within the analytical errors reported at the time (Allison, et al. 1971, Airey, et al. 1974, Dinçer and Davis 1984) and therefore the original figures by Allison and Hughes (1977) were used in this study.

Allison and Hughes (1977) did not report estimated tritium concentrations in precipitation for 1956-57 as they consider their results to be anomalously high. They did report a close ratio (0.96 – 1.06) between the tritium in precipitation in the lower South East region and Kaitoke (New Zealand). Sites at similar latitudes (and geographical settings) tend to display a strong correlation for tritium in precipitation (Dinçer and Davis 1967). Figure 4.2 shows the location of Kaitoke in relation to the study area. Following Allison and Hughes (1977) the annual mean tritium in precipitation for Kaitoke was used for the rainfall input model for the 1956-57 year.

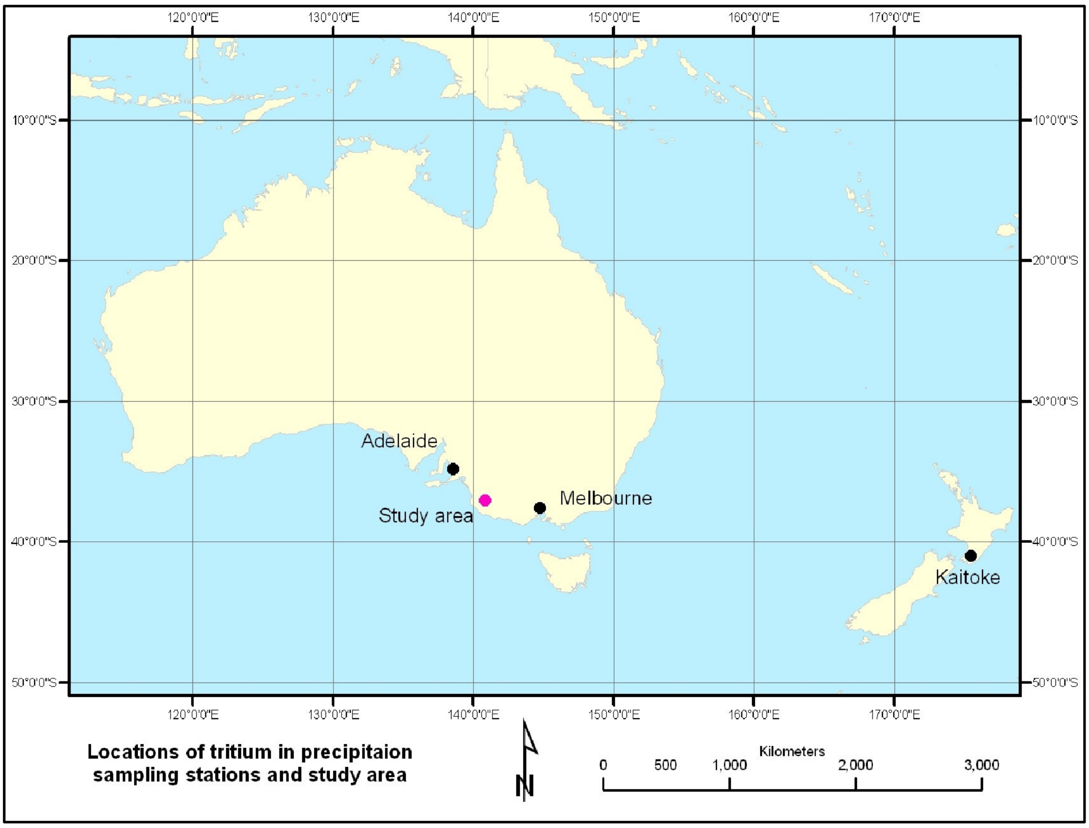


Figure 4.2: The location of tritium rainfall monitoring sites relative to the study area

Although the majority of the tritium in the hydrosphere is now stored within the world's oceans (Eisenbud, et al. 1978), the concentration of tritium in the oceans is very low. Allison and his colleagues (1971) suggested that rainfall near the coastline will consist of a greater proportion of 'ocean-originated' water and therefore the tritium measured in the rainfall will be lower. Their view was that further inland, the water vapour in the troposphere will be either replenished from the stratosphere or from evaporated surface water which will both have higher tritium concentrations (during the 1970s). However the reasonably close proximity of the study area to the coast (less than 200 km), and the absence of sufficient data to provide confidence in any ‘coast-separation’ algorithm resulted in the decision not to incorporate this aspect into the estimation of the tritium input function for this study.

The monthly concentrations of tritium in precipitation were calculated for each month for the study area from the period July 1953 to December 1977. Prior to 1953 the average annual tritium concentration in precipitation was assumed to be 5 TU, which is generally accepted to be the ‘pre-bomb’ tritium concentration for precipitation (Mazor 1997).

The following assumptions were used to estimate the monthly tritium concentrations in precipitation for the study area for the period between July 1953 and December 1977.

- As the study area is equidistant from Melbourne and Adelaide, for any months where GNIP data existed for both sites, an average of the two records were used. A comparison of tritium concentrations recorded at Adelaide and Melbourne showed that there were a small number of extreme variations in their values. An assessment of the correlation for the 10th to 90th percentile values (which excluded these large variations) showed a strong relationship (r^2=0.83) for $T_{Melbourne} = 1.07 \times T_{Adelaide}$.

- For those months where data was only available for either Melbourne or Adelaide, the above relationship could have been used to estimate the tritium concentration in precipitation for the study area. However this would mean adjusting the values by about 3.5% (3.5% up for Adelaide results and 3.5% down for Melbourne results). This percentage was within the error values of the analysis and so would not improve the accuracy of the final predicted values. In these instances, the value for either Melbourne or Adelaide was directly adopted for the study area.

- Prior to 1960, GNIP data did not exist, and between 1960 and 1963, the GNIP data was not complete. For the period between 1953 and 1963, the annual tritium concentrations reported by Allison and Hughes (1977) were converted to monthly values using an adaptation of the model developed by Doney and his colleagues (1992). Instead of estimating the seasonal variability based upon the normalising factors proposed by that research, the average annual tritium predicted by Allison and Hughes (1977) was used. The monthly predicted values for this period were then estimated from the equation;

  $$C_{monthly}(t) = [1 + a_m \cos(2\pi(t - \phi))].[A_{year}] \qquad \text{Equation 4.1}$$

  where $C_{monthly}(t)$ is the estimated tritium concentration for the month t, α_m is the amplitude of the seasonal variation, and ϕ is the phase of the year when the peak tritium concentration in precipitation occurs, the month (t) is reported as a decimal month, and A_{year} is the annual average tritium concentration in precipitation as predicted by Allison and Hughes (1977). The values used for the study area for the amplitude and phase values were an average of the two values proposed for Melbourne and Adelaide (Doney, et al. 1992), namely $\alpha_m = 0.341$ and $\phi = 0.21$.

