

Hydrogeology, hydrochemistry and isotope hydrology of Palm Valley, Central Australia

Author:

Wischusen, John David Henry

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**HYDROGEOLOGY, HYDROCHEMISTRY
AND
ISOTOPE HYDROLOGY
OF
PALM VALLEY,
CENTRAL AUSTRALIA.**

John David Henry Wischusen

BSc, Grad. Dip. Appl. Geol., MSc

Submitted as a requirement in full for the degree of

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**SCHOOL OF BIOLOGICAL, EARTH AND ENVIRONMENTAL SCIENCES
FACULTY OF SCIENCE**

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ABSTRACT

The Palm Valley oasis in arid central Australia is characterised by stands of palm trees (*Livistona mariae*). How these unique plants, separated by nearly a 1000 kilometres of arid country from their nearest relatives persist, has long fascinated visitors. Defining the hydrogeology of the Hermannsburg Sandstone, a regionally extensive and thick Devonian sequence of the Amadeus Basin that underlies Palm Valley, is the major thrust of investigation. Appraisal of drilling data shows this aquifer to be a dual porosity fractured rock aquifer which, on a regional scale, behaves as a low permeability, hydraulically continuous resource. Groundwater is low salinity (TDS <1000 mg/L) and bicarbonate rich. Slight variations in cation chemistry indicate different flow paths with separate geochemical histories have been sampled. Stable isotope ($\delta^2\text{H}$, $\delta^{18}\text{O}$) results from Palm Valley show groundwater to have a uniform composition that plots on or near a local meteoric water line. Radiocarbon results are observed to vary from effectively dead (< 4%) to 87 % modern carbon. To resolve groundwater age beyond the radiocarbon window the long lived radioisotope ^{36}Cl was also used. Ratios of $^{36}\text{Cl}/\text{Cl}$ range from 130 to 290×10^{-15} . In this region atmospheric $^{36}\text{Cl}/\text{Cl}$ ratio is around 300×10^{-15} . Thus an age range of around 300 ka is indicated if, as is apparent, radioactive decay is the only significant cause of $^{36}\text{Cl}/\text{Cl}$ variation within the aquifer. A review of previous, often controversial, ^{36}Cl decay studies shows results are usually ambiguous due to lack of certainty when factoring subsurface Cl^- addition into decay calculations. Apparently, due to the thickness of the Hermannsburg Sandstone, no subsurface sources of Cl^- such as aquitards or halites, are encountered along groundwater flow paths, hence the clear ^{36}Cl decay trend seen. The classic homogenous aquifer with varying surface topography, the “Toth” flow model, is the simplest conceptual model that need be invoked to explain these isotope data. Complexities, associated with local topography flow cells superimposed on the regional gradient, signify groundwater with markedly different flow path lengths has been sampled. The long travel times (> 100 ka) indicate groundwater discharge would endure through arid phases associated with Quaternary climate oscillations. Such a flow system can explain the persistence of this arid zone groundwater-dependent ecosystem and highlight the possibility that Palm Valley has acted as a flora refuge since at least the mid-Pleistocene.

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1. Introduction

1.1. Background

This thesis examines the hydrogeology of Palm Valley in central Australia. Palm Valley lies within the Western MacDonnell Ranges of the Northern Territory and is the major natural attraction of the Finke Gorge National Park, central Australia (Fig.1.1). In this region mean annual rainfall is around 250 mm/yr and potential evaporation is around 2800 mm/yr; hence the evaporation to precipitation ratio is over 10. The valley is named after the Red Cabbage Palms (*Livistona mariae*) that grow in this area. The nearest similar species are found around 1000 km away in the tropical regions of north Australia (e.g. at Mataranka, Lawn Hill shown on Fig. 1.1). The incongruity of this tropical looking palm growing in an arid environment is a source of fascination to visitors. The palms are described by Latz (1975) and are commonly assumed to represent a relict stand that has survived since a wetter climate allowed a greater distribution. Preliminary results of a comparative DNA gene sequencing study of the morphologically very similar palms at Palm Valley and Mataranka to the north, had indicated significant genetic divergence, a potential sign of long time separation between populations, (Bowman, pers. com 2002).

The onset of aridity in central Australia is dated by Chen and Barton (1991) at around 0.9 to 1.6 Ma. Since around 0.7 Ma world climates have been controlled by 100 ka glacial cycles (Colman et al., 1995). In Australia there is evidence that Pleistocene dry and wet episodes have oscillated, broadly following worldwide glacial and interglacial events respectively (Nanson et al., 1992). In central Australia up to 85% of a Quaternary glacial period is thought to comprise of dry (glacial) to hyper arid (glacial maximum) conditions with the remainder of cycle wet (pluvial) (White, 1994). The last hyper arid (glacial maximum) period in central Australia is thought to have occurred around 20 ka. The last full pluvial period in central Australia was around 100 ka (Kershaw and Nanson, 1993) though there is some evidence that wetter conditions prevailed around 35 – 50 ka (e.g. Croke et al., 1996).

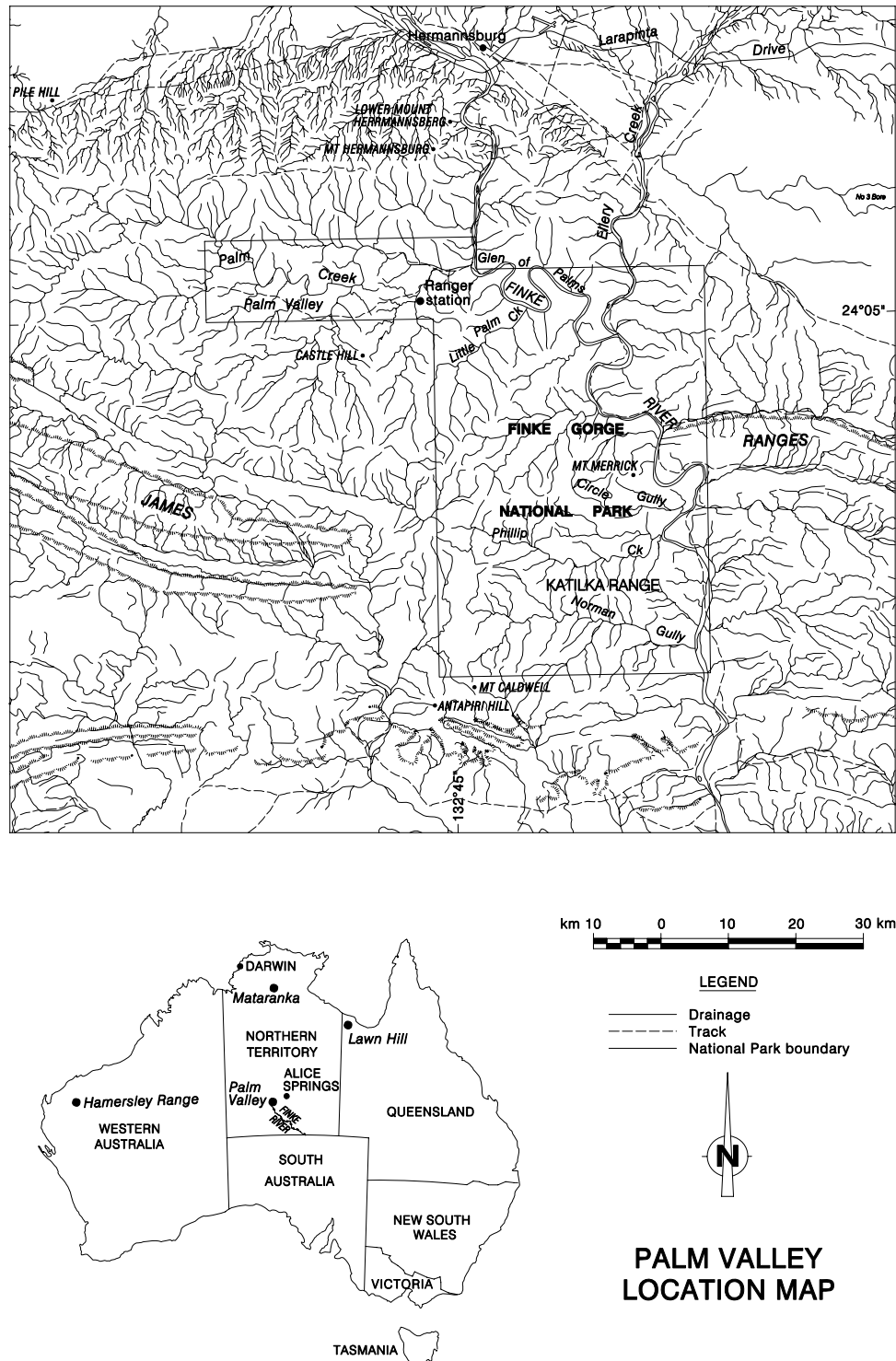


Figure 1-1 Location Map

Palm Valley is a part of the Finke Gorge National Park, central Australia, and lies about 130 km west of Alice Springs. Palm Valley, the main tourist attraction of this park, is a stand of *Livistona mariae* palm trees found along the Palm Creek, in the northwestern extension of the park. The nearest other populations of *Livistona* sp. in Australia are closer to the coast at the Hamersley Range, Mataranka and Lawn Hill locations marked.

Given this likelihood of protracted arid conditions in central Australia during the Pleistocene and the fact that many other rare flora (Latz, 1996) and fauna (e.g. Davis, 1995, 1997) are also found at Palm Valley, it is interesting to speculate on how long these palms have been separated from other *Livistona* species in tropical Australia. It may in fact be that Palm Valley represents a refuge that has functioned since the onset of aridity in central Australia.

Because of the modern day and past aridity of climate in this region, it has long been suspected that apart from a sheltered habitat, tapping shallow groundwater is how these palms survive dry times. In this study, the feasibility of groundwater sustaining the flora refuge at Palm Valley is examined. Because significant recharge may have last occurred during Pleistocene pluvial events, some of this study is orientated to dating groundwater. As hydrogeological and radiocarbon data indicated that very old (> 30 ka) groundwater may exist in this aquifer the ^{36}Cl decay method was applied. This method, which allows dating well beyond the 30 ka range of the more commonly applied ^{14}C decay method to ages of around 1 Ma (Phillips, 2000), has been controversial in some past studies because results are ambiguous. This is chiefly because inconsistent chloride concentration levels along perceived flow paths (possible evidence of Cl^- addition post recharge) complicate the interpretation of ^{36}Cl decay results. This complication is due to an equivalence phenomenon i.e. there is no way of proving that chloride has been added slowly and consistently along a flow path or near instantaneously either immediately post recharge or at some other time during flow (Andrews and Fontes, 1992). Thus, while ^{36}Cl decay dating offers a valuable tool for assessing groundwater systems with its long time frame resolution capability, on the other hand, it is also a technique which has resulted in debate about its veracity. Given the controversy regarding this technique I have devoted a significant portion of the overall effort to reviewing previous ^{36}Cl decay groundwater studies and recent developments in the literature that may affect the application of the method

The use of ^{36}Cl is potentially significant as any new insights gained on the application of this controversial technique may help future groundwater studies. The study of groundwater systems is an important endeavour in central Australia as in this region all industries, communities and presumably many ecosystems are reliant on groundwater. The characteristic high interannual variability of rainfall along with a lack of

hydrological data due to sparse populations, makes the study of groundwater in arid regions difficult (Lerner et al., 1990). Thus, in the central Australian region, reliance on annual or seasonal precipitation is not an option. Indeed many groundwater supplies are thought to tap old water and to even be non renewable in that the water stored in some aquifers is believed to be replenished only during past wetter climate regimes (e.g. the Alice Springs town water supply; Jolly et al. 1991; Jacobson and Lau, 1991). Consequently, this study of an apparently long lived groundwater dependent ecosystem, is relevant to the understanding and managing of groundwater in central Australia and potentially also other arid zone groundwater systems elsewhere.

1.2. Objectives

Thus the principal research objectives of this study are:

- 1) to evaluate the hydrogeology, hydrochemistry and isotope chemistry of the aquifer underlying Palm Valley.
- 2) to review the background theory and previous applications of ^{36}Cl decay dating of groundwater systems.
- 3) to apply the ^{36}Cl decay groundwater dating method at Palm Valley and critically assess results in the context of objectives 1) and 2).
- 4) to determine the feasibility that groundwater maintains the flora refuge at Palm Valley

These objectives are addressed in the following chapters. Chapter 2 outlines the methodologies adopted for this study. Chapter 3 characterises the environmental setting of Palm Valley. Chapter 4 defines the geology and aquifer characteristics of the Hermannsburg Sandstone at and near Palm Valley. Chapter 5 outlines the hydrochemistry of the Hermannsburg Sandstone. Chapter 6 examines the stable isotope and radiocarbon hydrology at Palm Valley. Chapter 7 reviews the background and theory of ^{36}Cl decay dating and examines the results from Palm Valley against some

critical factors known to complicate ^{36}Cl decay age interpretations. Chapter 8 looks at the relevance of this study by way of a review of previous ^{36}Cl decay groundwater studies and comparison of results from Palm Valley. Chapter 9 discusses ramifications of all these results and develops a hydrogeological conceptual model of the groundwater flow system at Palm Valley. Chapter 10 assembles all the key results and provides a summary of the evidence that support the hypothesis that groundwater can, and has, sustained the flora refuge at Palm Valley for a significant period.

2. Sampling and methodology

2.1. Introduction

This study started as a request by the National Park rangers for the then Water Resources Branch of the Northern Territory Government to examine the water supply sustainability in the Palm Valley portion of the Finke Gorge National Park in 1993. I was then working as a hydrogeologist for the Water Resources Branch and this job was assigned to me. Due to the complexity of this task and competing work interests this job carried on for many years unfinished. So to finish this job and put the study within a scientific context I made the project the basis of this thesis. Given this origin some aspects of the methods used for this study are slightly different from some University initiated projects. The main difference is that as a government worker when much of the data was gathered I had the luxury of a budget, in house labour and laboratories to undertake many of the analytical tasks associated with this project. While this has meant I have missed the experience of preparing my own samples and running analytical apparatus for chemical and isotope data, the use of professional laboratory services for this work at least ensures the accuracy of chemical and isotope analyses reported here. Similarly my role as a Northern Territory Government hydrogeologist equipped me with a familiarity with the database; this greatly assisted me in obtaining and analysing data from other bores drilled in the Hermannsburg Sandstone in the vicinity of Palm Valley. This was crucial for putting data from Palm Valley into a regional context. This comparison with a compilation of regional data from the Hermannsburg Sandstone also adds to the integrity of data from Palm Valley.

The complexity and scale of the physical and biological environments encountered by water as it moves through the hydrologic cycle indicate that application of one scientific discipline alone is unlikely to be sufficient to fully characterise a groundwater system. Consequently this study, like many other groundwater investigations, relies on a variety of techniques. In a similar vein, assessment of a groundwater system often involves consideration of large areas of country, so it is rare for any one project to supply all the necessary data to define a groundwater system. Instead, most studies build on previous work that has been compiled from when an aquifer is first drilled and exploited. This

can mean an important part of any groundwater study involves collating, assessing and interpreting relevant pre-existing groundwater data that have been collected by others. This study is no exception; great reliance is placed on previous groundwater drilling and chemical analysis data held in the Northern Territory Government database and, to a lesser extent, some previously published stable isotope data sets. Due to the setting of Palm Valley within a National Park, the remote and rugged terrain, potential procedural difficulties with drilling on Aboriginal owned land, and a lack of a large budget (a constructed water production bore costs over \$10 000 in this region) no new drilling was possible for this project. Thus only existing bores and springs were sampled for this study.

To allay any potential confusion about originality of data presented because of my ready familiarity with using data sourced from the Northern Territory Government database, I have cited the source of all data and interpretations not my own throughout the text. In essence, I collected all the data presented from Palm Valley, apart from the water bore drilling data (bores in place before study began) and some major ion chemical data. I also collected chemical and isotope (including ^{36}Cl) data from a water supply production bore at each of the surrounding Hermannsburg, Areyonga and Injatharra Aboriginal communities.

For this study I collated and surveyed bore and water levels to produce the potentiometric surface diagram shown in Figure 4.9.

2.2. NTG database

Groundwater resources are owned and managed by the Crown in Australia. Thus the Northern Territory Government (NTG) like other Australian Governments, acts as custodian of groundwater resource information. This information is gathered at the taxpayers' expense and is therefore a public domain resource. The NTG database comprises vast amounts of digital and hard paper copy information. The files for each NT registered water bore contain paper records of most relevant information. This bore record information is filed under the registered number (RN) of each bore. Other information such as water chemistry and bore hydrograph data are held in various

digital database systems and is often duplicated as a paper record on bore record files. Reports of all government groundwater investigations and many other pertinent external groundwater reports pertaining to the central Australian region are also held in the NTG database. These data are held by and are available from the NT Department of Infrastructure, Planning and Environment, Alice Springs, NT.

2.3. Survey data.

Bore elevations and heights (in metres of Australian Height Datum) of some springs and the main stand of palms were surveyed under my supervision by Scotty Balfour and Alan Russ of the NTG for this study in 1994. These data, which helped with construction of the potentiometric surface diagrams, are held in the NTG database in Alice Springs. Traditional dumpy level survey techniques were used for all elevations determined, apart from the elevation of bore RN14616 which was determined by differential GPS techniques. The dumpy level survey results were also crosschecked by the differential GPS method to ensure the level determined for RN 14616 was correct. These survey results are shown in Table 2.1

2.4. Geology

Apart from the cited published geological mapping, various other geological data were examined for this study. Results of various field and aerial photography mapping, conducted near Palm Valley for the petroleum exploration industry are available from company records held by the NT Geological Survey, Department of Minerals and Energy, Alice Springs. Data from petroleum wells drilled along the Palm Valley anticline are also available here. Some NTG water bore record files contain lithological logs compiled by various geologists from examination of drill cuttings and occasionally electric logging data. Nearly all bore records contain a lithological log compiled by the bore driller. Examination of these records and examination of drilling lithological samples held by the NTG were undertaken for this study. Field geology of the Hermannsburg Sandstone was examined at Palm Valley and elsewhere along the Krichauff Range to check the veracity of published and company record mapping.

Table 2.1 Survey results Palm Valley area

ID	REDUCED LEVELS AT PALM VALLEY			WL	GRID REFERENCE
	GL	MP	(metres AHD)		
RN 12024	551.08	551.39	544.39		
RN 4508	551.484	551.664	550.164		
RN 14903	554.71		DRY		
RN 14905	553.2		DRY		
Main channel next to palms at entrance to Cycad Gorge	556.124				
End of Denis Matthews long section	565.37				
Bottom Oasis	571.314		571.29	269336E 7336197N	
Top Oasis	571.409			269800E 7336700N	
Palms at road crossing			555.958		
Lone pine on creek	563.125		562.443		
RN 14616	614.08			264075E 7334536N	

NB. GL = ground level; MP = measuring point; WL = groundwater level; AHD = Australian Height Datum

2.5. Pump tests

Bore test pump data and interpretations are held as time versus drawdown charts on NTG bore record files. All tests were conducted by specialist NTG government field crews. Mono (positive displacement) pumps are set for these tests and discharge readings determined by orifice plates. Drawdown readings are taken by calibrated electrical “mega” lines. The tabulated readings taken during the pump tests are used to construct these charts and are held as paper records in the NTG database. Examination of these test pump records and previous groundwater studies conducted in the Hermannsburg Sandstone helped build an understanding of the aquifer characteristics. The supervision of various pump tests of bores sited in the Hermannsburg Sandstone at Areyonga and Palm Valley (Wischusen, 1994b, 1995a) also helped develop my understanding of this aquifer.