- For the months between July 1956 and June 1957, where Allison and Hughes (1977) did not report an annual average, equation 4.1 was used to predict monthly tritium values based upon the average annual concentration reported at Kaitoke (New Zealand) in Allison and Hughes (1977).

- For the period between July 1900 and June 1953, equation 4.1 was used to estimate the monthly concentrations of precipitation from the average annual concentration of 5 TU.

4.2.4 Determining Months Contributing to Recharge

The second aspect of the TIF is to determine the period of precipitation (and therefore relevant tritium concentration) that contribute to recharge.

Allison and his colleagues (1971) assessed vertical drainage through lysimeters 50 km south of the study area and suggested that a reasonable approximation for the TIF for a particular year would be the precipitation average during the time when precipitation exceeds evaporation, and adopted April-September as these ‘recharge months’. They reported that this approach would be suitable where the water table is within 2-3 metres of the surface. For the study area an assessment of historical rainfall and evaporation data was undertaken and it was identified that the months of June to September defined the appropriate ‘recharge period’.

Rainfall was compared to pan evaporation data (Clewett et al. 2003) for each month between July 1900 and December 1977. Transpiration was not estimated for the study area, as it was assumed that transpiration only dominated during the summer months (when evaporation exceeded precipitation and rainfall was not contributing to recharge).

4.2.5 Calculating the Tritium Input Function

For each calendar year, the tritium loading (weighted tritium concentration WT_y) was calculated;

$$WT_y = \frac{\sum_{i=1}^{n} T_i P_i}{\sum_{i=1}^{n} P_i} \qquad \text{Equation 4.2}$$

Where T_i is the concentration of tritium in the precipitation for month i, P_i is the amount of precipitation for month i, and n is the months where precipitation exceeds evaporation.

The Tritium Input Function for the study area is included in Appendix 5 along with the calculated monthly tritium concentrations in rainfall. The relationship between the TIF and measured tritium concentrations in precipitation is shown in Figure 4.3.

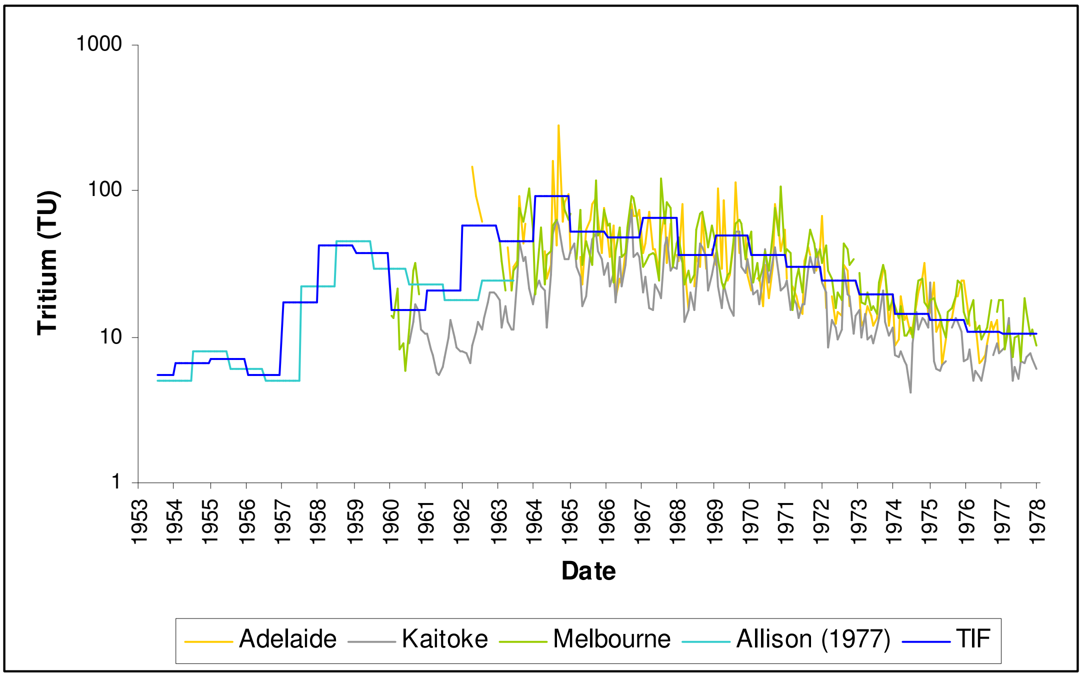


Figure 4.3: **The calculated Tritium Input Function of recharge water and the recorded tritium concentrations in precipitation**

4.3. RESULTS

4.3.1 Tritium Recharge Model

The estimation of recharge was adapted from the approach of Leaney and Allison (1986) where they studied vertical recharge to an unconfined limestone aquifer in the western portion of the Murray Basin using carbon-14.

In this study the tritium samples were collected from wells that intersected a small proportion of the total thickness of the Gambier Limestone aquifer, with 32 of the 36 bores sampled penetrating less than 10 metres into it. From

Chapter 2 the thickness of the Gambier Limestone aquifer through the study area is approximately 150 metres, and the study by Love and his colleagues (1993) indicated that the upper portions of the unconfined aquifer were dominated by local recharge (vertical drainage not lateral flow).

The model developed for this study therefore assumed that the lateral flow in the upper part of the aquifer was negligible. It follows from this assumption that annual recharge from surface infiltration will be retained in a layer, where the thickness of the layer will be the product of the volume of recharge and the saturated aquifer matrix. These assumptions relating to the aquifer flows are presented in Figure 4.4.

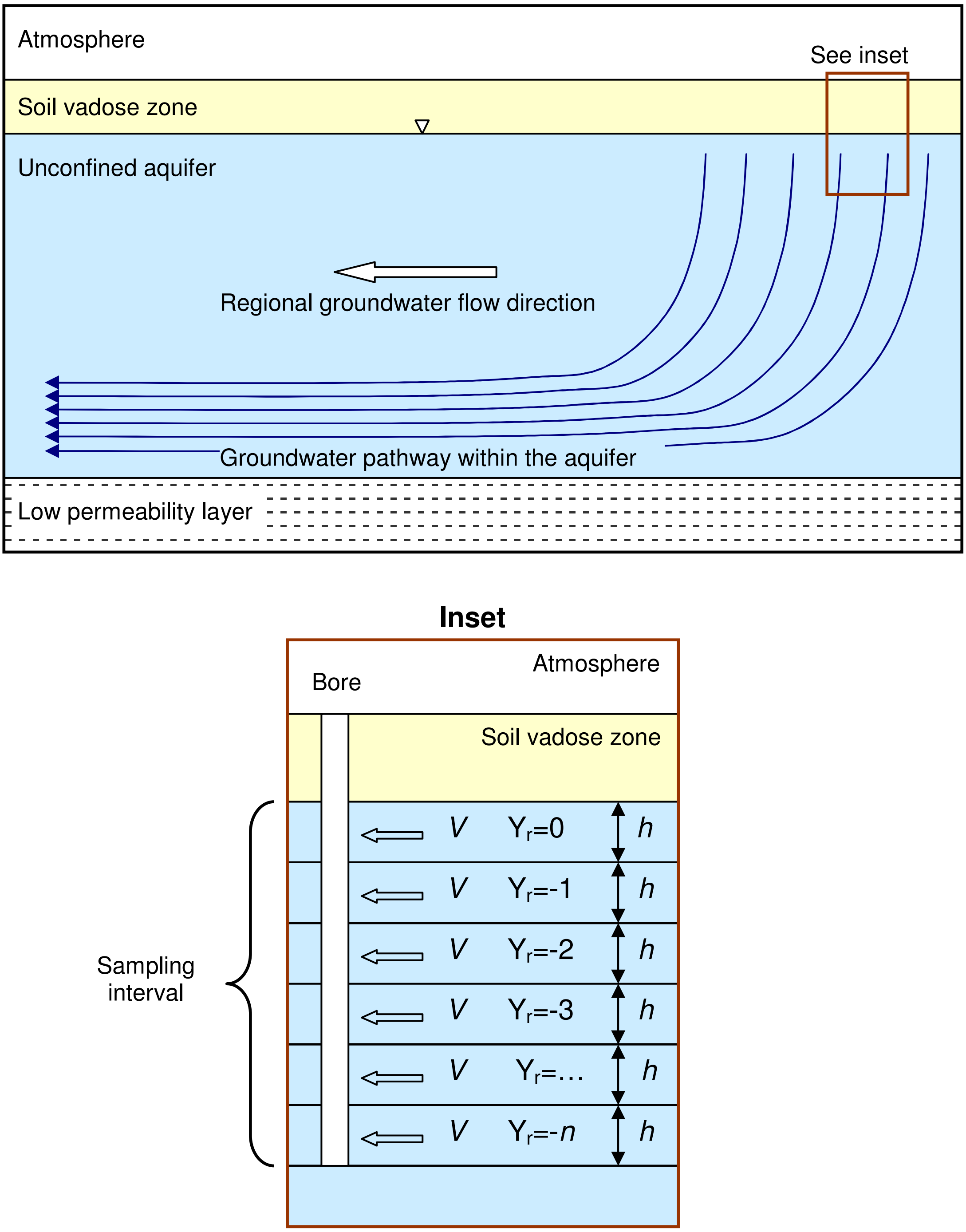
For the purposes of this study the average recharge rate was sought, and therefore the model assumed that the thickness of each "recharge-year" layer (*h*) was equal.

Based upon these assumptions, and by amending the approach of Leaney and Allison (1986), the following relationship was developed that describes the number of "recharge years" intersected by an open well;

$$n = \frac{D_B \alpha}{R} \qquad \text{Equation 4.3}$$

where n is the number of years of recharge intersected by the well, D_B is the depth in metres over which the well penetrates the aquifer, α is the porosity of the aquifer and R is the average annual recharge (m/yr).

The model developed by Leaney and Allison (1986) assumed that the volumetric contribution to any sample collected (Figure 4.4) would be same from each "recharge-year" layer. In this study only seven of the bores were recorded as having casing below the water table, with the rest known or assumed to be open hole construction (which is common in the South East region). Samples taken from these bores therefore are assumed to be composite samples from the phreatic surface to the total depth of the well.



V = Volumetric contribution from each “recharge-year” layer to a sample
Y_r = The year which the recharge layer infiltrated to the aquifer
h = The thickness of the “recharge-year” layer

Figure 4.4: **Conceptual cross-section of the unconfined aquifer illustrating the assumed aquifer flow and sampling contributions for the model**

Leaney and Allison (1986) reported that although many of their wells were cased to a particular depth below the water table, the outside of the casing was packed with gravel. In the South East region it is common practice that if wells constructed into the upper part of the Gambier Limestone aquifer are cased then the outside of the casing is backfilled with gravel. This is because the casing in these instances is used to prevent collapse of the wells and not to target specific levels of the aquifer. The gravel has a hydraulic conductivity significantly higher than the surrounding aquifer matrix and Leaney and Allison (1986) assumed that under pumping the wells acted as open holes.

Applying these assumptions, if groundwater samples are collected from a depth through an aquifer (from the water table), and the contribution to the sample is equally derived from across the aquifer interval, then the measured tritium concentration will be an average of the tritium concentrations of the depth of penetration. In Figure 4.4 the volume contribution (*V*) is equal from each “recharge-year” layer. These assumptions do not require that the aquifer is fully mixed over the sampling interval, only that the sample is equally derived from over the interval.

For this model an equation was developed that predicted the tritium concentration of any water sampled from the phreatic surface to a depth through taking an average of the residual tritium concentrations of each recharge year (corrected to the time of the sample), so that;

$$T_y = \frac{\sum_{i=0}^{n} \left(T_{t+i} e^{-\lambda(y-t+i)} \right)}{n} \qquad \text{Equation 4.4}$$

Where T_y is the tritium concentration measured in the bore sample in year y, T is the original concentration of tritium in the recharge water, λ is the decay rate of tritium, t is the year the water entered the aquifer, i is each discrete recharge layer within the aquifer, and n is the number of years of recharge layers that are intersected by the bore. Combining equations 4.3 and 4.4

produces an equation (4.5) to predict the tritium concentration in any sampled water from the phreatic surface to a known depth for any time;

$$T_y = \frac{R}{D_B \alpha} \cdot \sum_{i=0}^{n} \left(T_{t+i} e^{-\lambda(y-t+i)} \right) \qquad \text{Equation 4.5}$$

Due to the shallow nature of the aquifer, the permeability of the thin unsaturated zone and the winter response observed through hydrographs, it was assumed for this model that the recharge that occurred during the winter months entered the aquifer in the same year so that $y = t$.

Once a relationship between sample depth and radioactive isotopes is developed, Leaney and Allison (1986) demonstrated that theoretical recharge profiles could be constructed for bores by applying a number of categorised porosity and recharge rates.

The porosity values used for the upper portion of the aquifer matrix were 30%, 40% and 50%, with final mapping of recharge estimates based upon 40%. Porosity estimations from borehole geophysical logs for the Gambier Limestone aquifer in the region vary from 30 to 50%, with measured porosities from outcropped formations range from 48.6 to 60.6% (Love, et al. 1992). A porosity of 40% has been used in other regional studies when modelling recharge rates from groundwater tritium concentrations (Allison and Holmes 1973).

The profiles for two periods of October 1976 and March 1977 are provided in Figures 4.5 and 4.6. Included on these figures are the actual tritium concentrations measured from the sampling program.

Profiles were not generated for the other periods of data collection due to their reduced numbers of samples. However all samples were used to calculate recharge values based upon the model assumptions.