2.6. Hydrochemistry

Samples for major anion and cation analyses from bores and springs for this study were taken in new, one litre bottles, filled and rinsed 3 times with groundwater. For bore samples 3 bore casing volumes were purged and field pH and conductivity readings were steady before capping the sample bottle. Spring samples were taken in new bottles filled and rinsed 3 times; bottles were filled by submerging in the deepest part of the pool. In keeping with standard NTG protocols, samples are not fixed by acid or filtered in the field. Other bore chemical data used for this study from the NTG database are assumed to have followed a similar sampling protocol and analyses routine. However given the various vintages of analyses compared in this study it is possible that slight differences in methods used exist. Analyses of major cation and anion chemistry are determined by the water chemistry laboratory of the Department of Infrastructure, Planning and Environment in Darwin which uses the standard methods of the American Public Health Association (APHA, 1998). Iron (Fe^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+) ion concentrations were measured by flame atomic adsorption spectrometry (APHA, method 3111B). Calcium (Ca^{2+}) was determined by flame atomic absorption spectrometry (APHA, method 3111D). Chloride (Cl^-) concentration

was determined by argentometric titration (APHA, method 4500-Cl⁻ B), fluoride (F⁻) was measured by ion selective electrode technique (APHA, method 4500-F⁻ B). Total alkalinity (as CaCO₃), bicarbonate (HCO₃⁻), carbonate (CO₃²⁻) and hydroxide (OH⁻) were calculated by titration with acid (APHA method 2320 B). Sulphate (SO₄²⁻) was calculated by the colorimetric method of Goguel (1969). Nitrate (NO₃⁻) was calculated by Ultra Violet spectrophotometric screening technique (APHA method 4500-NO₃⁻, B). Silica concentrations were measured by colorimetry using a Molybdosilicate method (APAH method 4500-Si D). Total dissolved solids (TDS) were measured by evaporation of a sample at 180° C (APHA method 2540C). The pH (laboratory) was determined using instrumentation (APHA 4500-H⁺, B). Electrical conductivity (laboratory) was measured in microsiemens/cm at 25° C (APHA method 2510B). The uncertainty in analytical results for sodium, potassium, calcium and magnesium are ± 1 to ± 2 mg/L, for chloride, sulphate, bicarbonate, carbonate and nitrate ± 2 mg/L and for fluoride and iron ± 0.1 mg/L.

2.7. Chloride bromide ratios

Samples for chloride bromide ratio determination were taken in new 100 mL plastic bottles. The bottles were filled and rinsed three times before fixing pH with a few drops of concentrated nitric acid and capping. The Cl/Br ratios were determined by the University of New South Wales (UNSW) University Analytical Laboratory using standard ion chromatography to determine the chloride level and by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) technique for the determination of bromide from samples taken in 2002

2.8. Trace elements.

Samples for trace element analyses were taken in 100 mL plastic bottles. Bottles were filled and rinsed three times before fixing pH with a few drops of concentrated nitric acid and capping. Trace element chemistry was determined by Inductively Coupled Plasma Atomic Emission Spectra (ICPAES) at the School of Biological, Earth and Environmental sciences laboratory at the UNSW. Analyses at this laboratory are obtained by a run through a Perkin Elmer machine (Model: Optima 3000 DV).

Standards preparation and quality control follow the United States Environmental Protection Agency (USEPA) method 1620: Metals by Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption Spectroscopy.

2.9. Stable isotopes

The $\delta^{18}\text{O}$ over $\delta^2\text{H}$ ratios for this study were determined by standard mass spectrometry at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Isotope Laboratory in Adelaide, South Australia. Samples were collected in new 30 mL glass McCartney bottles after filling and rinsing three times with groundwater. Deuterium for mass spectrometry analyses at this laboratory (Harrington, 1999) is prepared by reducing 25 μL of water to hydrogen gas over depleted Uranium turnings at 800°C in the method developed and described by Dighton et al. (1997). Preparation of an oxygen sample for oxygen-18 analysis entails equilibrating 1 μL of water sample with CO_2 gas for several hours at 30°C using the method described by Socki et al. (1992). Stable isotope measurements are obtained by running the gases produced from the water sample outlined above through special stable isotope mass spectrometer. CSIRO quote an accuracy of $\pm 1\text{‰}$ for $\delta^2\text{H}$ and $\pm 0.15\text{‰}$ for $\delta^{18}\text{O}$ relative to the Vienna Standard Mean Ocean Water (VSMOW).

2.10. Carbon 13 and 14

Samples were collected in new 20 litre plastic bottles (to ensure enough carbonate was available for analyses) that were filled and rinsed three times from purged bores that recorded stable field conductivity. Samples from springs were collected in new 20L plastic bottles that were filled and rinsed with groundwater once before capping. All preparation of samples for analyses was undertaken by CSIRO in the Laboratory. In the laboratory carbonate is precipitated as BaCO_3 solid after the addition of BaCl_2 to the sample. At this laboratory the process (Harrington, 1999) involves adding 600 mL of 1.7 M BaCl_2 solution per every 20L of sample then raising the pH to between 9 and 10.5 by the addition of sufficient 10M NaOH. Overnight precipitation of the white BaCO_3 (and BaSO_4) is then facilitated by addition 5 – 10 mL of MAGNAFLOC-156.

The resulting precipitate is then acidified under vacuum using 9M HCl and the CO₂ gas produced is used for mass spectrometry analyses to determine the carbon-13 composition. CSIRO report an accuracy of ± 0.1 ‰ for stable carbon ¹³C results relative to the standard Pee Dee Belemnite Formation of South Carolina (PDB).

Much of the CO₂ evolved from the addition of acid on the BaCO₃ precipitate is also collected for radiocarbon analyses. The CO₂ is frozen using liquid N, water vapour is then removed via a series of ethanol/CO_{2(s)} traps prior to collecting CO₂ in gas flasks. The CO₂ gas is then stored for at least a month to ensure any ²²²Rn gas present in the sample has decayed. The CO₂ gas is then run through a Carbosorb/Permaflour mixture using the direct CO₂ adsorption method developed by Leaney et al., (1994). The resulting CO₂ saturated mixture is then collected in glass scintillation vials and an ultra low background Qantas liquid scintillation counter used for measuring ¹⁴C activity.

2.11. Chlorine 36

To ensure that no mixing of recent rain and groundwater occurred, particularly at the springs, all the ³⁶Cl samples were collected in October 1994 following several months of no rain at Palm Valley (see Fig. 2.1). Samples were collected in nitric acid washed, thoroughly rinsed with distilled water, one litre bottles that were prepared by the water quality laboratory of the NT Department of Infrastructure, Planning and Environment, in Alice Springs. Bottles were filled and rinsed three times before sealing. Samples were not filtered or pH fixed.

The water laboratory of the Australian Geological Survey Organisation (AGSO) in Canberra then prepared samples for analysis (using silver nitrate to precipitate silver chloride). The AGSO laboratory was geared up for sample preparation, as this organisation was a significant user of ³⁶Cl analyses for groundwater studies at the time. After this preparation, samples were analysed for ³⁶Cl by the Nuclear Physics Department of the Australian National University (ANU) in Canberra.

Determination of ³⁶Cl of a water sample involves several necessary processes to prepare a suitable sample of silver chloride for analyses by an Accelerator Mass Spectrometer.

Particulars of the steps necessary to prepare a sample, as followed by AGSO and also as detailed by Keywood (1995) for ^{36}Cl analyses by the ANU are listed below.

In a laboratory, under low light to prevent photo degradation of AgCl and using spectroscopically pure grade AgNO_3 and BaNO_3 and analytical grade NH_4 and HNO_3 , chloride from the water sample is extracted as AgCl and then purified to create a sulphur free sample. This is done by heating 100 to 150 ml of water sample on low heat for 1 to 2 hours, adding 5 ml of AgNO_3 and heating until a precipitate is formed. These samples were then cooled and left to stand overnight covered in parafilm. These samples are then centrifuged at around 3000 rpm for at least ten minutes. After repeating this process on all the supernatant, a bead of AgCl is formed in the bottom of the centrifuge tube.

This bead of AgCl is then dissolved using 1 ml of concentrated NH_4 solution and diluted by addition of 40 ml of Milli-Q[®] water and 5 ml of BaNO_3 added after 5 minutes heating in a water bath. After a further 10 minutes in a water bath these samples are taken out and left to stand overnight. The supernatant of these samples is then drawn off using cleaned disposable pipettes into a clean 50 ml centrifuge tube and the BaSO_4 and possible BaCO_3 precipitate discarded. This supernatant solution is then added to a prepared and heated mixture of 15 ml 2M HNO_3 , 10 ml Milli-Q[®] water and 5 ml 10% AgNO_3 , a precipitate of AgCl is then formed. After an hour of heating at a low level the samples are cooled, covered in parafilm and left to stand overnight. The precipitate is then transferred to a centrifuge tube and centrifuged at 3000 rpm for around five minutes. The bead of AgCl formed in the bottom of the centrifuge tube is then rinsed and centrifuged two more times. The centrifuge tube and bead of AgCl is dried overnight in an oven. This purified bead of AgCl is then ready for ^{36}Cl analyses in the ANU accelerator mass spectrometer. In each batch of samples prepared, a solution of sodium chloride of known ^{36}Cl concentration (Weeks Island Halite) and Milli-Q[®] is prepared and also run through the preparation process to provide a control for the procedure.

Details of the method of analysis, accuracy of results and a description of the Accelerator Mass Spectrometer (AMS) used at the ANU for ^{36}Cl determinations are outlined by Fifield et al. (1987, 1990, 1994). The process begins at ANU when the

prepared AgCl sample is imbedded into a substrate of high purity (Merck, AR grade) AgBr that coats a copper sample holder used for AMS analysis. This reduces the amount of rouge ^{36}S that can be produced if the caesium ion beam mistakenly strikes the copper sample holders used (Fifield et al., 1990). In simple terms the AMS involves the sample of AgCl being bombarded with a caesium ion beam from a sputter source and the beam of chloride ions produced being accelerated in the ANU 14UD AMS machine. En-route to the heavy ion detector for counting, the chloride ions are stripped to Cl^{10+} ions and accelerated by a terminal voltage of 14 MV and then accelerated again (tandem acceleration) back to ground voltage. A Faraday cup is used to count stable $^{35}\text{Cl}^{10+}$ and $^{37}\text{Cl}^{10+}$ ions, the Faraday cup can be retracted and an in line propane filled ionisation chamber (heavy ion detector) then used to determine $^{36}\text{Cl}^{10+}$ ion counts. This system, where stable and radioactive isotopes are transported in the same beam, allows the $^{36}\text{Cl}/\text{Cl}$ ratio to be determined without reference to a standard (Fifield et al., 1990). The high energies of ions produced also allow clear separation of ions in the beam so that the ^{36}S isobar and stable ^{37}Cl isotope do not complicate the ^{36}Cl count. Each suite of samples prepared by the AGSO laboratory includes one sample prepared from the Weeks Island Halite which has a known $^{36}\text{Cl}/\text{Cl}$ ratio of below 1×10^{-15} (Fifield et al., 1987). An analysis of this sample provides a quality assurance on the sample preparation process. In addition, for each run through the AMS, one of the 12 sample holders contains AgCl prepared from a standard of known $^{36}\text{Cl}/\text{Cl}$ ratio (GEC standard with weighted mean value of $436 \pm 2 \times 10^{-15}$ $^{36}\text{Cl}/\text{Cl}$). ANU reported no deviations from the expected $^{36}\text{Cl}/\text{Cl}$ ratios for the Weeks Island Halite blank sample or the GEC standard during any of the analyses performed for this study, consequently no analytical errors are expected for the ^{36}Cl results reported here. Fifield et al. (1994) report reproducibility of ^{36}Cl measurements is within $\pm 2\%$ based on regular measurements of the GEC standard.

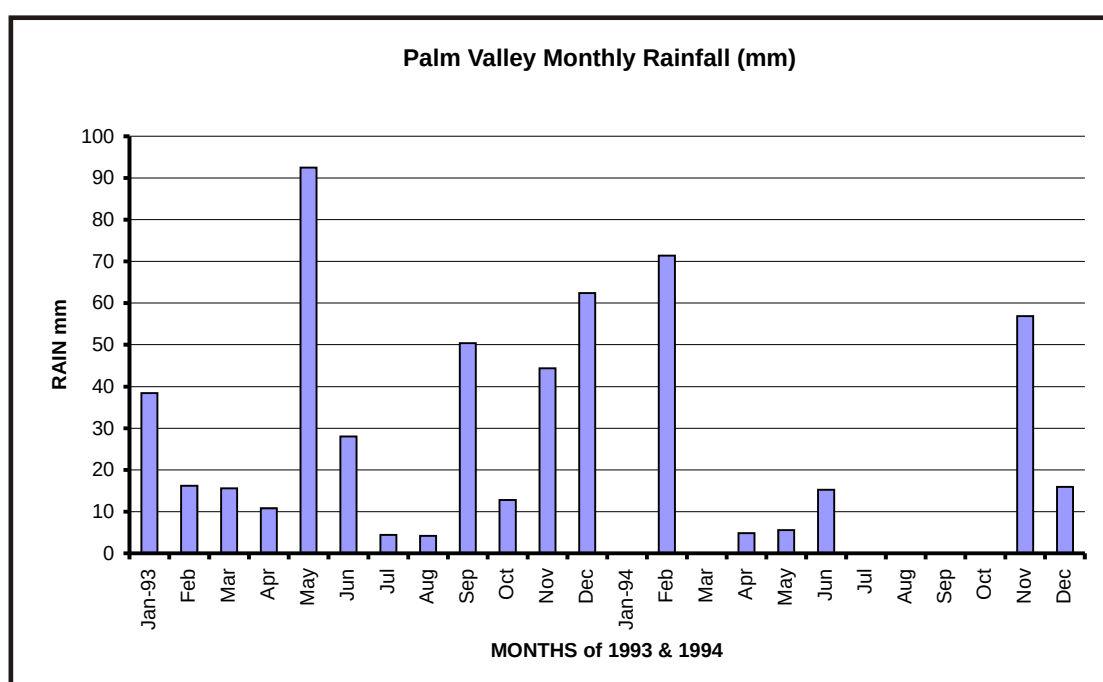


Figure 2-1 Monthly rainfall at Palm Valley 1993- 1994

When sites at Palm Valley were sampled for ^{36}Cl analyses during October 1994 it can be seen that no rain had fallen for months, which reduced the likelihood of contamination of spring water with modern rainfall.

3. Environmental setting

3.1. Introduction

Palm Valley is located in central Australia, 130 km west of Alice Springs. Palm Valley lies within, and is the major tourist attraction, of the Finke Gorge National Park, central Australia (Fig. 1.1). The valley is renowned for a unique arid zone floral assemblage with Red Cabbage Palms (*Livistona mariae*) (see Plate 3.1) being the obvious unique vegetation in the valley (see Plate 3.2). A quarter of the plant species recorded from central Australia occur here. The valley also supports 37 rare, relict and restricted central Australian distribution plant species (CCNT, 1992). The Palm Valley Gas Field (Do Rozario, 1991), which supplies Darwin and Alice Springs with natural gas, lies immediately north of the park. A first management priority of the park is the conservation of the *Livistona mariae* palm tree population.

3.2. Climate

3.2.1. Rainfall

Palm Valley lies within the low rainfall arid area defined by the Australian Bureau of Meteorology (BOM) shown in Figure 3.1. This region is described by the BOM (www.bom.gov.au) as being dry for much of the year, and having an erratic rainfall pattern, with a slight summer maximum. Rainfall can occur in any month but is more likely in summer months. Summers are hot and winters cool in this region. Based on a limited period of available rain records (1981 – 2002) mean annual rain at Palm Valley is 325 mm yr⁻¹. Monthly mean rainfalls for this period are shown in Figure 3.2.

This chart shows summer rainfall to be in excess of winter rainfall, which is typical of the central Australian region (e.g. Hesse, 2004). This rainfall mean may be skewed because the short rainfall record period at Palm Valley which encompasses the extremely wet years of 2000 and 2001, as seen in Figure 3.3 below.

The mean annual rainfall data based on over 100 years of record for the Hermannsburg community, only 15 kms north of Palm Valley, is 234mm. Thus it may be that the

pattern for monthly rainfall data where summer rain is in excess of winter rains, based on over 100 years of record for the Hermannsburg community, shown in Figure 3.4 gives a truer representation of long term rainfall pattern at Palm Valley. Figure 3.3 illustrates the variable nature of rainfall in central Australia where rainfall in 1996 (78 mm) is an order of magnitude less than in 2000 when over 1100 mm of rain was recorded for Palm Valley. Spatial variation of rainfall in this region is also evident as the unusually wet year of 2000 resulted in around 300 mm less annual rainfall at other rain stations within a 125 km radius of Palm Valley: Wallace Rockhole, 50 km east, 780mm; Ormiston Gorge National Park, 65 km north, 820mm; Watarrka National Park, 125 km west, 824mm. This difference could result from Palm Valley catching one or two more heavy thunderstorms during 2000 than at some other rain stations. The wettest month at all these stations was February 2000 when heavy rain was widespread across central Australia. This event was caused by a rain-bearing tropical depression, the former Tropical Cyclone Vincent, moving south into central Australia.

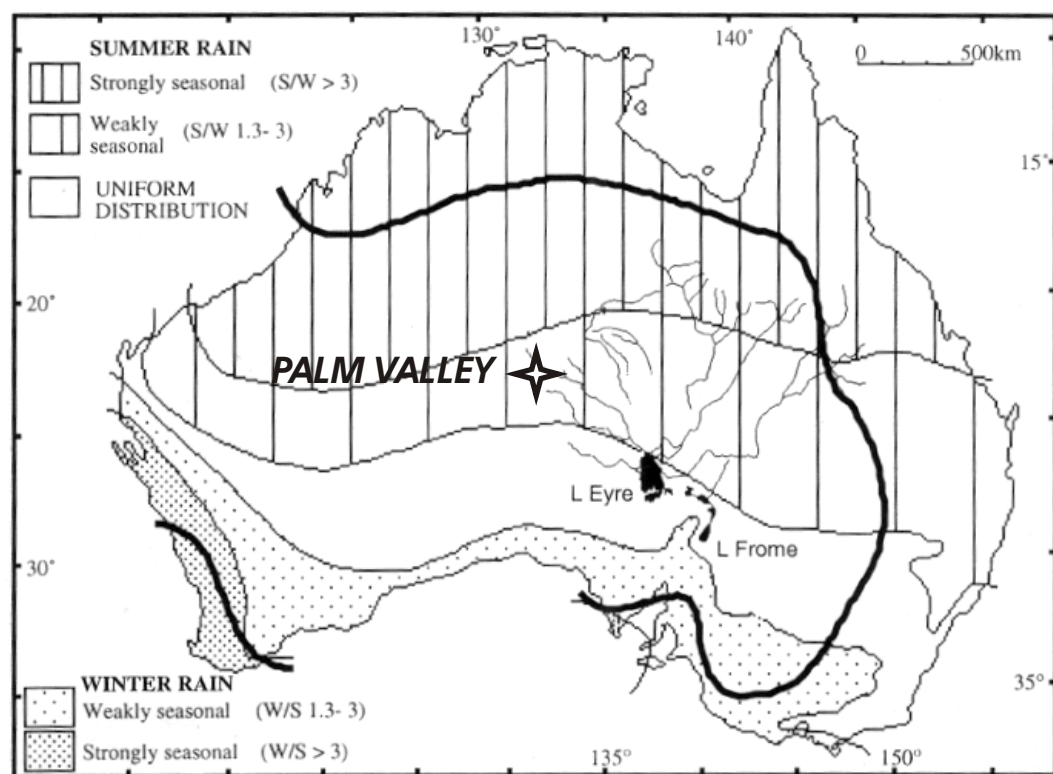


Figure 3-1 The Australian Arid Zone and rainfall seasonality

The arid zone of Australia lies within the solid black line. Palm Valley lies near the middle of the Arid Zone where summer rain is usually 1.3 - 3 times winter rainfall. Adapted from Quaternary International, Vol 118-119, Hesse et al. 2004, "late quaternary climates of the Australian arid zone: a review" p 87-102, ©2004 with permission from Elsevier.