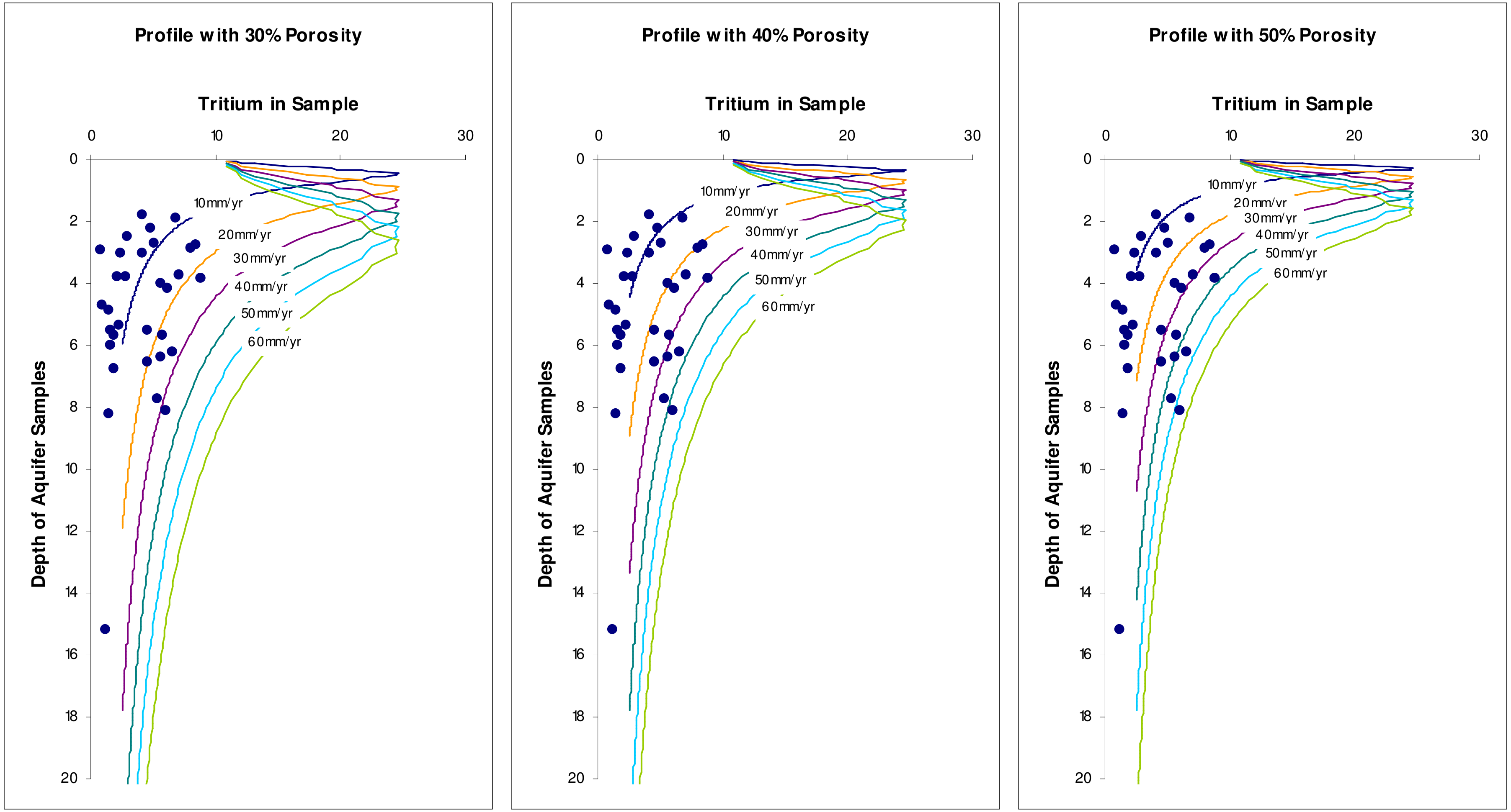


Figure 4.5: The groundwater samples (October 1976) compared to predicted tritium concentrations for recharge estimates

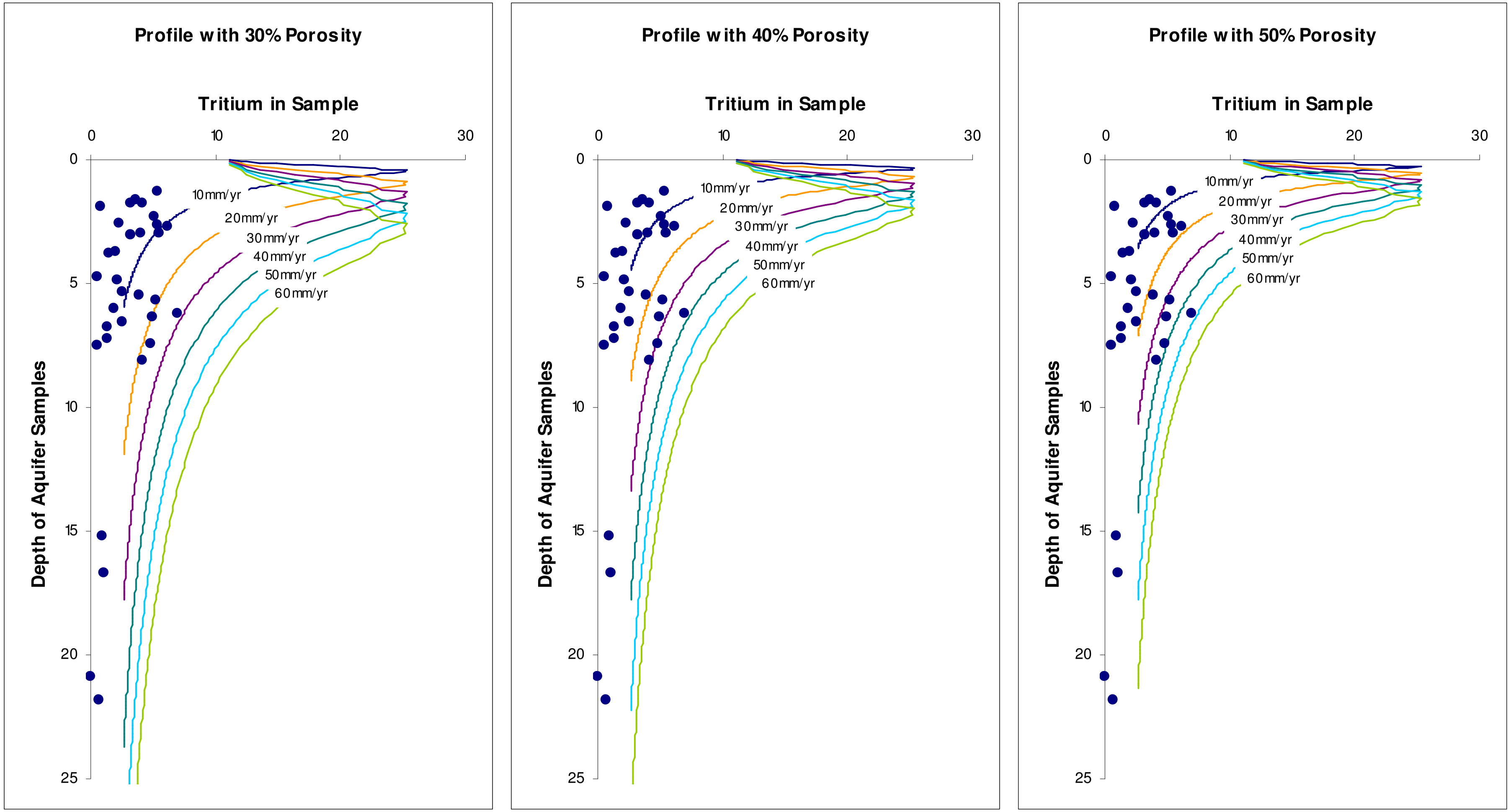


Figure 4.6: The groundwater samples (March 1977) compared to predicted tritium concentrations for recharge estimates

The calculation of individual recharge estimates for all bores is possible because of the assumption that the recharge of each year is consistently represented in the aquifer as an equal thickness layer. These values were calculated within the model using a rearrangement of equation 4.4 to solve for *n* (the number of years of recharge that contributed to the sample). The average recharge was then determined from a rearrangement of equation 4.3:

$$R = \frac{D_B \alpha}{n} \qquad \text{Equation 4.6}$$

Figure 4.7 shows that the concentration of a groundwater sample from the phreatic surface to any depth is made up of the corresponding years of recharge.

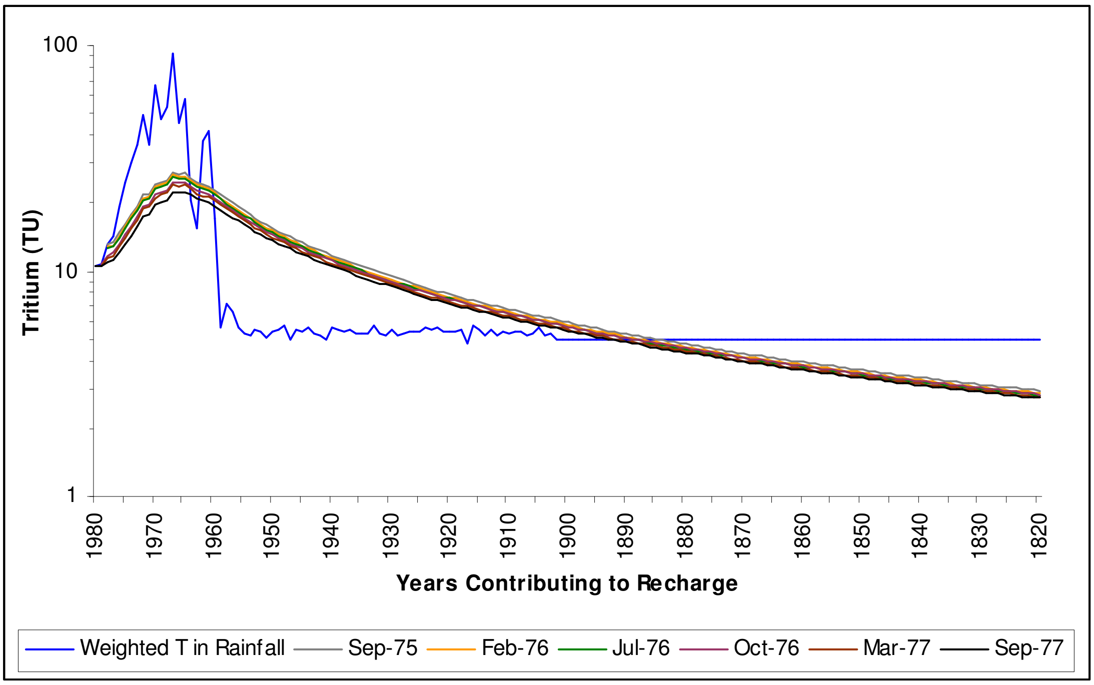


Figure 4.7: **Modelled tritium concentrations in composite groundwater samples corrected to each sample date**

Figure 4.7 also illustrates that there may be difficulties in estimating recharge using this method if the groundwater concentrations were greater than 10 TU as the years of contribution could be either of two possibilities. The highest tritium concentration measured in the groundwater samples was 8.5 TU and so this difficulty was avoided.

The model produced slight variations between the estimations for recharge from the same well on different sampling occasions. This variation is most noticeable when comparing the estimated recharge values from the October 1976 to the March 1977 sampling events. These two sampling events included 64 of the 105 samples available and therefore provided the greatest capacity for comparison.

A comparison of the two sampling dates shows that the recharge estimated from the October 1976 sampling data appears to have a tendency to estimate higher recharge rates than those estimated by most of the other sampling dates, but most noticeably for the March 1977 dataset. Figure 4.8 compares recharge rates estimated for October 1976 with all of the estimates from other sample dates. Those markers below the 1:1 ratio line signify that the estimated recharge rate was higher in the October 1976 dataset. Figure 4.9 shows a scatter plot of the recharge values of March 1976 compared to the other years, illustrating the absence of any bias.

While a bias appears to be shown in Figure 4.8, for those bores sampled at both times, the recharge rates estimated from the October 1976 data (mean = 17.06, SE = 2.07) were not significantly higher than those estimated from the March 1976 data (mean = 13.22, SE = 1.80). This assumed a porosity of 40%, however the use of other porosity values did not result a statistically significant difference between the two datasets.

The July-September winter rainfall for both 1976 and 1977 was in the bottom quartile of the dataset (1900-1977) with 403 and 371 mm respectively (average being 486 mm), while in 1975, the July-September winter rainfall was slightly above average at 498 mm. As there were very few samples collected after the 1975 and 1977 winters it was not possible to further investigate whether there were seasonal influences upon the results.