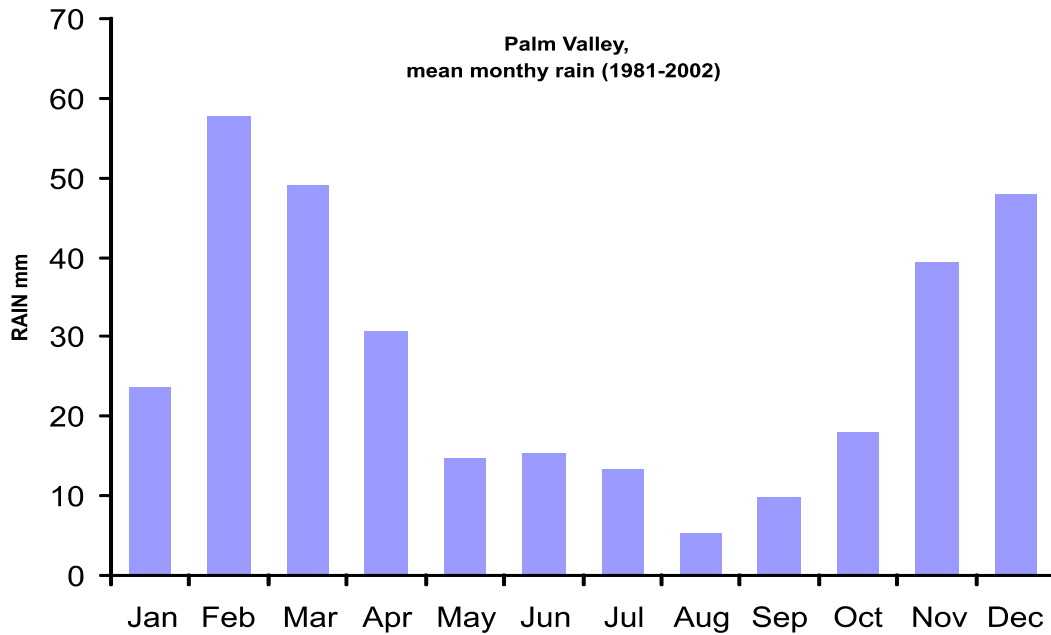


Figure 3-2 Mean monthly rain (mm) from Palm Valley
Mean monthly rain (mm) at Palm Valley, Finke Gorge National Park, Northern Territory (BOM, station number DR015663).

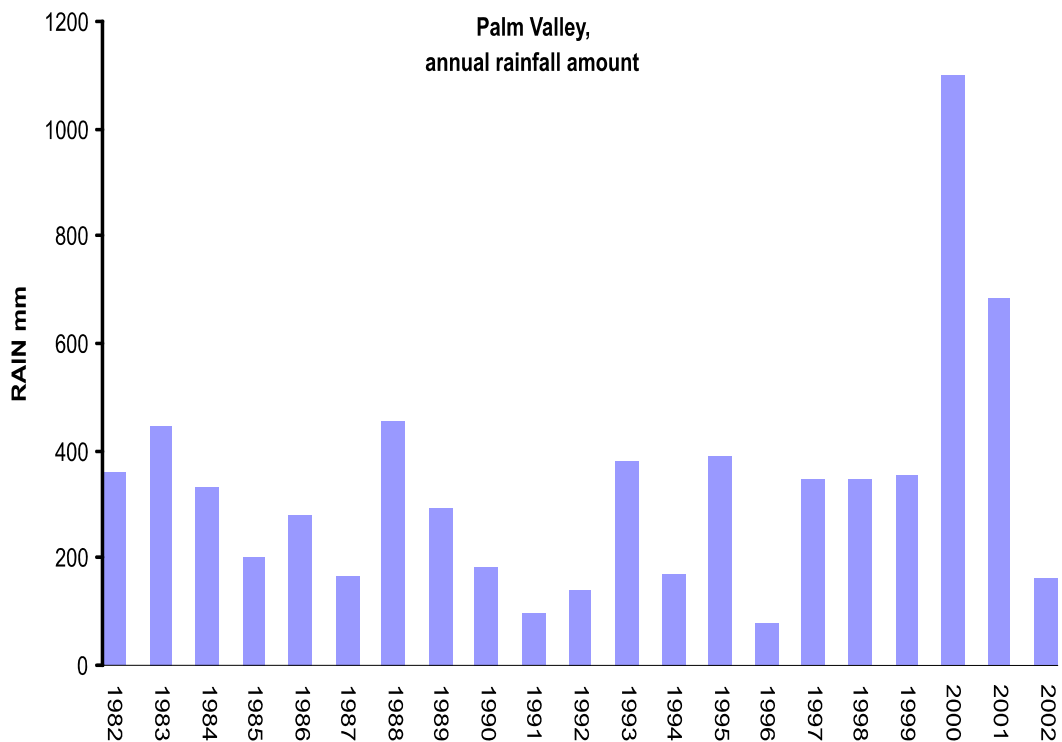


Figure 3-3 Yearly rainfall totals at Palm Valley
Yearly rainfall totals at Palm Valley, January 1982 to December 2002. (BOM, station DR015663).

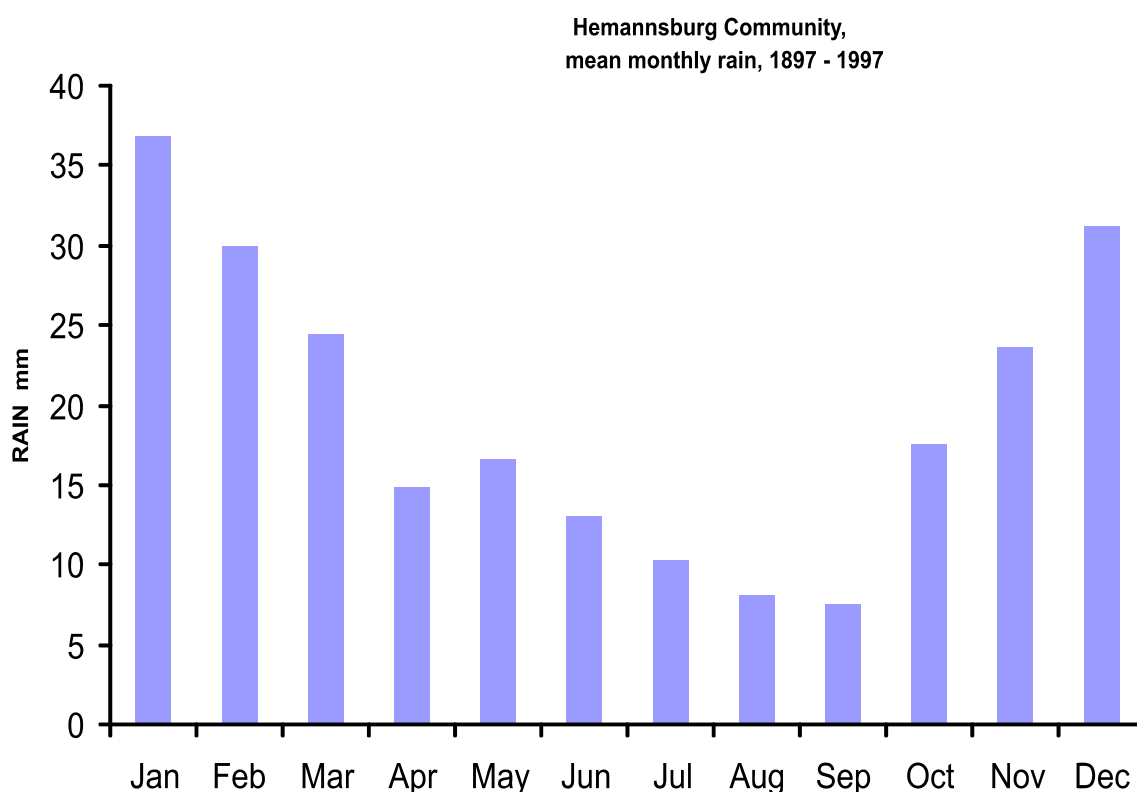


Figure 3-4 Mean monthly rainfall totals at Hermannsburg from 100 yrs of record
Mean monthly rainfall totals at Hermannsburg from 100 yrs of record (BOM, station DR015531).

The Bureau of Meteorology website gives an extensive general overview of climate and rainfall pattern in central Australia. Much of the discussion below on central Australian rainfall is sourced from the extensive data contained on this website (www.bom.gov.au). The rare large widespread summer rainfall events, such as February 2000 discussed above, are attributed to southerly incursions of the northern monsoon, bringing decaying tropical cyclones or the monsoon trough south into central Australia.

Variability in rainfall is probably also partly linked to variations in the Southern Oscillation Index (SOI), a measure of major air pressure shift between the Asian and east Pacific regions that is calculated from the monthly or seasonal fluctuations in the air pressure difference between Tahiti and Darwin. Sustained positive values of the SOI (La Nina events) are associated with stronger Pacific trade winds and warmer sea temperatures to the north of Australia. Together these give a high probability that eastern and northern Australia will be wetter than normal and an earlier than normal

start to the northern monsoon season will occur. The best-known extremes associated with the SOI are the opposite to La Nina and are known as El Niño events which are characterised by sustained negative SOI values. These events impact most strongly on southern and eastern Australia and are associated with drought conditions. (www.bom.gov.au).

Analyses of years with positive SOI from 1910 to 1988 by the Bureau of Meteorology, show that winter- spring rainfall is at the 8th decile on average for these years in central Australia. It is noted, however, that there is not a direct correlation between high SOI years and central Australian rainfall as not all La Nina years have resulted in above average rainfall years.

When the high rainfall years at Palm Valley of 2000 and 2001 (see Fig. 3.3) are compared to records of the SOI, as shown in Fig. 3.5, it can be seen that these extreme rainfall years do correlate with a sustained period of positive SOI. When total monthly rainfall record at Palm Valley is compared to monthly SOI values as shown in Figure 3.6, it can be seen that not all periods of sustained positive SOI have resulted in above average rainfalls. Thus while the La Nina phenomenon may influence central Australia summer rain patterns, there is not a direct correlation with positive SOI (La Nina) events. La Nina years are more likely to result in a longer and more intense northern monsoon, which in turn then increases the opportunity for favourable synoptic conditions to occur that allow a southerly incursion of decaying tropical cyclones and/or the monsoon trough. This fact probably best explains the occasional correlation of extreme summer rain and La Nina events in central Australia. The occasional nature of this relationship is shown on Figure 3.5, where it can be seen that even though the SOI was strongly positive from the spring of 1998 to autumn 1999, no significant summer rain occurred. In contrast, it can be seen that during the following summer, positive SOI values are associated with the heavy rains of February and April 2000.

Thus while the causes of heavy rainfall in central Australia are understood, confident prediction of rainfall is not possible and the Bureau of Meteorology classification of the rainfall pattern in central Australia as being erratic seems the most apt description.

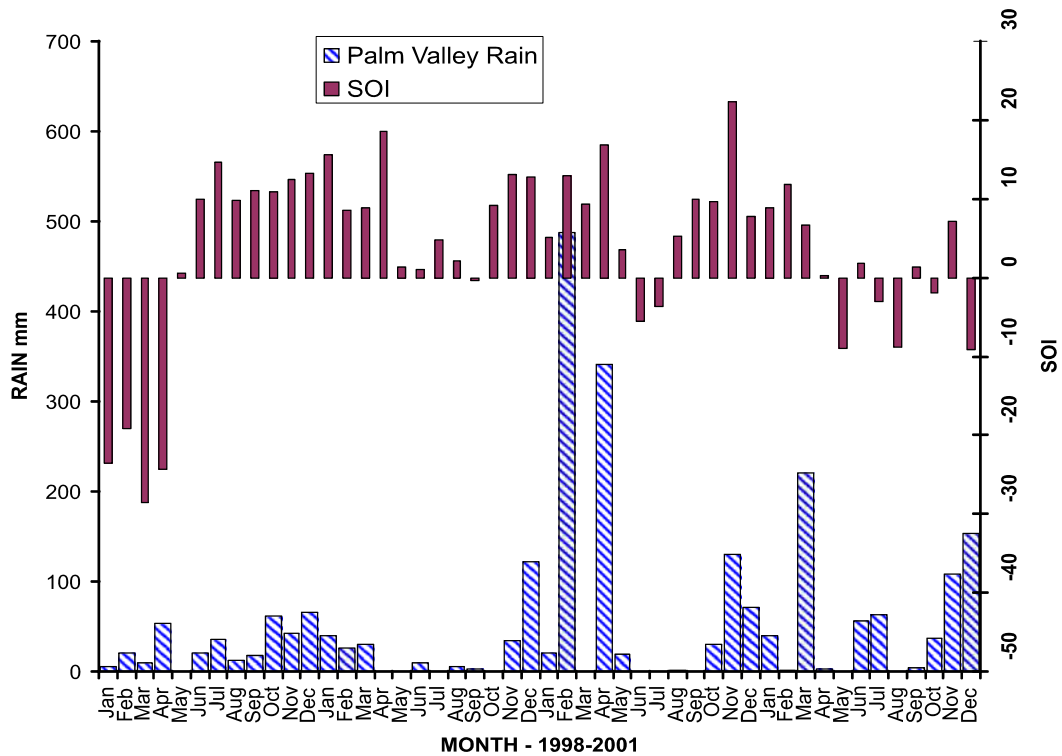


Figure 3-5 Monthly rainfall records and value of the Southern Oscillation Index (SOI) compared for Palm Valley 1998–2001. It can be seen that although a positive SOI existed for three summer periods in a row (1998–1999; 1999–2000; 2000–2001) extreme rainfall occurred only during the 1999–2000 summer. Data from BOM (www.bom.gov.au).

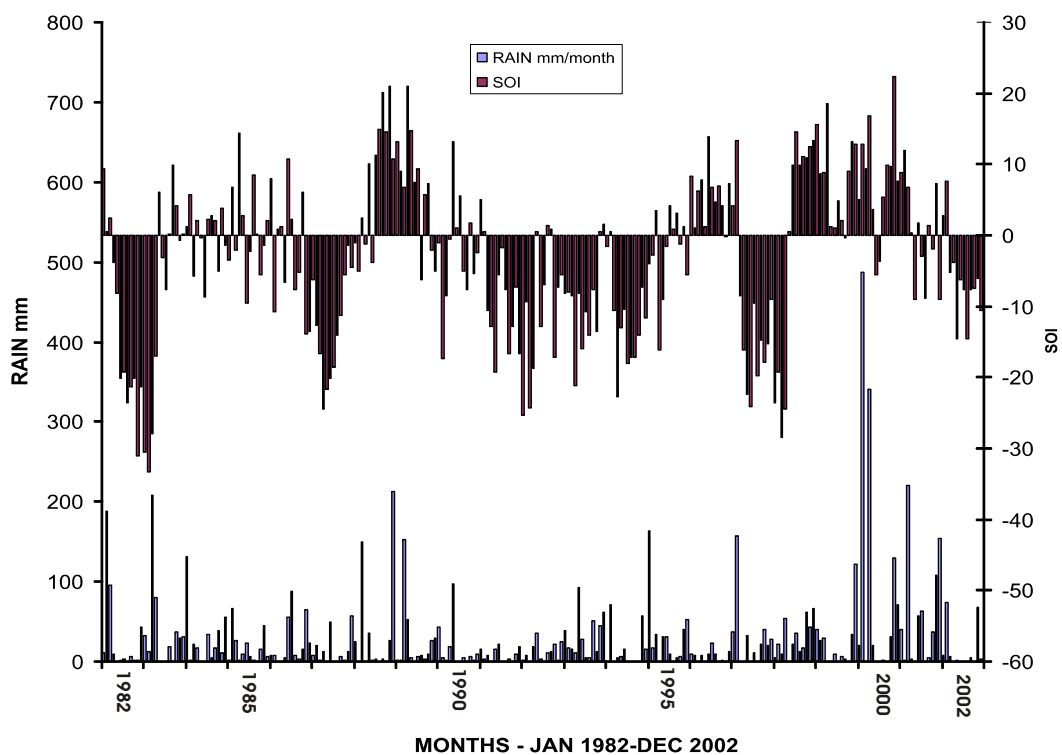


Figure 3-6 Monthly rain records and value of the Southern Oscillation Index (SOI) compared for Palm Valley. The majority, but significantly not all of the wettest months (> 150mm), seem to correlate with long periods of positive SOI. Data from BOM (www.bom.gov.au).

3.2.2. Temperature and Evaporation

Along with this low and variable rainfall, temperature and evaporation rate are high during summer in this region. Figure 3.7 shows the mean maximum and minimum temperatures for Alice Springs; large seasonal and diurnal variations are evident. Mean monthly maximum temperatures in January are over 36 °C while the minimum mean temperature is around 21°C. Conversely, in July mean maximum temperature is less than 20 °C (19.6) and mean minimum temperature is 4 °C (www.bom.gov.au; weather summary, Alice Springs Airport.).

Evaporation rate is also high in this region. Figure 3.8 shows the mean monthly class A pan evaporation for Alice Springs. When the monthly evaporation is compared to the monthly rainfall data, it can be seen that evaporation can be expected to far exceed rainfall even in winter months. The fact that the 9th decile monthly rain totals shown on Figure 3.8 are also well below evaporation rates indicate it is a rare month indeed for rainfall to exceed evaporation. Mean annual evaporation (3068mm) exceeds mean annual rainfall (285 mm) by an order of magnitude (i.e evaporation / precipitation is 10.8).

3.2.3. Summary

In summary the climate of central Australia is characterised by hot summers and cool winters. Rainfall is low and erratic with rain more likely in summer months. Rare incursions of the northern monsoon can result in widespread rain and thunderstorms in summer months.

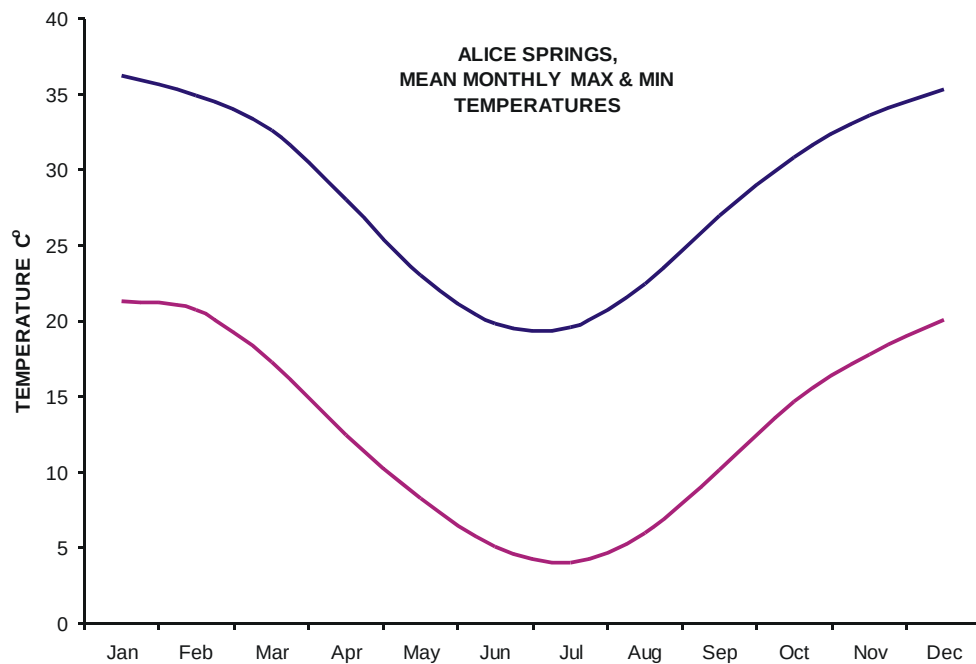


Figure 3-7 Mean monthly maximum and minimum daily temperatures (°C) at Alice Springs Airport (BOM station 015590).

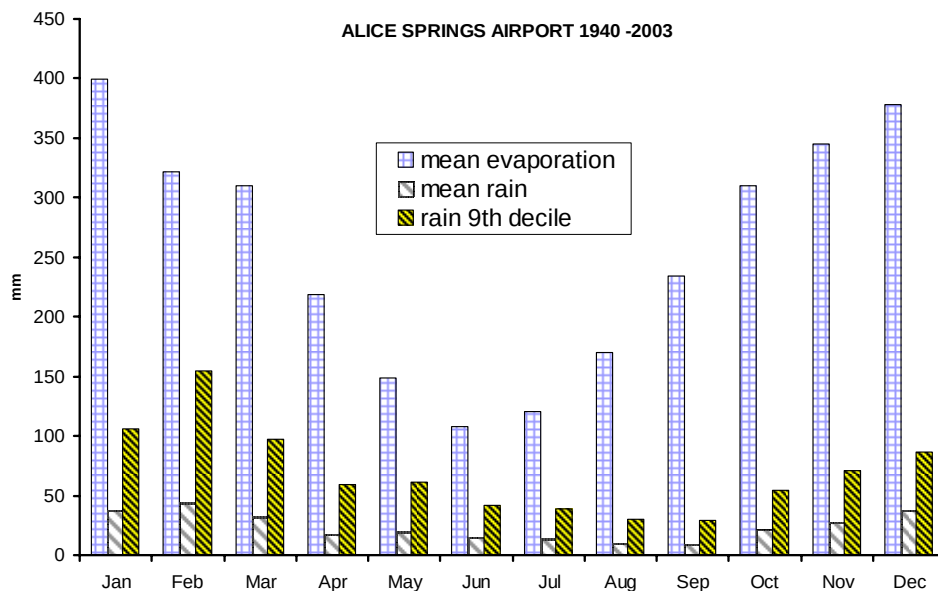


Figure 3-8 Mean monthly class A pan evaporation with mean and 9th decile monthly rainfall totals at Alice Springs Airport (BOM station 015590).

3.3. Topography

Palm Valley is surrounded by rocky ranges (Plate 3.3). These ranges rise up to 400 metres above the main stand of palms. The topography of the area surrounding Palm Valley is shown in Figure 3.9. Palm Valley is situated in the flatter area surrounded by ranges (known locally as Palm Paddock), as shown by the area of wide spaced topographic contours. The surrounding ranges are steep, as shown by the closeness of the 20m contours. Simpson et al. (1991) note the range country to be steep to moderately undulating with slopes of 15-30° common and some erosion gullies to have sandstone walls with over 200m of relief. The majority of the area, shown in Figure 3.9, drains to the Finke River. This river runs for hundreds of kilometres south eastwards towards Lake Eyre from Palm Valley (Fig. 1.1).

3.4. Land Systems

Land systems are areas or groups of areas throughout which there is a recurring pattern of topography, soils and vegetation (Low et al., 2004). Perry et al. (1962) have mapped and defined the land systems of the Alice Springs region. The Palm Valley region of the Finke Gorge National Park is mapped as being Krichauff land system. This system is noted by Perry et al. (1962) to occur in sandstone range country throughout central Australia. They describe the geomorphology of this system as eroded and dissected sandstone plateaux with superimposed drainage of narrow gorges and joint-controlled tributaries. The dominant vegetation is described as sparse shrubs and low trees over Spinifex grasses. River Red Gums, Ghost Gums and Ironwoods can also occur along river channels that dissect the sandstone plateaux. Dames and Moore (1982) determined the soils of this land system as Lithosol shallow (<10 cm depth) skeletal sands with little pedological development. These soils are noted to be coarse-textured, noncalcareous, lacking in coherence and chemically and physically infertile. In larger drainages such as the Finke River, coarse sands are common. Simpson et al. (1991) describe soils near the apex of the Palm Valley anticline to be comprised of quartz sands and sandstone fragment framework and note these red to reddish yellow soils are thin and rich in secondary iron oxides. The soil matrix is described as kaolinite with traces of illite, montmorillonite and iron oxides.

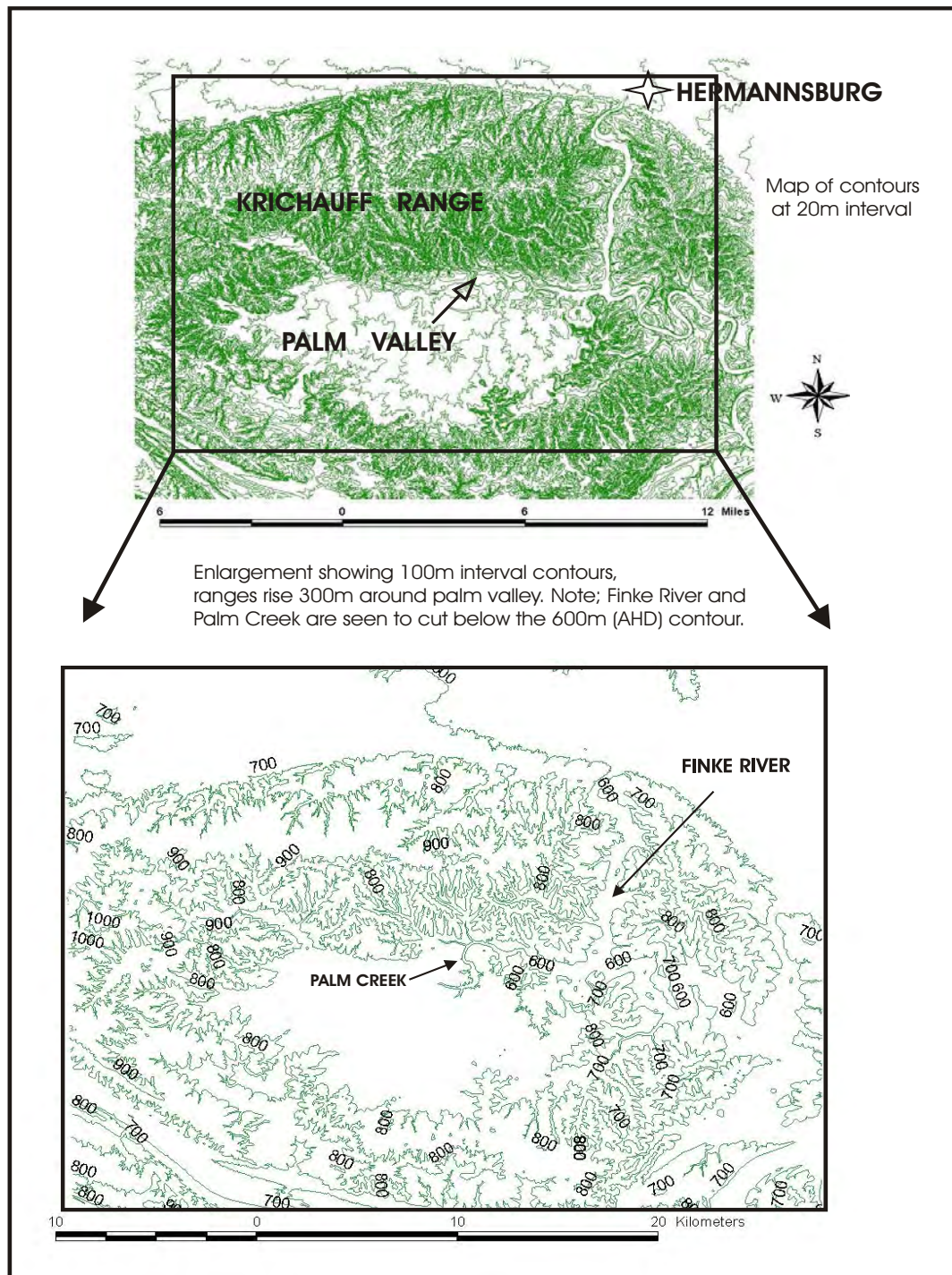


Figure 3-9 Topography of the area surrounding Palm Valley. The upper map shows the topographic contours at 20m intervals. The close spacing of these contours prevents annotation with contour heights at this scale but an appreciation of the steepness of terrain and relative flatness of the plain, known as Palm Paddock, is discernible. The path of the Finke River as it cuts through the ranges is clearly marked as a line of no contours in the upper right corner of this map. The lower map is a plot of only the 100m (AHD) contour data with heights annotated. The Finke River and Palm Creek drainage lines are seen to cut below the 600m AHD contour. Contour data are from AusLig, via Finke Gorge National Park.

Given the name of this land system is taken from the Krichauff Ranges that border Palm Valley, it is likely the description of this land system well matches the country around Palm Valley. Figure 3.10 shows a schematic diagram of this land system and highlights some of its component land units. Land unit number 6 on this diagram, described by Perry et al. (1962) as narrow valley floors of major through-going drainage, is noted by Low et al. (2004) to contain a broad diversity of plant species and represents the habitat within the Finke Gorge National Park where the majority of rare and relict plant species occur. Figure 3.11 shows a map of the number and distribution of endemic species near Palm Valley. From this figure, it can be seen that the sheltered gullies running south from the Krichauff Ranges hold the greatest number of endemic species. Details of the flora and fauna of the land units of the Krichauff Land system are given by Dames and Moore (1982) and Low et al. (2004).

3.5. Flora

3.5.1. Introduction

Latz (1996) discusses and rates the relict nature of many of the plant species found in Palm Valley. The palms are described in some detail by Latz (1975) and are commonly assumed to represent a relict stand that has survived at Palm Valley since a wetter climate allowed a wider distribution. In recognition of this relictuality *Livistona mariae* is listed by the Australian and New Zealand Ecological Conservation Council as a vulnerable species worthy of conservation (Morton et. al., 1995). The NT government information sheets on threatened species series note this palm is listed by the Federal Environment Protection and Biodiversity Conservation (EPBC) Act (1999) as a threatened species with a vulnerable status.

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Figure 3-10 Schematic of Krichauff land system. Numbers mark the various units that make up this land system. Land unit number 6 is the narrow valley floor of through-going drainage and represents the habitat in which most rare and relict plant species occur in the Palm Valley region. (After Perry et al., 1962).

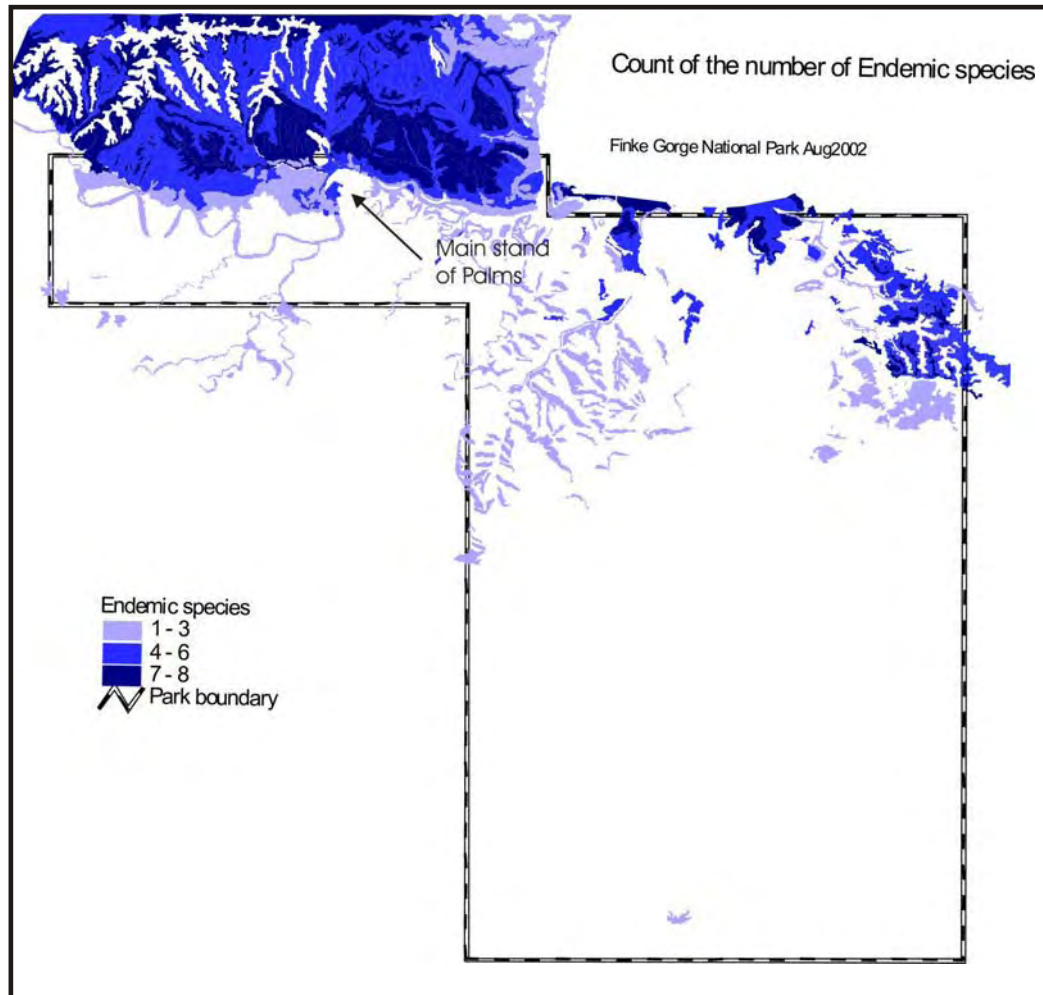


Figure 3-11 Schematic of distribution of endemic plant species around Palm Valley. (Image from Dennis Matthews, Finke Gorge National Park.)

3.5.2. *Livistonia mariae*

This palm (Family: *Arecaceae*) was first described, by the naturalist F. von Mueller in the 1870s, from specimens collected from the Finke River by the explorer Ernest Giles. Rodd (1998) reviews several of these descriptions and notes there is some confusion as to which publication actually defines the *mariae* species, but notes that by 1878 this name was associated with the central Australian palm. For a long time (first described in the 1870s by Mueller, Rodd, 1998) perhaps encouraged also by the geographical separation, the Palm Valley *Livistonia mariae* were regarded as a distinct species. Similar palms to the north at (e.g. Mataranka and Lawn Hill, Fig. 1.1) were classified as a separate species, *Livistonia rigida*. In a comprehensive review of the *Livistonia* species in Australia, Rodd (1998) has now reclassified some of these palms. Due to the very similar morphology of the *Livistonia rigida* found at Mataranka, eastern Arnhem Land and far north west Queensland and some remote palms in the Kimberly region of Western Australia (King Leopold and Durack Ranges) with the Palm Valley *Livistonia mariae*, Rodd (1998) regards these three geographical populations as subspecies of *Livistonia mariae*. The Palms at Palm Valley are designated *Livistonia mariae* subsp. *mariae*, the northern palms (formerly *Livistonia rigida*) as *Livistonia mariae* subsp. *rigida* and the Kimberly palms as *Livistonia mariae* subsp. *occidentalis*.

Rodd (1998) acknowledges that the assignment of the central Australian palms as being conspecific with the various northern Australian populations is potentially controversial. However, apart from the slight but consistent differences in leaves and fruits he notes between these populations, he concludes that the striking resemblance of most organs is overwhelming evidence that these populations are the one species. Detailed description and definition of these three subspecies are given by Rodd (1998).

How long the palms have been separated from their nearest relatives 1000 km away in the wet-dry tropics of northern Australia is uncertain. Given the arid climate of central Australia and the fact that Rodd (1998) notes *Livistonia mariae* sp. to always occur near permanent water even when found in northern Australia suggest groundwater is crucial to the palms survival at Palm Valley.

3.5.3. Genetic evidence of isolation

3.5.3.1. *Livistona* species

Preliminary results of a comparative DNA gene sequencing study of the morphologically very similar palms at Palm Valley and Mataranka to the north indicated significant genetic divergence and thereby gave an indication of long time separation between populations (Bowman, pers. comm., 2002). This seemed to support the hypothesis that a refugium operates at Palm Valley. However, subsequent analyses of the chloroplast DNA by Japanese researchers have been unable to detect a genetic difference between these two populations (Isagi, pers. comm., 2003). In fact phylogenetic differences between *Livistona mariae* and other morphologically diverse northern Australian species (*Livistona humilis* and *L. inermis*) could not be recognised from these analyses of chloroplast DNA. (see Fig. 3.12). Thus, given this indication that in some instances speciation may not be registered by changes in chloroplast DNA, further work, perhaps utilising DNA from other types of cells, is needed to determine which, if any, genetic differences exist between the central and northern Australian *Livistona mariae* subspecies.

A comparison of allozymes from an isolated stand of *Livistona australis* in south eastern Australia with the nearest major stand 180km further north by Orscheg and Parsons (1996) had similar results in that no genetic differences were discernible and hence no insight into how long these two populations may have been separated was gained.

Thus, as apparently standard genetic testing methods do not give clear information on genetic differences between populations and sometimes species, more work on the genetic characteristics of the *Livistona* species may be needed for useful comparisons between separate populations to be made.

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Figure 3-12 Preliminary unpublished phylogenetic tree of some Australian *Livistona* species based on analyses from 6 loci in chloroplast DNA. Reliability of this tree is considered uncertain by its creators, as genetic variations are very low based on these data. Additional analyses of these species genetics is ongoing; however, this diagram illustrates the possibility that the *Livistona mariae* (Palm Valley) and *Livistona rigida* (Mataranka) species are genetically indistinguishable. Data from Isagi, pers comm. 2003.

3.5.3.2. Cycads

The other well known endemic, seemingly wet climate plant species that exists in central Australia and at Palm Valley, the cycad fern (*Macrozamia macdonnellii*) occurs in shaded apparently moist gorge habitats throughout the MacDonnell ranges (Morton et al., 1995). Other Australian cycads occur only in wetter regions along the north, east and south west coasts (see distribution map Fig. 3.13) so this species, like the *Livistona mariae*, has also been considered a relict from when a wetter climate prevailed in central Australia. Sharma et al. (2004) in a study of genetic variation of cycads in northern New South Wales noted that even some morphologically distinct species of *Macrozamia* had very low genetic differences, which makes it very difficult to genetically characterise these morphospecies as distinct species. Thus even if cycads were adopted as a surrogate for the central Australian palms in an attempt to use genetic differences between central Australian and coastal populations to determine how long seemingly wet climate relict fauna have existed in the region, results may also prove inconclusive. Sharma et al. (2004) note that a range of molecular genetic techniques may be needed to adequately gauge genetic differences between some species of cycad.