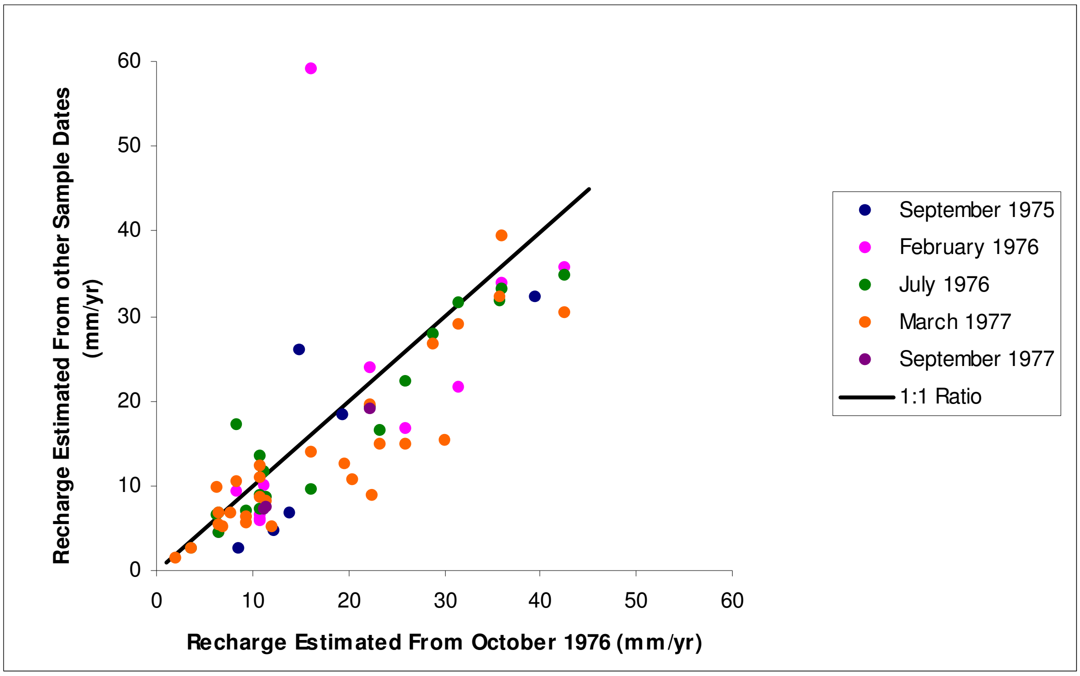


Figure 4.8: Estimated recharge rates predicted from the October 1976 dataset compared to all other sample date datasets

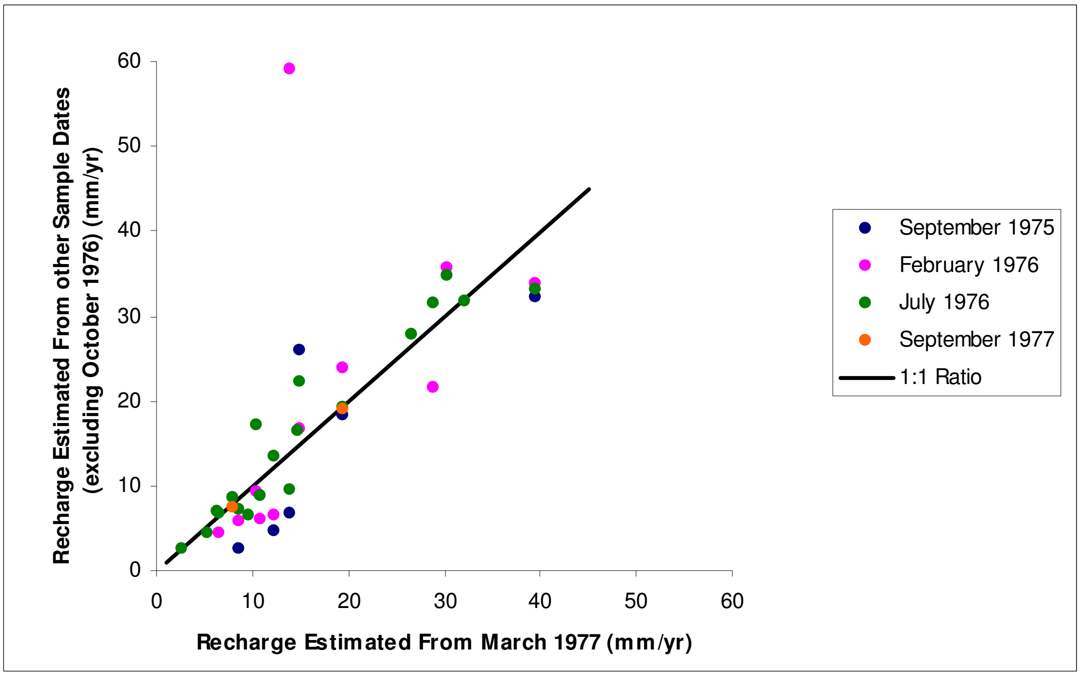


Figure 4.9: Estimated recharge rates predicted from the March 1977 dataset compared to other sample date

The mean estimated recharge rates for the study area presented in Figure 4.10 are calculated from the all of the available sample results assuming a saturated aquifer porosity of 40%. The longer term recharge into the upper unconfined aquifer is generally between 6.7 and 22.1 mm/yr (25th and 75th percentiles) with a median recharge rate of 10.9 mm/yr.

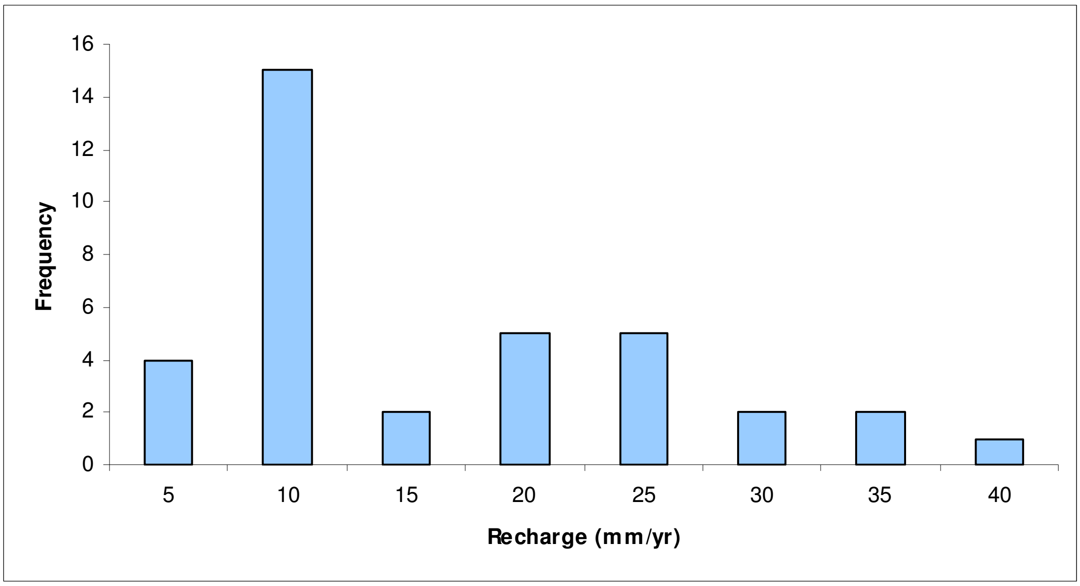


Figure 4.10: The frequency of recharge rate estimates for the study area assuming aquifer matrix porosity of 40%

When reviewed spatially, this variability in recharge estimates suggests that recharge rates are neither consistent nor random; with the majority of the higher recharge estimates being located in the centre of the study area.

Figure 4.11 illustrates the estimated recharge rates for each bore location for both the summer (February to July) and winter (September to October) sampling periods. This figure demonstrates that the centre of the study area is subject to higher recharge rates than other parts of the study area. Using the inferred area of high recharge to differentiate the recharge values, the modelled data indicates that particularly for the winter sampling results, the modelled recharge in the centre of the study area is considerably higher than the remainder of the study area. This comparison is provided in Figure 4.12.