3.5.3.3. Discussion

Until rigorous genetic analyses are conducted, other explanations for the existence of the incongruent tropical flora in central Australia are possible. For instance transportation of plant seeds by water birds travelling along chains of natural waterholes less than 200 km apart that link Palm Valley to the south and north of the continent is proposed by Latz (1996) as a plausible explanation for the presence of tropical (non relict) like vegetation at Palm Valley. However, the lack of palms in the intervening country or at other known refugia (Morton et al., 1995) in the central Australian MacDonnell ranges does not lend support to a bird-borne propagation of this palm. Orscheg and Parsons (1996) also note the possibility of bird or even mammal transportation of seed may explain the existence of the isolated stands of *Livistona australis* in western Victoria (southeastern Australia). The cycad fern (*Macrozamia macdonnellii*) has a similar distribution to the palms, in that no occurrences link the coastal and central Australian cycad populations, hence a bird-borne propagation

mechanism, if applicable, has also failed to leave a trail in the intervening country between cycad occurrences. In fact Sharma et al. (2004) note cycads have no mechanism for long distance dispersal. Given these points, the explanation of these “wet climate” plant types being relicts marooned in the arid interior since a previous wetter time seems more likely. Whether this isolation has operated since the onset of aridity in central Australia or since some Quaternary pluvial period when perhaps climate allowed connection to coastal populations along river corridors is yet to be determined.

3.5.3.4. Conclusion

Application of genetic studies has the potential to give an insight on the genetic divergence between the so called relict isolated central Australian “wet climate” flora of palms and cycads with distant analogues that grow in modern day wetter climates. Unfortunately, straightforward techniques such as comparison of allozymes (Orscheg and Parsons, 1996; Sharma et al., 2004) and DNA sequencing (Isagi, pers. comm., 2003) do not necessarily allow ready determination of genetic divergence for these two types of plants. Thus, a study of the relict nature of palms (and cycads) in central Australia from genetic characteristics will seemingly require a specifically orientated comprehensive study using various techniques. The results of any such study would be of interest as apart from period of separation an indication as to how long shallow groundwater has discharged at Palm Valley may also be gained.

3.5.4. Water Requirements

It has long been inferred that groundwater sustains these palms (Chapter 1), actual proof that this is so and what the water requirements of this family of palm are yet to be determined. There is circumstantial evidence that supports a groundwater dependency for the *Livistona mariae*, the palms seemingly survive protracted dry spells here and exist no where else in the arid zone. The populations of relict fish that exist in nearby spring pools (Davis, 1997) support the notion of a permanent groundwater supply being available to the palms at Palm Valley. Protracted dry periods of over 200 days are occasionally recorded in central Australia (e.g. at Tempe Downs, 130 km south west of Palm Valley, Bureau of Meteorology records show that no rain at all was recorded for over 250 consecutive days during both 1894 and 1944).

The fact that date palms thrive at mound springs but nowhere else in the desert surrounding the Great Artesian Basin fed Dalhousie springs in the driest part of the continent in northern South Australia shows at least one other species of palm that also is inferred need a groundwater source to survive in the Australian arid zone. In central Australia there are some data on Date Palm tree water usages, at the Northern Territory Government Arid zone research institute block at Alice Springs where Date Palms are irrigated and closely monitored for research purposes Nesbitt (pers. comm., 2005) reports that drip irrigated mature Date Palms use an average of 200 litres of water each per day.

The investigation of *Livistona* palm plant water use physiology is apparently yet to be done. Indeed two of the leading experts on *Livistona* Palm species, John Dransfield at the Royal Botanic Gardens, Kew, England and the Australian expert John Dowe at James Cook University in Townsville, Queensland both acknowledge that the link of groundwater to palm growth in desert regions around the world has never been proved to their knowledge, even though the postulated water requirements of these species of plant suggest that this is so. For instance John Dransfield (pers. comm. 2005) notes " ...there are several palms that occur along water courses in areas of very low rainfall, and it has always been assumed that it is availability of near surface groundwater that allows these palms to grow in otherwise very hostile environments." John Dowe (pers. comm. 2005) notes "I don't know of any studies or research projects that have assessed the water requirements of *Livistona mariae*."

There are, however, some studies in tropical Australia where plant water use has been studied e.g. Eamus et al., 2001; Cook et al., 1998; Lamontagne et al., 2005. These studies have not, however, concentrated on any *Livistona* species. Interestingly the recent study by Lamontagne et al. (2005) managed to determine deuterium values for xylem water from several tree species and by comparison to soil, river and groundwater deuterium values in the area estimate which tree species were groundwater dependant during the dry season. Thus it may be that given sufficient data some future adaptation of this technique may yet confirm groundwater dependency of the *Livistona mariae* at Palm Valley.

Given the above it seems that, like the studies of *Livistona sp.* DNA mentioned above, much is yet to be learnt on the physiology of the *Livistona mariae* or indeed any other *Livistona* species.

3.6. Aboriginal connection

The northern section of Finke Gorge National Park in which Palm Valley lies is surrounded by Aboriginal Land. Aboriginal people lived in central Australia before European settlement in the 19th century. It is not known exactly how long people have inhabited the Palm Valley area; however, human occupation has been dated to around 22 ka, 150 km west of Palm Valley in the Cleland Hills by Smith (1987, 1989). Latz (1995) notes that the *Livistona mariae* palm features strongly in Aboriginal mythology throughout the central Australian region.

When the township at Hermannsburg (15 km north of Palm Valley) was settled in 1877 as a Lutheran mission, the local Aranda speaking Aboriginal people slowly began to congregate at this site. Descendants of these “Western Aranda” people (Stead, 1982) have strong traditional links to the country around Hermannsburg where most of them now live. In the late 1990’s a small portion of the Finke Gorge National Park, which included the main stand of palms in Palm Creek (Palm Valley), was subject to an Aboriginal Land rights claim under the Federal Government Land Rights (Northern Territory) Act, 1976. In a report of this land claim, Gray (1999) details the strong affiliation many Aboriginal people have with Palm Valley, which is known as *Ntarea* in the Aranda language. In order to determine what group had claim to this land under the Act, Justice Gray took evidence from interested Aboriginal parties on their spiritual connections with sites on the *Ntarea* estate.

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Figure 3-13 Distribution of cycads in the Australian region (after Jones, 2002). The *Macrozamia macdonnellii* of central Australia, found at Palm Valley and elsewhere in nearby ranges, is seen, like the *Livistona mariae* palms, to be an isolated mid-continent dwelling species.

The main “dreaming” sites connected to Palm Valley are the *Ratapa*, or Twins Dreaming, the *Lakabara*, or Black Falcon Dreaming and the *Yelka*, or Bush Onion Dreaming. At one of the main dreaming sites *Itaratara*, which lies in the bed of the Palm Creek near the upstream extent of the main stand of palms (see Fig. 3.14), marks in the bedrock represent the twins of the *Ratapa* Dreaming. Custom has it that lying on one of the twins will enable a person to become fat or thin, depending on which twin is selected (Gray, 1999).

One of the outcomes of the Palm Valley land claim was that a group of 978 Aboriginal people, the Renkeraka/Ratara group who mainly come from Hermannsburg, were determined to be the traditional Aboriginal owners of Palm Valley. The connection of Aboriginal people to Palm Valley has long been recognised by Finke Gorge National Park management. Consultations on park management issues are routinely made. In fact one of the senior Aboriginal custodians for Palm Valley lives on an outstation 8km south of Palm Valley. This allows for ready communication between park staff and traditional owners.

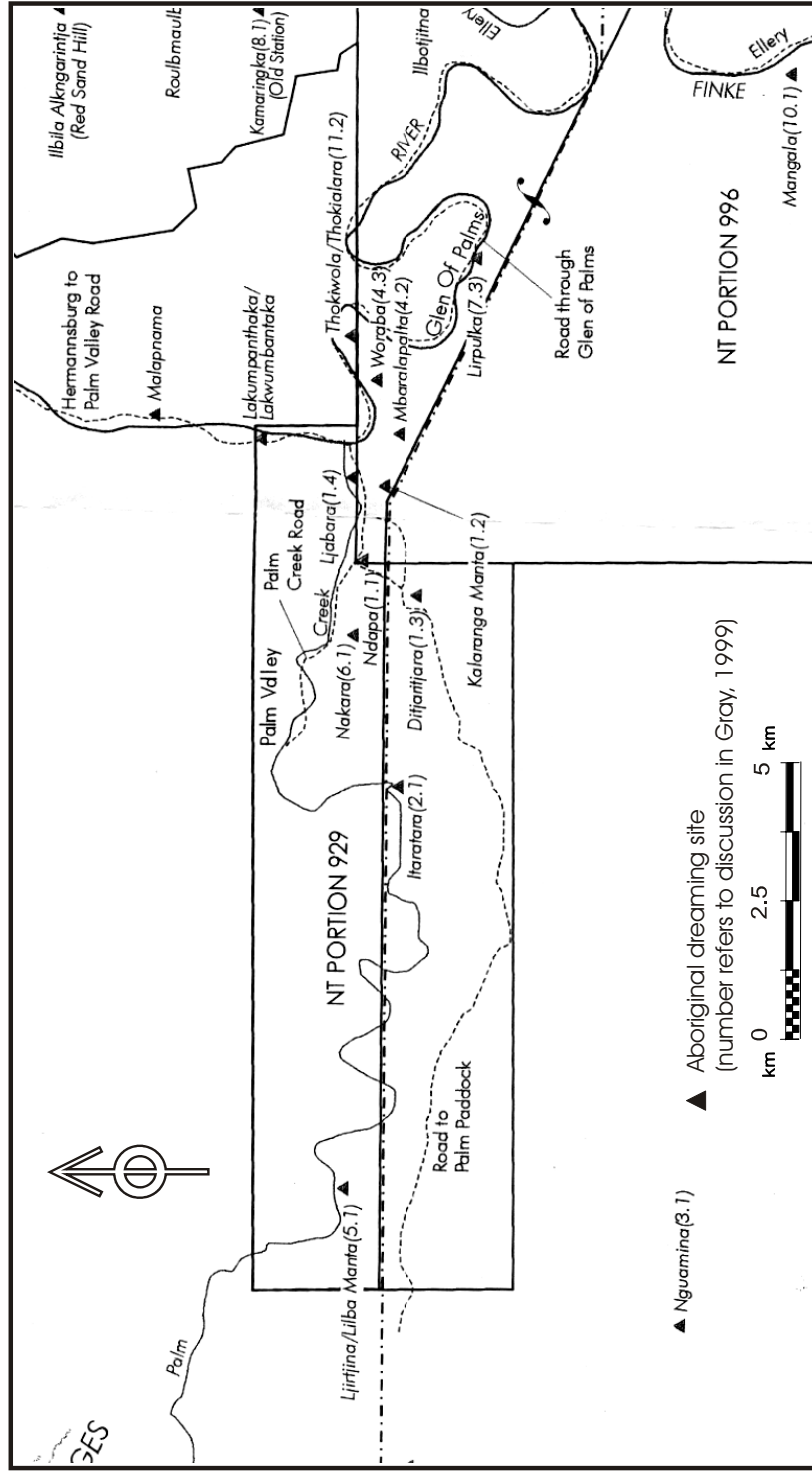


Figure 3-14 Location and Aranda name of Aboriginal dreaming sites near Palm Valley as listed during a Land Claim hearing. The site marked Itaratara (2.1) is located near the main stand of palms at Palm Valley and represents a significant place in the Ratapa or Twins Dreaming. Image adapted from Gray (1999).

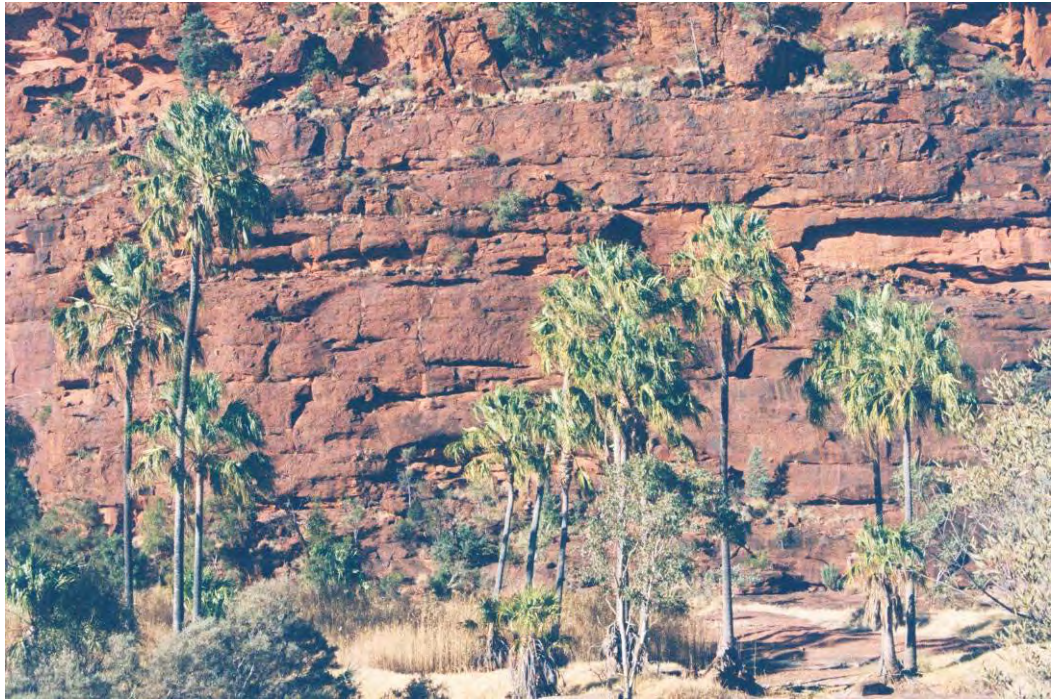


Plate 3-1 *Livistona mariae*, Palm Creek, Palm Valley. Red Cabbage Palms (*Livistona mariae*) growing in Palm Creek at Palm Valley. The Hermannsburg Sandstone forms the gorge wall in the background.



Plate 3-2 Palm Valley; roughly half of the main stand of Palms in Palm Creek looking east towards the Finke River from the top of the northern gorge wall. Vibrant community with all stages from seedlings to mature trees present.



Plate 3-3 Palm Plain as seen looking southwest from Palm Valley 8 gas well site on top of the Krichauff Range from the eastern side of the Finke River (cream coloured sand and river gums along the Finke are seen in the bottom right of the photo.). The contrast between the Palm Plain and surrounding topography is evident. The vast extent of Hermannsburg Sandstone is also illustrated by this photo, as all hills shown are outcrops of this sandstone.

4. Hydrogeology

4.1. Geology

4.1.1. Introduction

The first systematic government geological mapping program to cover Palm Valley was reported by Ranford and Cook (1964) in a set of notes and map covering the Henbury 1:250 000 sheet area. A detailed account of prior geological work is given in these notes; reconnaissance appraisals by various geologists and exploration mapping for minerals and petroleum comprise most of these earlier reports. These notes represent a part of the Australian Government's Bureau of Mineral Resources (BMR) systematic mapping program of the Amadeus Basin, a sediment filled intracratonic depression that covers a large area of central Australia. Mapping and photo-geological studies by various petroleum companies prior to this mapping program had identified various potential petroleum traps based on surface structural expression. One of these features is named the Palm Valley anticline due to its proximity to Palm Valley. In 1965 a successful petroleum (gas) exploration well (Palm Valley No. 1) was drilled on the Palm Valley anticline (a few kilometres north east of Palm Valley on the banks of the Finke River). This well has subsequently led to the development of a commercial gas field along this anticline (Do Razzio, 1991).

4.1.2. Mapping

In 1968 the first geological map of the Henbury 1 : 250,000 sheet which covers the Palm Valley area was published (Cook, 1968). In 1970 detailed results of the BMR mapping program of the whole Amadeus Basin was also published (Wells et al., 1970). Figure 4.1 shows the extent of the Amadeus Basin, distribution of some relevant lithological units, and the location of Palm Valley within the Amadeus Basin.

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Figure 4-1 The Amadeus Basin, distribution of relevant lithological units and the location of Palm Valley. (Reproduced from Simpson et al., 1991)

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Figure 4-2 Geology near Palm Valley. On this map the unit Pertnjara group (annotated as Pzp on the diagram) coincides with the distribution of the Hermannsburg Sandstone in the area shown. The Pertnjara Group had not been formally separated into members such as the Hermannsburg Sandstone at the time this geology map was compiled. After BMR, 1970.

Figure 4.2 shows the geology near Palm Valley. On this more detailed map a unit called the Pertnjara Group is annotated as Pzp on the diagram. The Pertnjara Group was first proposed by Chewings (1931), with the name pertnjara which means 'many stones' in the local aboriginal Aranda language being an appropriate name for a unit which contains conglomerates. The Hermannsburg Sandstone is a member of this group and the outcrop shown surrounding Palm Valley is in fact solely comprised of Hermannsburg Sandstone (see Figs 4.2 and 4.1). The Pertnjara Group has been differentiated on later larger scale maps. For instance the Henbury 1: 250 000 geological map (Cook, 1968) clearly shows Palm Valley to be surrounded by Hermannsburg Sandstone. It should be noted that as the Palm Valley area lies near the boundary of two 1:250,000 map sheets the older smaller scale mapping image has been presented (Fig 4.2) for clarity. The Pertnjara Group was divided into three members (Parke Silstone, Hermannsburg Sandstone, Brewer Conglomerate) by Wells et al., (1970). The Hermannsburg Sandstone is named after Mount Hermannsburg which lies about 7 km north of Palm Valley in the Krichauff Ranges (see Fig. 1.1).

The geology of the Hermannsburg Sandstone near Palm Valley has been of ongoing interest to petroleum companies, and other mapping covering the Palm Valley area has been presented by Thigpen (1973) and Pancontinental (1984). In all this mapping the Palm Valley area is shown as an anticline with gentle dips. Palm Valley lies on the southern flank of Palm Valley anticline and a syncline axis is mapped just south of the Palm Creek. Dips are very flat at around 5 or less degrees along the southern flank as seen on examination of Figure 4.3. Detailed structural mapping of the Hermannsburg Sandstone, while potentially being of interest as a clue to the structure of deeper gas bearing strata to petroleum companies, has been hampered by a lack of distinct marker horizons (Magellan, 2003).

4.1.3. Stratigraphy

Palm Valley lies on a vast outcrop of the Hermannsburg Sandstone (Figs 4.1, 4.2). The Palm Plain area generally has only superficial Cainozoic cover with the Hermannsburg Sandstone usually within 1 m of the ground surface. Palm Creek, in which the main stand of palms is found, is incised into this sandstone and drains into the Finke River,

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Figure 4-3 Map of geological structure near Palm Valley. The Palm Valley anticline axis and shallow dips of the limbs are clearly seen.
After Do Rozario et al., 1991.

one of the major rivers of central Australia. The Devonian Hermannsburg Sandstone is part of the Amadeus Basin stratigraphic succession as illustrated in Figure 4.4. The middle to Upper Devonian event, the Pertnjara Movement, initiated the deposition of the Hermannsburg Sandstone in the Amadeus Basin. A subsequent Late Devonian event, the Alice Springs Orogeny, resulted in the folding of the Hermannsburg Sandstone (Wells et al., 1970).

Jones (1991) has further refined the relationship of lithology to tectonics and links variation in distribution, facies and grainsize of the whole Pertnjara Group with several distinct tectonic events or pulses during the Alice Springs Orogeny. Initiation of the Hermannsburg Sandstone deposition is linked to the Henbury Movement. The predominantly medium grained, red-brown quartzose sandstone with very few siltstone lenses suggest deposition on an extensive braid plain. The lack of coarse scale detritus indicates either a low relief or distant source area (Jones, 1991).

The upper Ljiltera Member of the Hermannsburg Sandstone defined by Jones (1972), which is distinguishable from the lower undifferentiated Hermannsburg Sandstone, by the presence of medium and coarse grained pebbly sandstones, was deposited in response to the subsequent Brewer Movement. The presence of larger detritus indicates a more intense uplift along the northern edge of the Amadeus Basin is associated with the Brewer Movement than with the Henbury Movement. The following deposition of 3000+ metres of coarse Brewer Conglomerate above the Ljiltera Member (see Fig. 4.4) indicates the intensity of this movement continued to increase in the Early Famennian. Major folding of the Pertnjara Group that produced numerous intra-basinal anticlines (e.g. the Palm Valley anticline) separated by broad synclines in the Amadeus Basin is inferred by Jones (1991) to have taken place during the Late Carboniferous.

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**Figure 4-4 Stratigraphy of the north east and south central Amadeus Basin.
After Oaks et al., 1991.**

4.1.4. Lithology

The red brown Hermannsburg Sandstone near Palm Valley is observed to be the upper Ljiltera Member (Warren and Shaw, 1995). This upper sequence is described by Jones (1972) as orange to reddish brown litharenite and rare sublitharenite, fine to very coarse sand which is commonly trough cross stratified in co-sets varying from 1 to 5 m in thickness. Pebbles and mudclasts up to 7 cm in size are common at the base of these cosets. The cosets generally become finer grained upwards and may merge into smaller scale tabular cross stratified beds or flat beds. The sequence can therefore be divided into numerous partially complete sedimentary cycles.

The Hermannsburg Sandstone is described by Jones (1972) as cross stratified and minor flat bedded medium to very coarse grained sandstone. Fine grained sandstones are rare and sandy siltstone beds are very rare. The main difference of the Ljiltera Member from the rest of the section is that generally pebbles or clasts are rare below the Ljiltera Member.

4.1.5. Structure

The Hermannsburg Sandstone is described by Lindsay and Korsch (1991) as a synorogenic molasse-like succession. This sandstone thins southwards away from the northern Amadeus Basin margin, though Jones (1972) infers the Hermannsburg Sandstone to be over 1000 m thick with the upper Ljiltera Member, characterised by the presence of occasional pebbly facies, being over 200 m thick near Palm Valley.

The Hermannsburg Sandstone is gently folded in the Palm Valley region (Ranford and Mikolajczak, 1963). The Palm Creek area is on the southern flank of the Palm Valley anticline with a syncline axis mapped through Palm Plain. The anticline is mapped as an arcuate (convex to the north) structure at the surface (Hermannsburg Sandstone) and from seismic data with steeper dips on the northern flank (Do Rozario and Baird, 1987). The anticline axis can be traced for over 40 km at the surface.

In outcrop, this sandstone is jointed near Palm Valley. Thigpen (1973) mapped the joints/lineaments from airphoto interpretation in this area as part of early petroleum exploration by Magellan Petroleum. These lineaments/joints were studied to help understand the nature of the fractured gas reservoir at depth in the Pacoota Sandstone. Figure 4.5 shows a portion of this fracture mapping (with other features) near Palm Valley. Analysis of the fracture patterns identified two major trends, a north westerly and a north easterly. Do Rozario and Baird (1987) interpret these patterns as evidence of one or more conjugate systems of shear fractures formed by compression during folding associated with Alice Springs Orogeny. Other trends, as shown on Figure 4.5, are thought to possibly reflect other episodes of folding and/or younger fracturing due to post folding horizontal rotation or tensional unloading of the anticline.

Mah et al. (1995) using edge enhancement techniques of satellite images and some field mapping along the crest of the Palm Valley anticline have classified some east-west and north-south fracture trends as additional major lineaments. On the basis of these additional trends, some of which seem to have been previously mapped (Fig. 4.5) by Thigpen (1973), Mah et al. (1995) propose a possible two stage deformation model for the formation of the Palm Valley anticline. The first stage, with principle north south stress direction is believed responsible for an east west trending anticline. The second stage with an east to west principal stress direction is then inferred to have transformed the east west Palm Valley anticline into an arcuate anticline. Most other workers (Lindsay and Korsch, 1991; Warren and Shaw, 1995) favour several pulses of north south compression during the Alice Springs Orogeny to have caused the structural features such as the Palm Valley anticline.

While the exact structural history is an important consideration to oil companies interested in the timing of gas entrapment etc, the present day structural and fracture configurations are the most relevant aspects of structural geology to groundwater studies.

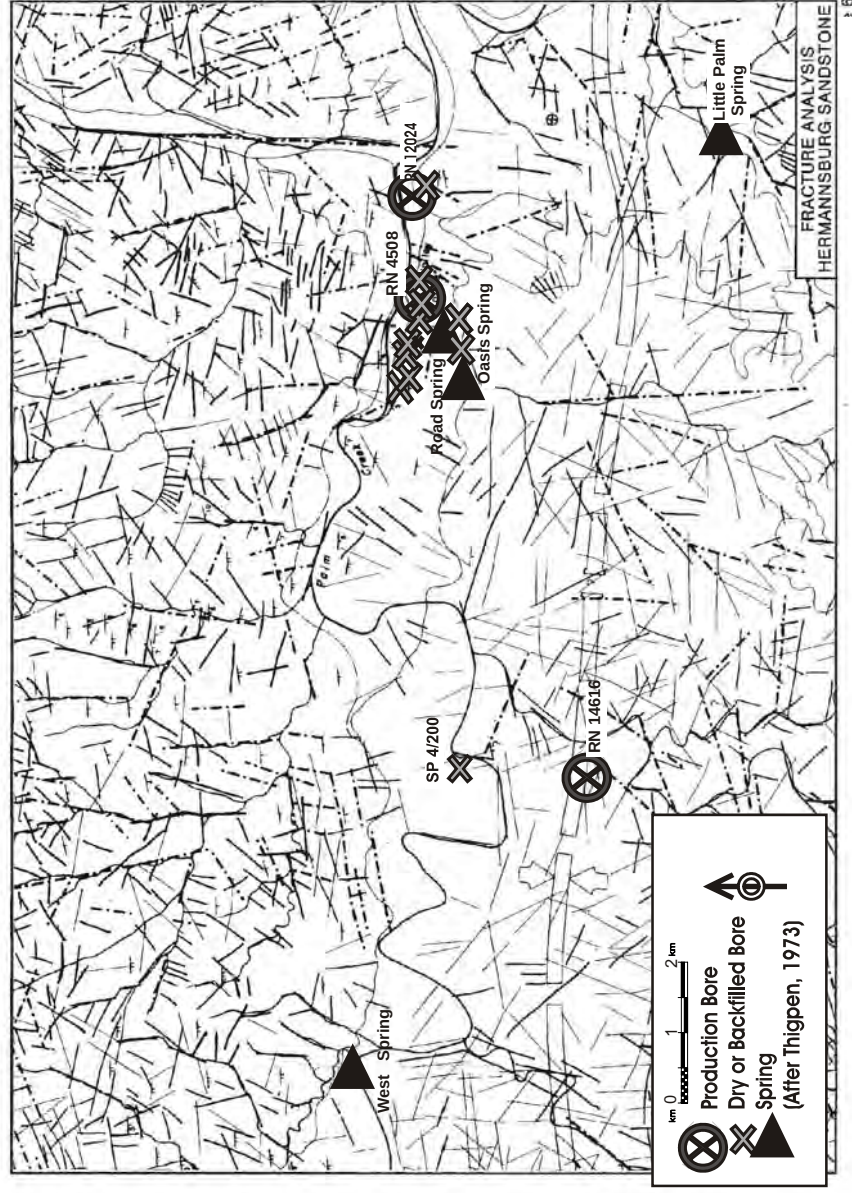


Figure 4-5 Aerial Photograph Lineament Interpretation, Hermansburg Sandstone
Air photo interpretation of lineaments (fractures/joints?) in the Hermansburg Sandstone near Palm Valley (After Thigpen, 1973).
Hydrogeological features such as bores and springs are also shown. There is a probable association of these hydrogeological features and enhanced permeability due to the mapped lineaments.

4.2. Background - Aquifer characteristics

4.2.1. Introduction

The aquifer characteristic usually calculated from test pumping is aquifer transmissivity. When observation bores in addition to the pumped bore are available aquifer storage parameters can also be calculated. For an unconfined aquifer, the storage parameter sought is known as specific yield, and is defined by Hazel (1975) as "the volume of water which will drain under gravity from a unit volume of aquifer" and thus is expressed as a dimensionless ratio. It is usually noted that this parameter, while obviously associated with the aquifer's porosity, refers only to the drainable volume of stored water; surface tension and lack of interconnected voids will result in some portion of water being retained within the aquifer once the specific yield is released. Transmissivity is a measure of the aquifer's ability to transmit water and is related to the fundamental equation of groundwater flow, known as Darcy's law (Freeze and Cherry, 1979). The derivation of Darcy's mid-nineteenth century empirical law is described in most hydrogeology texts. Krusemann and de Ridder (1970) define Darcy's law thus "the rate of flow through a porous medium is proportional to the head loss, inversely proportional to the length of the flow path, and proportional to a coefficient k , and may be expressed by

$$Q = kiA \quad (4.1)$$

where Q is the flow rate (m^3/day), k is a constant (m/day), i is the hydraulic gradient, i.e. the loss of head h over a distance l , A is the total cross section perpendicular to the flow (m^2) or

$$Q/A = v = ki \quad (4.2)$$

where Q is the flow rate (m^3/day), k is a constant (m/day), i is the hydraulic gradient, i.e. the loss of head h over a distance l , A is the total cross section perpendicular to the flow (m^2) and v is the Darcy velocity (m/day)".

Transmissivity (T) is related to the Darcy flow equation coefficient k by the relation;

$$T = kb \quad (4.3)$$

where b is the aquifer thickness (Hazel, 1975). The Darcy flow equation coefficient k is known as the hydraulic conductivity and is defined by Hazel (1975) "as the rate at which water is transmitted through a unit area under a unit gradient." It should not be confused with velocity, as the dimension of length / time is a shortened version of $\text{length}^3 / \text{length}^2 \times \text{time}$. Transmissivity is then the rate of flow, under a hydraulic gradient equal to one, through a cross-section of unit width over the whole thickness of the aquifer. It is commonly designated by the symbol T and has the dimensions of $\text{length}^3 / (\text{time} \times \text{length})$ or $\text{length}^2 / \text{time}$ and is usually expressed in the units m^2/day (Krusemann and de Ridder, 1970).

4.2.2. Fractured aquifers

The extensive mathematical equations used to determine aquifer characteristics under various hydraulic conditions are mostly based on the Darcy flow equation (Hazel 1975). However, the vast majority of test pumping equations presented in the literature, where the analysis of groundwater flow to bores allows the determination of aquifer characteristics, are based on many assumptions of ideal aquifer performance and usually restricted to groundwater flow through granular porous media only (Freeze and Cherry, 1979). These assumptions include that the aquifer is homogeneous, isotropic and of uniform thickness and that flow to the well is radial, laminar and horizontal (Krusemann and de Ridder, 1970).

The porosity and permeability of the Hermannsburg Sandstone is well documented in studies of this unit over 100 km east of Palm Valley as part of investigations associated with the Alice Springs borefield. Read and Paul (2000) present data from cores within the upper Hermannsburg sandstone where helium porosity of around 20% and permeability to water around 50 milli Darcy i.e. a hydraulic conductivity of 0.04 m/day). Lau, (1989) measured an average permeability and porosity of 80 milli Darcy

(0.07 m/day) and 24 % respectively in the Ljiltera member of the Hermannsburg Sandstone in a cored hole at the Alice Springs town water supply borefield at Roe Creek.

For fractured sandstone aquifers such as the Hermannsburg Sandstone where some of the flow to the well is via fractures of potentially various orientations and dimensions, the usual assumptions made for test pumping analysis and therefore any aquifer characteristics derived, may not be valid for this aquifer type. For example, groundwater flow in any sort of fractured rock aquifer is potentially very complex to analyse as flow may be non-laminar (Mackie, 1982) or non-radial (Milne-Home, 1988) near to pumping bores. This excludes the determination of transmissivity from test pumping methods commonly used to analyse granular porous media. Some alternative testing and interpretation methods for tests conducted in fractured aquifers have been proposed by some workers (e.g. Barker, 1988; Acuna and Yortos, 1995; Novakowski and Bickerton, 1997).

As the Hermannsburg Sandstone can be expected to behave as a double porosity aquifer (fracture and matrix permeability), due to the porous sandstone matrix, still other types of test pumping analyses of data may be more applicable for this type of aquifer. Lods and Gouze (2004) review some of the detailed studies that have previously been undertaken in an effort to combine fractured flow and double porosity concepts (e.g. Hamm and Bidaux, 1996) in analysing test pumping results; they present a computer model that may help characterise flow in some double porosity aquifers. However, the use of averaged hydraulic properties is still a requirement of the method presented. Furthermore, Jourde et al. (2002) demonstrate that in some instances where flow is only within two different fracture systems, results may erroneously be interpreted as double porosity flow behaviour (delayed yield like response) and consequently warn that test data from a single well should be used cautiously when assessing flow properties of fractured aquifers.

In a straightforward approach Boehmer (1993) notes that double porosity aquifers should respond in a similar manner to tests conducted in porous media that display a delayed yield response.

Some test data from the Hermannsburg Sandstone (e.g. RN012026, NTG bore file) certainly show a decrease in the rate of drawdown some time (log of time scale) after a constant rate test has begun (i.e. delayed yield). This suggests use of double porosity analyses techniques (e.g. Kruseman and de Ridder, 1991) may provide some additional information (e.g. storage data) on aquifer characteristics for some bores. However, other test pumping results do not show an obvious double porosity delayed yield effect (e.g. at the Hermannsburg community borefield, Childs (1990) notes most tests show a straight line response on drawdown against log of time plots). Thus it seems some bores within the Hermannsburg Sandstone only display a porous medium like response when test pumped. This is further evidence that a dual porosity aquifer system characterises flow in the Hermannsburg Sandstone.

In their classic text book on test pumping analysis and evaluation, Krusemann and de Ridder (1991) warn that "in spite of the intense research that fractured rocks have undergone in the last two decades, the problem is still the subject of much debate." A decade on, the problem of interpreting flow in fractured aquifers was noted to still be at the frontier of research in hydrogeology (Berkowitz, 2002). Indeed Berkowitz (2002) notes that the inherent structural and hydraulic complexity of fractured formations drastically limits the nature and quality of data that can be obtained from field and test pump results, which in turn limits the certainty of any hydrological conclusions drawn from such data.

Most textbooks (e.g. Singhal and Gupta, 1999) and reviews of flow in fractured media (e.g. Berkowitz, 2002) note the analysis of flow in fractured rock aquifers can be approached either as a discrete problem where the hydraulics of flow in individual fractures is examined or by a continuum approach where the fractured media is taken as a representative continuum in which spatially defined values of hydraulic conductivity, porosity, storage, etc are assigned, and it is assumed the fractured media then acts in a hydraulically similar fashion to granular porous media. It is worth noting that some detailed experiments that have compared the discrete and continuum approaches to the analyses of flow in fractured rocks have provided evidence of the validity of the continuum approach (e.g., Cacas et al., 1990; Troisi and Vurro, 1988). The work in a deep mine in Switzerland (Cacas et al., 1990) required setting packers to isolate discrete fractures in boreholes and then testing hydraulic properties for each fracture. Such

detailed work to gain hydraulic information on discrete fractures is rarely practical, particularly at remote Northern Territory water bores drilled in the Hermannsburg Sandstone.

This problem of characterizing groundwater flow in fractured media has inspired attempts to simulate flow by developing apt computer models of fractured systems. Many recent studies adopt stochastic approaches as this method can better simulate the expected wide variations (orders of magnitude, Cacas et al, 1990) of hydraulic properties in fractured media compared to the deterministic models commonly applied in granular porous terrains. This strategy of modelling still requires a choice of whether a discrete or continuum approach is adopted. For example Tsang et al. (1996) develop a stochastic continuum model of a fractured medium and account for double porosity affects by assigning a small fraction of the medium higher hydraulic conductivities concentrated along the perceived fracture planes. In contrast, Masciopinto (in press) uses a concept of discrete parallel fractures to develop a stochastic model of flow in carbonate terrain in the Salerno region of Italy. Berkowitz (2002) gives a thorough background on the theory and types of modelling techniques deployed in fractured rock media.

The relation of matrix and fracture flow in fractured rock aquifers has also been examined by finite element modelling techniques. Matthai and Belaynech (2004) by way of field data-based finite element simulations have examined the flow interaction between matrix and fractures in double porosity double permeability systems. They found that stagnation of flow within matrix blocks (a concept used to simulate fractured flow in some earlier studies) would not be expected to occur unless the fracture to matrix hydraulic conductivity ratio exceeded 10^5 and note that this result implies matrix permeability below that expected in hydrocarbon reservoirs. This result would suggest that, as the Hermannsburg Sandstone is porous and permeable, groundwater can be expected to flow both within the matrix and along fractures in this aquifer.

Detailed field studies like some of those mentioned above are seldom possible for groundwater investigations. In the absence of readily useable models to mimic flow through generally unknown fracture patterns, representing the fractured media as an equivalent effective volume of porous media (continuum approach) is often the only

available approach to studying some groundwater systems (Freeze and Cherry, 1979). Berkowitz (2002) notes this approach is applicable when the interaction between the fracture network and the porous/permeable host rock allows sufficient interaction to establish a local equilibrium. This then suggests if the scale of study allows such conditions then a continuum approach is a valid concept to apply. Selecting the appropriate scale to match the available data is stressed as being an important consideration when evaluating fractured rock aquifers (Cook, 2003; Berkowitz, 2002). For example Cook (2003) notes that calculating regional groundwater flow rates by multiplying regional head data by aquifer hydraulic conductivity determined from bore test pump test results may overestimate the rate of flow in some fractured terrains. This may arise due to the different scales from which the two data sets are obtained. For instance, if the nature of fracture patterns is such that fractures are not well connected away from the individually tested bores, then the regional flow rates would better be calculated by considering only the matrix hydraulic conductivity rather than the fracture-enhanced characteristics determined from well testing.

4.3. *Hermannsburg Sandstone – Regional data*

4.3.1. Introduction

Aspects of the hydrogeology of the Hermannsburg Sandstone have previously been described by McQueen and Knott (1982), Lloyd and Jacobson (1987), Jacobson et al. (1989) and Lau and Jacobson (1991). Palm Valley lies in the Amadeus Basin folded rock aquifer province defined by Lloyd and Jacobson (1987). The Hermannsburg Sandstone is a reliable source of potable groundwater (Lau and Jacobson, 1991). Bores are usually deep (>50 m) with modest yields. This aquifer is generally regarded as unconfined, though higher permeability zones such as fractures / joints can result in marked water strikes at depth during drilling. Lau and Jacobson (1991) ascribe the aquifer characteristics of the Hermannsburg Sandstone to both fracture and porous permeability.

4.3.2. Test pumping

When Darcy flow conditions are assumed, tests in the Hermannsburg Sandstone can be analysed as for standard porous media. When analysing unconfined aquifers most workers note the problem of adequately compensating for vertical components of flow to the well, as the aquifer is dewatered during the test. However, later during the test the flow pattern around the well is commonly considered to be a fair approximation of radial flow in a confined aquifer and consequently the standard methods developed for analysing flow in confined aquifers can be used (Freeze and Cherry, 1979; Hazel, 1975; Krusemann and de Ridder, 1991).