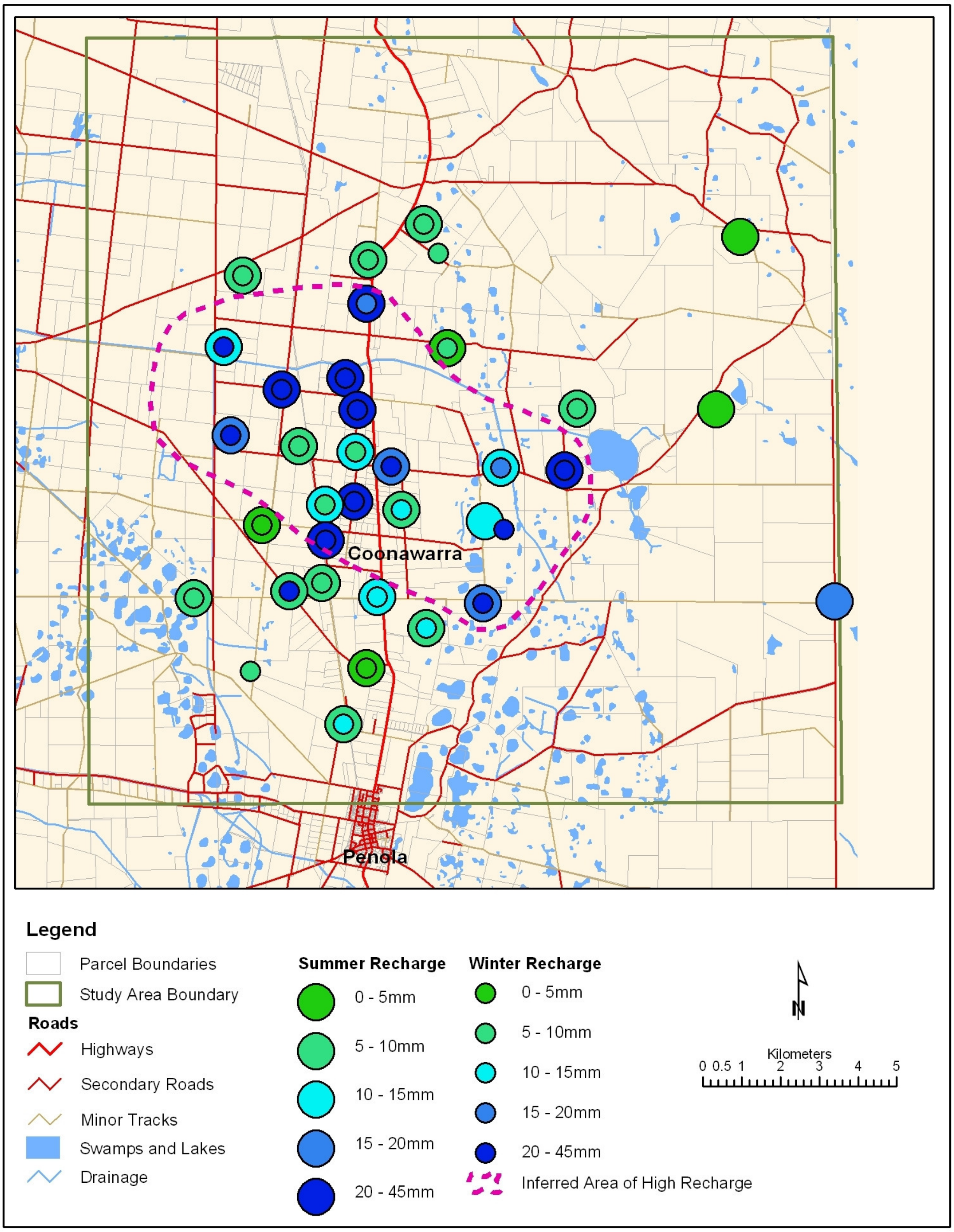


Figure 4.11: The estimated recharge rates within study area (matrix porosity of 40%) based upon summer and winter modelling periods

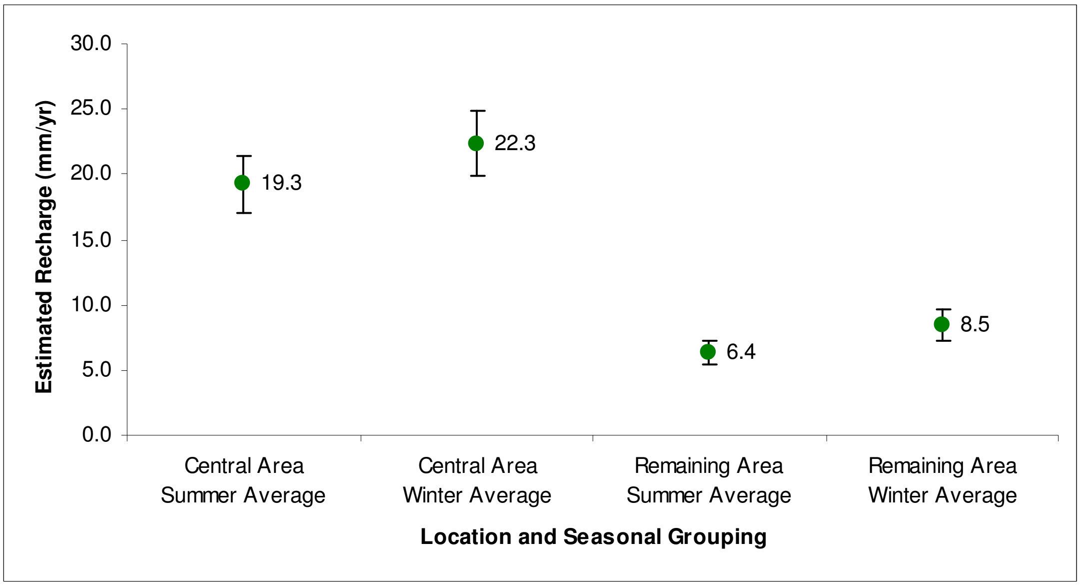


Figure 4.12: The average estimated recharge rates between the centre of the study area (inferred area of high recharge) and the outer parts of the study area based upon summer and winter modelling (matrix porosity of 40%)

As shown in Figure 4.12, the differences in winter and summer estimates for recharge are not significantly different, however the recharge estimates between the inferred area of high recharge and the remaining parts of the study area are significantly different. This observation provides further support that the modelling approach is not statistically sensitive to intra-seasonal variations. Removing the seasonal classification results in an estimated annual recharge within the central area of high recharge of 20.8 mm/yr (SE = 1.7) and for the remaining area 7.4 mm/yr (SE = 0.8).

It was not possible to identify the factors contributing to this spatial recharge pattern. Spatial analysis was undertaken using soil texture and landuse information (reported in Chapter 5), and a one-dimensional leaching model (reported in Chapter 7) to further investigate this landuse relationship.

4.4. DISCUSSION

4.4.1 Predicted Recharge Rates

Modelling of the tritium data provided an estimate of recharge rates and their variability throughout the study area.