One of the commonest methods used to analyse single bore test pump data is the graphical procedure known as Jacob's straight-line approximation (Mackie, 1989) where the method of Cooper and Jacob (1946) is approximated and transmissivity is determined by the equation:

$$T = \frac{2.3Q}{4\pi \delta S} \quad (4.4)$$

where T = transmissivity, Q = discharge per day (m^3/day) and δS = slope of graph (drawdown per log cycle of time).

Values of transmissivity determined by Northern Territory Government technical officers using this (semi-log) graphical technique are presented in Table 4.1 and cited by other studies (e.g. Lau and Jacobson, 1991; McQueen and Knott, 1982). It should be noted that most of these results are computed from pump tests of eight to 24 hour duration on individual bores; few observation bores are available. Values are determined for the latest times of constant rate tests in an effort to meet the confined aquifer behaviour assumption outlined above. The Jacob drawdown correction for thin unconfined aquifers (Hazel, 1975) is usually not applied.

Table 4.1 Location and aquifer characteristics of bores drilled in the Hermannsburg Sandstone

SampleID	Easting	Northing	Area	Name / type (NT database)	Depth (m)	SWL (m)	T (m ² /day)	k (m/day)	Yield (L/s)	Conduc- tivity (μ S/cm)
G0055007	269461	7349064	H'burg area	Kaporitja Spring						740
G0055029	279846	7335932	Palm Valley	Little Palm Spring						444
G0055030	269249	7336285	Palm Valley	Oasis (South) Spring						892
G0055057	264180	7336891	Palm Valley	PV04/200 Shot Hole	8.0	6.0				811
G00Shotline1	254640	7340422	Palm Valley	PV01/608 Shot Hole	8.0	3.0				
G0ROAD	269850	7336853	Palm Valley	Road Spring						774
G0WEST	259550	7337669	Palm Valley	West Spring						802
RN000052	222706	7335104	Areyonga	Production No. 1	55.8	3.70			0.5	970
RN000291	222671	7335209	Areyonga	Production No. 2	137.2	5.50			0.9	930
RN002830	222533	7335586	Areyonga	Production No. 3	108.8	0.60	10	0.092	1.8	824
RN002934	267561	7349576	H'burgtown	Production No. 2	97.5	4.30	3.4	0.036	1.4	885
RN003280	269494	7348731	H'burg area	Station No. 1	54.9				1.3	1140
RN003618	273198	7348641	H'burgtown	Production No. 3	193.0	8.80	1.5	0.008	1.3	1590
RN004508	270745	7336876	Palm Valley	Camp Ground Bore	91.5	1.50	0.14	0.002	0.2	1190
RN005740	282620	7341616	H'burg area	Old Station	36.6	6.40			0.5	1090
RN006949	332731	7346883	Owen Springs	5 Mile	85.3	46.00			1.3	723
RN007175	270160	7349106	H'burgtown	Production No. 4	171.0	1.20	1.5	0.009	3.1	1130
RN007291	271031	7348963	H'burg area	Ironwood	165.3	0.52	3	0.018	3.0	1050
RN007292	267110	7349354	H'burg area	Rainbow	140.7	0.00	14	0.100	8.8	747
RN010209	353853	7340751	Owen Springs	Southern Cross	243.8	121.90			1.0	1018
RN010774	222537	7335609	Areyonga	Production No. 5	182.0	1.49	2.4	0.013	4.5	809
RN011338	282496	7341704	H'burg area	Apmakuaputa	122.0	5.50	0.34	0.003	1.0	1800
RN011341	280243	7344111	H'burg area	Tukarara	129.0	7.00	0.43	0.004	0.7	1160
RN011342	281423	7342791	H'burg area	Ilpiulalknarrintja	129.0	6.70	0.59	0.005	0.8	1695
RN011343	244171	7345840	H'burg area	Lyalaitum	61.0	11.40	6.5	0.131	2.3	1220
RN011439	241806	7347200	H'burg area	Ilkarialalama	61.0	2.68	29	0.497	2.5	840
RN011440	244171	7345840	H'burg area	Ltaltoma	83.5	15.36	4.3	0.063	1.0	1050
RN011446	280158	7344050	H'burg area	Coultards	137.0	11.40	0.6	0.005	1.0	1130
RN011447	282069	7342228	H'burg area	Ilpiulalknarrintja	152.5	6.70	0.4	0.003	1.0	1705
RN011448	286478	7337658	H'burg area	Yankee	122.0	41.83	0.4	0.005	0.9	1000

Table 4.1 Location and aquifer characteristics of bores drilled in the Hermannsburg Sandstone

SampleID	Easting	Northing	Area	Name / type (NT database)	Depth (m)	SWL (m)	T (m ² /day)	k (m/day)	Yield (L/s)	Conduc- tivity (μ S/cm)
RN011831	377000	7341597	Owen Springs	Railway Bore	432.9	108.40	2.5	0.008	2.0	1450
RN012022	270128	7337171	Palm Valley	Rangers House 1 (1978)	200.0	10.30			0.1	950
RN012023	269128	7337171	Palm Valley	Rangers House 2 (1978)	100.0	1.80			0.1	1120
RN012024	270128	7337171	Palm Valley	Production Bore	67.0	7.70	22	0.371	1.9	971
RN012025	279128	7347171	H'burg area	Arkankaputa	200.0	12.22		0.000	0.1	920
RN012026	278924	7345393	H'burg area	Arkankaputa	168.0	10.00	0.2	0.001	1.1	1190
RN012549	277172	7346094	H'burg area	Tjanukura	150.0	29.70	0.7	0.006	1.0	1360
RN012650	319092	7343058	Owen Springs	Desert	152.0	91.00			2.3	970
RN013652	343489	7318839	Owen Springs	McGinnis	110.0	51.00			1.0	1227
RN013653	363515	7339374	Owen Springs	Rock Hole	330.0	99.70			1.5	500
RN014164	263278	7349604	H'burg area	Tnyimipirta	128.0	14.42	2.3	0.020	2.3	875
RN014165	271018	7348931	H'burgtown	Production 7	166.0	0.00	2.77	0.017	3.6	1075
RN014166	304759	7329716	Wallace	Production	220.0	91.30	3.77	0.029	3.2	1050
RN014616	264224	7334708	Palm Valley	Palm Paddock	121.0	0.80	0.4	0.003	0.8	802
RN014952	288338	7337271	Injarrtharna	Production	194.6	50.00	4	0.028	2.0	704
RN014956	253180	7348321	Ljiljera	Antjakwera	78.8	5.55	8	0.109	10.0	1150
RN014957	258672	7349160	Ljiljera	Production	112.2	6.50	3.1	0.029	2.0	832
RN015006	271268	7349371	H'burgtown	Monitoring	250.0	5.03			2.0	1280
RN015007	270538	7349000	H'burgtown	Monitoring	220.0	5.98	4	0.019	4.0	1084
RN016359	288338	7337291	Injarrtharna	Standby	192.7	41.20			1.5	860
MEAN VALUES of WATER BORE DRILLING										
					148	34	4.6	0.06	1.8	1065

N.B. SWL = standing water level measured below top of casing or ground level.
Hydraulic conductivity (k) calculated by dividing transmissivity (T) by assumed saturated thickness, i.e. Depth minus SWL.

A shortfall in aquifer testing data is recognised for the aquifer characteristics determined for the Hermannsburg Sandstone from Northern Territory Government testing because:

- (1) the aquifer is a fractured sandstone and may not behave as a Darcian continuum.
- (2) observation bore data are limited.
- (3) delayed yield effects from the double porosity aquifer may have been missed due to brevity of test.
- (4) hydraulic boundaries may have affected drawdown graphs.

Nevertheless, the similarity of transmissivities recorded in the Hermannsburg Sandstone (Table 4.1) is an indication of the suitability of late time transmissivity calculations from the single bore tests. This also then implies that taking mean aquifer characteristics for the purpose of regional analyses should be justified. That is, the continuum or equivalent porous media approach is a valid method to assess groundwater flow in the Hermannsburg Sandstone.

It should be noted that such assumptions are commonly made when assessing groundwater resources at a regional scale. For example Nastev et al. (2004) apply a continuum approach when assessing the fractured rock aquifers of south western Quebec, Canada. It should also be noted that the method used by the NT government for determining transmissivity in a fractured rock aquifer is not without precedent. Krusemann and de Ridder (1991) outline the Warren-Root method where transmissivity is also calculated by use of the Jacob straight line method on late time drawdown data from a single well test, although in this case a confined fractured aquifer was tested.

4.3.3. Previous assessments

Lau and Jacobson, (1991) compiled drilling data from many water bores drilled in the Amadeus Basin and tabulated drilling statistics. This work and other regional studies have included an appraisal of aquifer characteristics for the Hermannsburg Sandstone. Lau and Jacobson (1991) note transmissivity (T) in the Hermannsburg Sandstone

averages around 100 m²/day (includes an anomalous T value of 1500 m²/day). Analyses of test pumping in the north eastern Amadeus Basin region (McQueen and Knott, 1982) gave a typical transmissivity (T) range of around 0.2 – 20 m²/day and hydraulic conductivity (k) range of 0.04 to 1.0 m/day. Nearby to Palm Valley, drilling along the northern flank of the Krichauff Range generally shows less permeable aquifer characteristics for the Hermannsburg Sandstone. Childs (1990) notes that all but one bore drilled for the Hermannsburg community borefield have a T below 4.5 m²/day. These bores are all deep (97 - 220 m) and water levels are at or near the surface, thus hydraulic conductivity must also be low, (i.e. 100 m saturated thickness with T= 4.5 m²/day represents k = 0.045 m/day). Elsewhere along the north side of the Krichauff Range bores drilled into the Hermannsburg Sandstone for outstations show similar aquifer characteristics to the Hermannsburg borefield, that is, the value of k ranges from 0.04 to 1.0 m/day and T ranges from 4 to 20 m²/day (Salas, 1987).

4.3.4. Hermannsburg Sandstone - aquifer characteristics

A compilation of bores drilled into the Hermannsburg Sandstone at a similar latitude to Palm Valley is presented in Table 4.1. These bores from the Northern Territory Government database were determined to tap the Hermannsburg Sandstone by examination of drilling records and published geological mapping. This compilation was undertaken to put the data from Palm Valley in a regional context and represent bores from a similar mid-Amadeus Basin position. The location of the bores presented in Table 4.1 is shown in Figure 4.6.

At Palm Valley bore RN 12024 was tested at T = 22 m²/ day, k = 0.3 m/day in 1994 (Wischusen, 1995a). Other bores near Palm Valley have recorded lower hydraulic characteristics. From Table 4.1 it can be seen that RN 14616 and RN 4508 had T values of 0.4 and 0.14 m²/day and k of 0.003 and 0.002 m/day respectively when tested.

The discrepancy of these aquifer characteristics from the regional compilation of Lau and Jacobson (1991) may reflect variation in facies and/or structural (joints fractures) features occurs elsewhere in the Amadeus Basin. It should be noted, however, that the highest yielding bore in the Hermannsburg Sandstone cited by Lau and Jacobson (1991) RN 11169, is now regarded by Northern Territory Government geologists (Read and

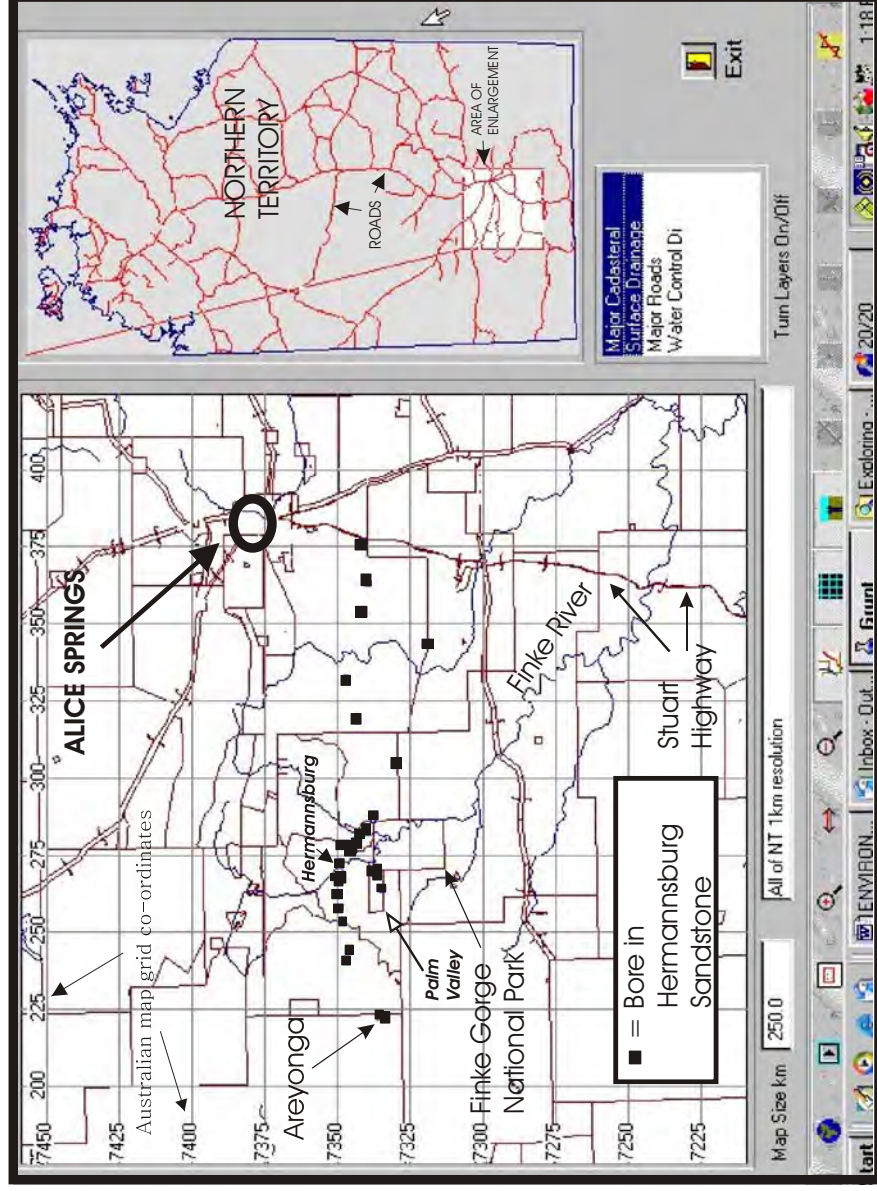


Figure 4-6 Location of bores drilled into the Hermannsburg Sandstone at similar mid Amadeus Basin position to Palm Valley. The hydraulic characteristics of these bores are presented in Table 4.1

Paul, 2000) to be drilled into the Mereenie Sandstone, a much higher yielding aquifer in the Amadeus Basin. Given this reclassification of Bore RN 11169 and the small sample ($n=12$) used to compile Hermannsburg Sandstone aquifer characteristics by Lau and Jacobson (1991), it is likely that without this bore, aquifer characteristics would be computed to be closer to that shown on Table 4.1, where $n = 29$. (The complete list of bores used to compile the Lau and Jacobson (1991) aquifer characteristics data is not known, so mean values cannot be re-calculated excluding RN 11169).

Given these aquifer characteristics are usually derived only from the testing of successful production bores and not all bores drilled, estimates of hydraulic characteristics of the aquifer, as a whole, are likely to be at or below the lower end of the range.

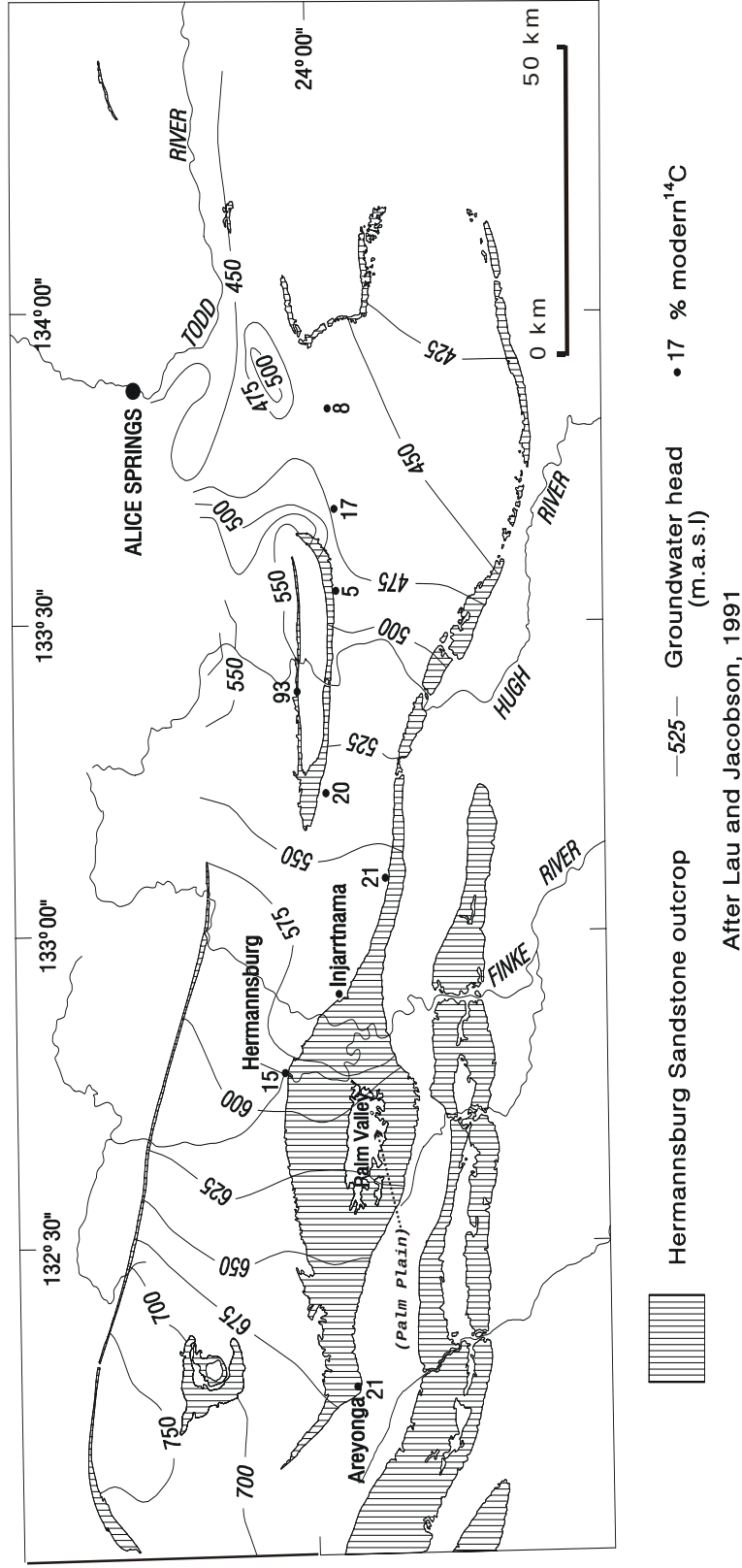
4.3.5. Groundwater flow

Lloyd and Jacobson (1987) estimated head in the Hermannsburg Sandstone and constructed a regional potentiometric surface diagram in the folded rock province of the Amadeus Basin. This diagram with some additional radiocarbon information from Jacobson et al. (1989) is shown in Figure 4.7. Regional groundwater flow is clearly seen to be from west to east in this diagram.