The modelled recharge rates are comparable to those estimated through other studies. Slightly to the north of the study area at Joanna, Walker and his colleagues (1987) used chloride profiles to estimate recharge in improved pasture grazing land of 1.5 – 13 mm/yr. Their sites generally had greater depth to groundwater than the majority of the study area, but they are comparable to those of its eastern portion. Their study included an estimated recharge of 80 mm/yr for a site that they believed was subject to inundation. For comparison, the highest recharge estimate from the present tritium model was 59.0 mm/yr (α=40%). In this same area, and revisiting one of the same sites as Walker and his colleagues (1987), Leaney and Herczeg (1995) used a variety of methods to estimate a diffuse recharge rate of 10 mm/yr. Further north at Padthaway, Allison and Hughes (1975) calculated local recharge to be 27 mm/yr based upon modelling of groundwater tritium concentrations.

The estimated recharge rates produced with the tritium model are less than those of both De Silva (1994) and Bradley and others (1995) however, who used groundwater hydrographs, soil texture associations and landuse to estimate annual recharge of 20 – 120 mm/yr within the study area.

The modelled recharge rates are also less than those estimated using a variety of techniques south of the study area. Allison and Holmes (1973) estimated recharge over the Gambier Plain area to be 120 mm/yr. Allison and Hughes (1974) estimated recharge at three sites around Mount Gambier to be between 40 and 140 mm/yr. In a later more extensive study of the same area, Allison and Hughes (1978) predicted recharge rates of 50 – 270 mm/yr for a variety of soil types, with the highest recharge estimates being for skeletal soils (such as those that occur in the eastern portion of the study area), and 130 – 150 mm/yr for terra rossa soils. Such terra rossa soils occur in the centre of the study area. More recently, studies have indicated that recharge under plantation forestry in the lower south east is negligible when compared to recharge under other agricultural landuses (Dillon et al. 2001).

That the recharge rates are less than those of the lower south east are not surprising, as recharge to the unconfined aquifer decreases from south to north in the region (Love, et al. 1993). However the large variability in recharge indicated by these other works is not easily explained.

Modelled recharge rates are variable across the study area. This conclusion is independent of the estimates of aquifer porosity used in the model. The central portion of the study area produced higher recharge estimates compared to those areas to the south, east and north. The strong spatial relationship and the significant difference in recharge rates suggested that this has an environmental explanation. The inferred area of higher recharge (Figure 4.11) has a marked similarity to that of the nitrate plume in groundwater identified by MacKenzie and Stadter (1981) (Figure 1.3).

Two possible factors which could influence the rate of recharge are: (i) the recharge could be higher due to environmental factors such as the soil type, or (ii) the elevated tritium concentrations are a result of irrigation during the summer months which maintains a higher soil moisture level so that vertical drainage occurs quicker in these areas once winter rains commences. This latter factor was proposed by Allison and Hughes in their study (1975) and an investigation of this is reported in Chapter 7. It is possible that both environmental factors and land management practices associated with this central area contribute to its increased recharge.

Although groundwater levels in the central part of the study area are not elevated (as might be predicted under high localised recharge), this is likely to be due to the high transmissivity of the upper parts of the tertiary limestone aquifer (Mustafa and Lawson 2002). As indicated by MacKenzie and Stadter (1981), the groundwater in this central area exhibits a lower electrical conductivity than the surrounding study. This is an indication of fresh water input to the aquifer from the surface; as recycling of irrigation water alone would be expected to result in an increase in electrical conductivity.

Assumptions which could affect the accuracy of the model must be kept in mind. Rainfall data from Mount Gambier has been combined with tritium concentrations (sometimes estimated from annual recording) from locations away from the study site. Also in some cases, the standing water level on the day of sampling has been extrapolated from the available datasets (Appendix 4). Also, in the eastern portion of the study area where the overlying unsaturated zone is thicker, and the landcover means that the recharge may take more than a few months to reach the aquifer. The assumption that recharging water reaches the aquifer within the year of the rainfall season may then not be appropriate.

Regardless of these possible limitations, the predicted recharge rates and their spatial variability are consistent with other studies and field observations.

4.4.2 Application of the Tritium Model

The model used in this study is simplified from that developed by Vogel (1966) but should be applicable where sampling is undertaken over a small upper portion of the total thickness of an unconfined aquifer.

The approach used in this study is an adaptation of that developed by Leaney and Allison (1986). Although they developed their model for a semi-arid environment using carbon-14 for the estimation of age, the approach can also accommodate the estimation of recharge to a shallow unconfined aquifer where moderate annual recharge is occurring.

Although the technique of using tritium to measure recharge is now limited (due to the relatively low levels of tritium experienced in the southern hemisphere in the 1960s, the ongoing decrease of tritium in precipitation, and the decay of tritium in the soil and groundwater) the approach adopted here could be applicable to other radioactive tracer methods such as the use of ^{3}H/^{3}He.

The accuracy of the model would be improved with improved data on groundwater level. Further, sample site selection could focus on wells that intersect a thinner portion of the aquifer (e.g. 5 m). This will provide recharge rates that are applicable for more recent timeframes (e.g. averaged over the last ten years rather than 40 years) which would provide a more contemporary estimate of annual recharge. In addition, the model does not specifically account for irrigation within the study area. Irrigation water (sourced from lower in the aquifer) will have had tritium concentrations less than rainfall.

4.4.3 Implications of Modelled Recharge

The model predicts increased recharge in the centre of the study area over a similar areal extent to that of elevated nitrated concentrations in groundwater. Recharge rates can be a key contributor to the transport of nitrate into groundwater systems. In this instance, the model indicates that accelerated leaching from the surface may be one of the factors resulting in the elevated nitrate concentrations in groundwater observed through the 1970-1980s.

The estimation of recharge rates through the tritium model does not provide evidence of the recharge pathways, and therefore cannot identify the source(s) of nitrates in groundwater under the study area. This will require further assessment, such as through nitrate isotope analysis (Chapter 6).

Despite this, the model indicates the potential for degradation of groundwater quality; either from nutrients or other surface generated sources. The increased flux to the aquifer in the centre of the study area suggests that contaminants have a reduced time to attenuate before entering the aquifer system compared to other parts of the study area.

4.5. CONCLUSION

Tritium concentrations in groundwater have provided evidence that recharge variability through the study area is a contributing factor to the observed elevated groundwater concentrations of nitrate.

A recharge model estimated long term (~40 year) recharge rates across the study area in the vicinity of 10.9 mm/yr. Recharge rates are significantly higher in the area immediately surrounding Coonawarra - 20.8 mm/yr for this central area compared to 7.4 mm/yr in the remainder of the study area.

These estimates of recharge have the same magnitude as other estimates supporting the validity of the model.

Given that rainfall (and tritium input) is consistent across the study area, it is suggested that a combination of land management practices, particularly irrigation, and soil types may have resulted in the recharge variability; particularly the increased vertical drainage into the unconfined aquifer in the centre of the study area.