Brown et al. (1990) used a horizontal and vertical k of 0.03 and 0.003 m/day respectively when modelling flow through this aquifer. If such aquifer characteristics are representative, then slow flow through the Hermannsburg Sandstone can be expected. If aquifer hydraulic conductivity and porosity are known, Darcy's Law can be used to estimate the travel time of water over a specified distance under a given gradient by the formula:

$$T = \frac{x\theta}{ki} \quad (4.5)$$

Where T = travel time (in days) over distance x , x = distance in metres, θ = porosity, i = gradient and k = hydraulic conductivity in m/day.



REGIONAL POTENTIOMETRIC SURFACE - HERMANSBURG SANDSTONE

Figure 4-7 Regional Potentiometric Surface – Hermannsburg Sandstone.

This Figure shows the potentiometric surface over a large area of central Australia (After Lau and Jacobson, 1991). A west to east gradient is clearly seen in the Palm Valley area. This diagram was constructed without the benefit of water level data from Palm Valley but highlights how the local data shown in Fig. 4.9 fits with the regional pattern. The locations of communities where bores that tap the Hermannsburg Sandstone have been sampled for this study are also shown.

If a regional gradient of a 100m drop every 50km (Fig. 4.7, $i = 2 \times 10^{-3}$) and a porosity of 6% (Magellan Petroleum, 1966)) along with a horizontal hydraulic conductivity of 0.03 (Brown et al. 1990) are used to determine travel time assuming Darcy flow conditions T is calculated (Eq. 4.5) as $T = 9.85 \times 10^{-4}$ m/day. The average linear velocity V can be calculated by use of the formula:

$$V = 365 \frac{ki}{\theta} \quad (4.6)$$

Where V = average linear velocity, k = hydraulic conductivity in m/day, i = gradient and θ = porosity (i.e. effectively $365 \times T$.)

From the regional data discussed above average linear velocity is then calculated to be 0.36 m year^{-1} . When the k values near those estimated for bores RN 4508 and RN 14616 (Table 4.1) near Palm Valley are used (i.e. $k = 0.0025 \text{ m/day}$), calculated average linear velocities are around 0.03 m yr^{-1} . Both these average linear velocity estimates and the modelling of Brown et al. (1990), with an average linear velocity of 0.06 m year^{-1} through the Hermannsburg Sandstone, highlight the potential for very slow groundwater movement through this aquifer.

4.4. Local Hydrogeology

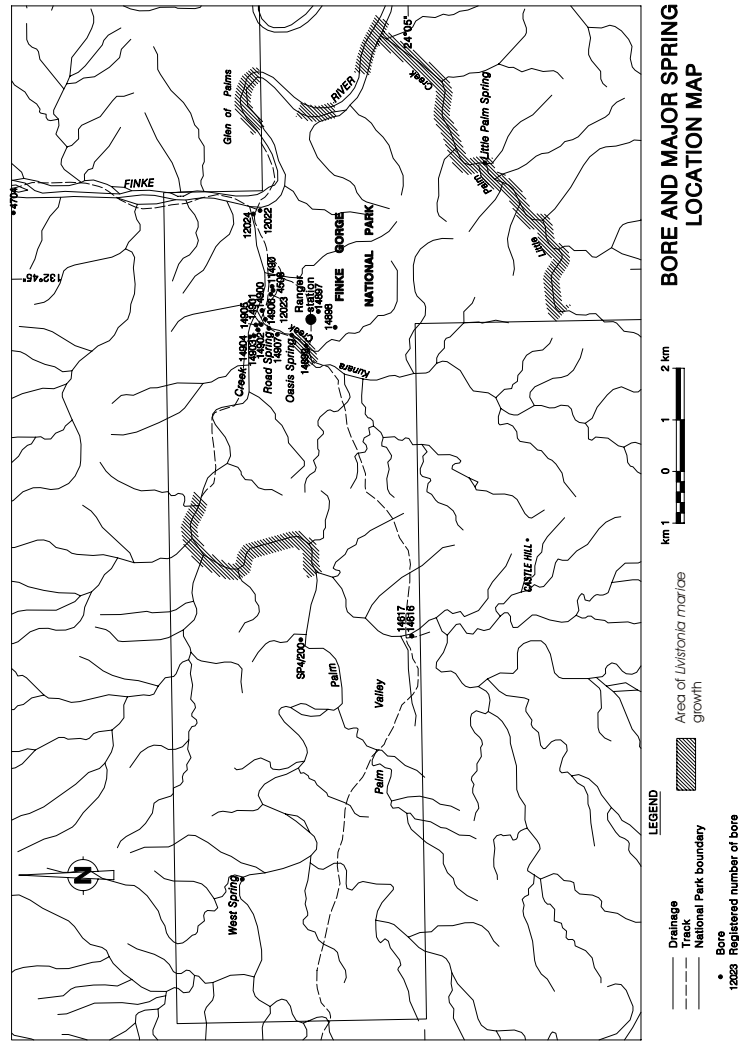
4.4.1. Previous work

The first bore at Palm Valley was drilled near the Campground to service a chalet that then existed in the area. This bore (numbered out of sequence in the Northern Territory data base as RN011490) was drilled in 1961 to depth of 51 m in the Hermannsburg Sandstone. Records are scarce for this bore but it apparently flowed at 0.2 L/s after initially being thought a dry hole. In 1964, the current campground bore RN 4508 (Fig. 4.8) was drilled, a yield of 0.2 L/s and water level of 1.5 m below ground was recorded. In 1978, following the drilling of several exploratory bores, the bore RN 12024 was drilled and constructed as a production bore. In 1986 this bore was deepened in an attempt to increase yield, and a bore for an outstation (Conrads bore for Intyiamangama outstation) in Palm Paddock RN 14616 was drilled (Fig. 4.8).

An investigation was then undertaken in 1988 (Warne and Prowse, 1988) to look for additional water supplies for planned expansion of the campground at Palm Valley. Eleven shallow (40-60m) holes were drilled within 2 km to the west of RN 4508 (Fig. 4.8) but no supply greater than 0.1 L/s was encountered, and all these holes were backfilled (bores RN 14897-14907, Table 4.2).

Based on the results of this and nearby drilling, Warne and Prowse (1988) considered joint/fracture development was limited. They went on to develop a concept that only a limited shallow band of fractured Hermannsburg Sandstone, locally recharged from creek flow, stored groundwater in this region. The potential for intergranular storage was discounted. This concept raised concern about the possibility of competition between the unique vegetation of this park and tourists for the then perceived locally restricted groundwater supplies.

Given these concerns the existing bore RN 12024 was examined to see if its use presented any danger to the palms groundwater supply (Wischusen, 1995a). This report concluded that interference to the palms' water supply from park domestic extractions from bore RN 12024 would be most unlikely. The reasons were considered to be the large distance (7 km), potentiometric surface drop between the bore and main stand of palms of more than 30 m, and limited propagation of drawdown effects in low permeability aquifers (Theis, 1940) indicated interference to be unlikely. Furthermore, even discounting additions from aquifer throughflow and induced drainage, something in the order of 30 m of 6% porosity aquifer over a radial area of 7 km² would need to be dewatered (i.e. around 270 ML) before affecting the palms. This interpretation readily allayed fears that the modest groundwater extraction for park use would adversely affect palm tree health. From analysis of test pump data, it was concluded a yield of 30 m³/day is sustainable from RN 12024 (Wischusen 1995a). This yield, along with the occasional use of the bore at the campground (RN 4508), easily meets the requirements of park visitors and rangers.



4.4.2. Groundwater features

4.4.2.1. Introduction

Figure 4.9 shows local groundwater features and bores drilled in the Palm Valley region. A summary of drilling data from these bores is shown in Table 4.2. The regional west to east gradient shown through the Hermannsburg Sandstone in Figure 4.7 is corroborated by the potentiometric data available in the Palm Valley region shown in Figure 4.9.

Figure 4.5 shows the distribution of joints and fractures in the Hermannsburg Sandstone mapped from air photos near Palm Valley by Thigpen (1973). The position of production bores and springs are seen to have some correlation with these mapped fractures. Most of the dry or low yield backfilled bores shown plot away from mapped fractures. The lack of supply noted for Bores RN 14897 – 14907, drilled in the vicinity of Road Spring and Bore RN4508, illustrate how the low k of the Hermannsburg Sandstone can limit the observed yield of shallow rotary air blast drilled holes when no fractures are encountered.

4.4.2.2. Discharge sites

Groundwater seepage sites are commonly observed at many locations along the creek beds in the vicinity of Palm Valley. Low yielding seepages, some of which dry up in the heat of the day, appear to be bedding related. That is, groundwater apparently oozes (Plate 4.1) from small lenses of slightly coarser, cleaner sandstone (i.e. at the base of some crossbed cosets which Jones (1972) notes can be coarser grained). Groundwater is also seen to seep from joints (Plate 4.2). The line of calcrete deposits associated with the discharge mark the joint plane.

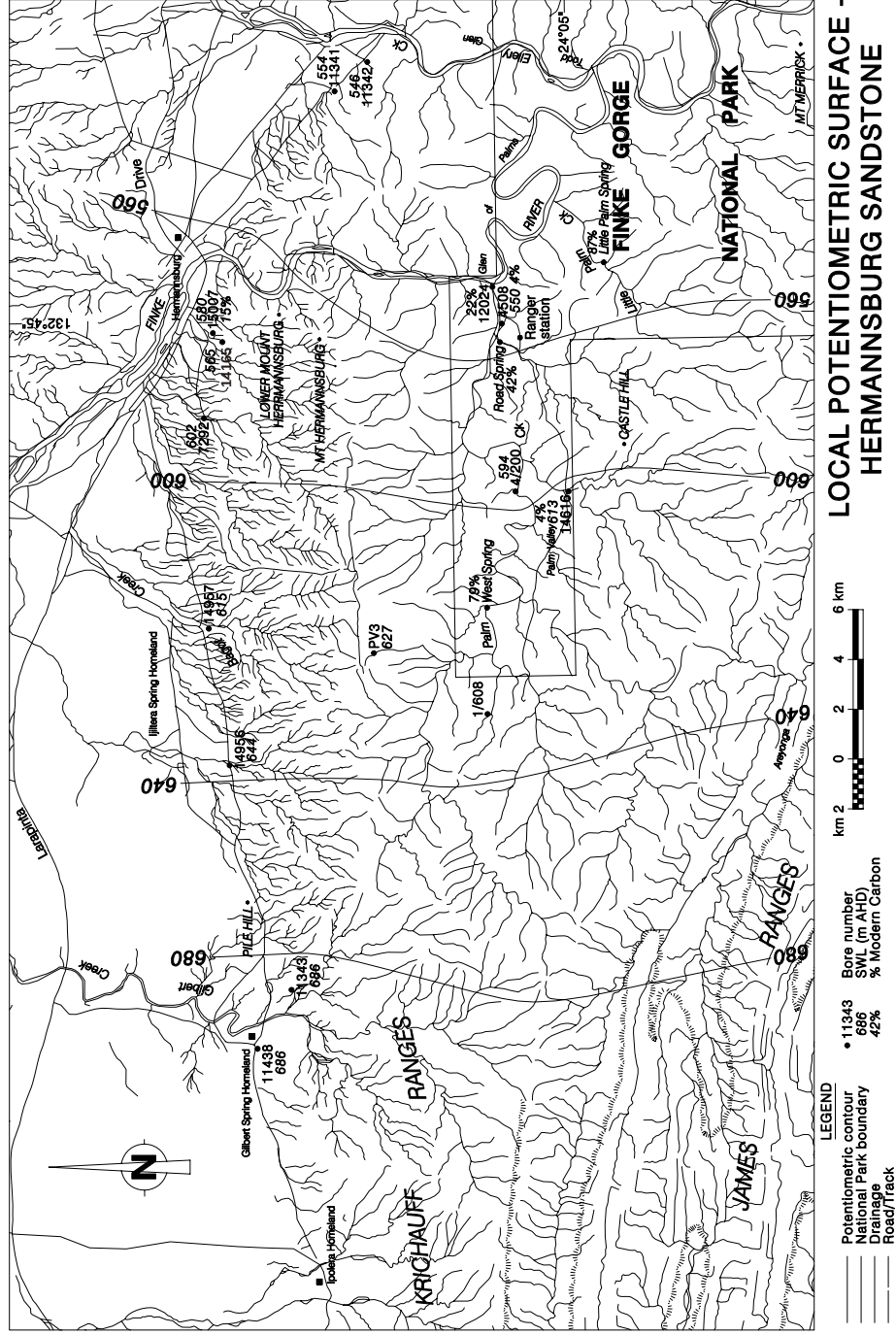


Figure 4-9 Potentiometric surface – Hermannsburg Sandstone in Palm Valley and Hermannsburg community region. Bore and springs are shown with radiocarbon and standing water level (SWL; reduced to Australian Height Datum (AHD)) data, where available. Potentiometric surface is a composite of readings derived from the different most recent dates available in the NTG database.

Table 4.2 Palm Valley area drilling data

BORE RN	LOCATION	Depth (m)	SWL (m)	Supply (L/s)	Status
4508	Palm Valley	92	1.5	0.2	Production
10774	Areyonga	180	3	8	Production
11940	Palm Valley	55	surface	0.2	Backfilled
12022	Palm Valley	200	10.3	0.13	Open hole
12023	Palm Valley	100	1.8	0.13	Backfilled
12024	Palm Valley	67	8.4	1.9	Production
14616	Palm Valley	121	0.8	0.8	Production
14897	Palm Valley	60		0.1	Backfilled
14898	Palm Valley	40			Backfilled
14899	Palm Valley	40			Backfilled
14900	Palm Valley	30			Backfilled
14901	Palm Valley	40		0.01	Backfilled
14902	Palm Valley	30			Backfilled
14903	Palm Valley	30			Backfilled
14904	Palm Valley	30			Backfilled
14905	Palm Valley	30			Backfilled
14906	Palm Valley	30			Backfilled
14907	Palm Valley	30			Backfilled
14952	Injarrtnama	195	41	2	Production
14165	Hermannsburg	166	surface	3	Production
1/608	Palm Valley	8	3		Shot hole
4/200	Palm Valley	8	6		Shot hole

The groundwater appears saturated with calcite, as most seep sites are associated with calcrete deposits. These deposits may be precipitated when the solubility of the calcite decreases as water temperature rises during the heat of the day. In many instances active seepages are surrounded by dry calcrete deposits, (Plate 4.3). These dry deposits appear to be blocked, former seep sites. Calcrete deposits are also common elsewhere out of the creeks on the surface of the Hermannsburg Sandstone at Palm Valley. Some of these deposits may represent where seeps from an ancient, higher, potentiometric surface have occurred (Plate 4.4). Apart from these observable discharge features, it is also possible that unseen diffuse discharge through the less permeable sandstone matrix occurs and/or resultant mineral precipitation from evaporation clogs near-surface fine matrix pores.

The springs shown in Figure 4.9 are evident as 20 – 100 m² pools of water around 1m deep. Thick vegetation grows near these springs. Only West Spring has no *Livistona mariae* palms nearby. West Spring (Plate 4.5) and Road Spring (Plate 4.6) are known as permanent springs (Finke Gorge Park rangers, pers. comm. 1992). These two springs are evident as several square metres of pooled water over 1 m deep within bare sandstone outcrop along creek lines. Small active seepage sites surround each of these springs and the main pools of water are intersected by vertical joint planes in the sandstone. Oasis (bottom water) spring (Plate 4.7) is also positioned near a vertical joint plane. This spring, which has a population of fish, may also be permanent, though the heavily vegetated upstream main spring area (Oasis Spring, Plate 4.8) could provide a permanent refuge for fish. It should be noted that this main spring area is so heavily vegetated that no significant pools of water to obtain samples from were found here.

Another reputed permanent spring is in the Little Palm Creek. This spring is observed to vary markedly in size and, when sampled, had water of much lower conductivity than at the other springs and bores in this region (Table 5.1). In contrast to other springs it was sampled after summer rains in March 1993. The lower conductivity was taken to indicate that mixing with recent rain had occurred. For this reason and also due to budget constraints, a full suite of isotope analyses was not run for samples from this site.

Davis (1995, 1997) regards all three of these springs as permanent water bodies on the basis of limnological studies that describe relict fauna at each site.

All of these springs are taken to represent groundwater discharge from enhanced permeability conduits, such as joint planes or cleaner sand lenses within the low permeability Hermannsburg Sandstone

4.4.3. Aquifer type

If the Hermannsburg Sandstone is taken to be a low permeability saturated sandstone with intermittent joints/fractures providing conduits of enhanced permeability, as evidenced by occasional springs and higher yielding bores, then the drilling results of Warne and Prowse (1988) at Palm Valley can be interpreted differently. That is, rather than showing no groundwater in the Hermannsburg Sandstone, it may be that the shallow drilling encountered no significant joints/fractures and that insufficient aquifer area was exposed for groundwater seeping to the hole be noticed during rotary air blast drilling. All these holes were backfilled immediately after drilling so no recovery of water level data could be observed. Bore RN 6503, 3 km south of Hermannsburg and RN 11490 at the campground (Fig. 4.8) when drilled, were thought to be dry but subsequently flowed. Two bores, RN 7292 and RN 14165 at the Hermannsburg borefield also flow.

The drilling data either side of the Krichauff Range at Hermannsburg and Palm Valley can be interpreted as evidence that the Hermannsburg Sandstone - while having a low hydraulic conductivity unless enhanced by joints/fractures - is a saturated intergranular aquifer, often with potentiometric levels at or near the ground surface. The porosity, areal extent and thickness (up to 1300 m; Wells et al., 1970) of the Hermannsburg Sandstone indicate that large volumes of groundwater may be stored within this aquifer. Such an interpretation is in keeping with regional hydrogeological studies of the Amadeus Basin (Fig. 4.7).

4.5. Summary

The Hermannsburg Sandstone aquifer is a double porosity aquifer with low matrix k (Table 4.1). Permeability is occasionally enhanced by fractures. In unfractured regions deeper bores are often required for viable yield. At Palm Valley occasional permanent pools of water (springs) are found on Hermannsburg Sandstone outcrops. These springs result from increased discharge associated with localised permeability enhancement.

On face value (consistent geology and potentiometric trend), it appears this shallow groundwater originates from a vast resource of water moving slowly through the regionally extensive Hermannsburg Sandstone. As groundwater is likely to be crucial to the ongoing survival of the Palm Valley ecosystem, examination of other aspects of the hydrogeology is warranted.



Plate 4-1 Bedding related seeps, Hermannsburg Sandstone.

Water seeping from the Hermannsburg Sandstone (dark areas within the paler calcrete regions, ruler in photo centre is 30 cm long). These weeps seem bedding related with associated calcrete deposits showing both active and former discharge sites. Features such as this show that the watertable is at, or above, the surface in areas of Palm Valley.



Plate 4-2 Joint related seeps, Hermannsburg Sandstone
Water seep site from a joint in the Hermannsburg Sandstone within Palm Creek.
The pale calcrete deposits associated with discharge clearly mark the joint plane.



Plate 4-3 Calcrete deposit associated with a seep site.
Seep site in Hermannsburg Sandstone near West Spring where a plant has taken root in an associated calcrete deposit.



Plate 4-4 Calcrete deposit above current potentiometric surface.
Thick calcrete layer on the Hermannsburg Sandstone along the edge of Palm Creek near West Spring. This calcrete (seen as a pale bed on top of the darker Hermannsburg Sandstone) which is now above the potentiometric surface, may have formed by groundwater discharge when the potentiometric surface was higher some time in the past.



Plate 4-5 West Spring.
Some of the ponds of water at West Spring, Palm Valley. No palms grow near to this Spring.



Plate 4-6 Road Spring.
viewed looking westwards from high on a hill. The lone *Livistona* palm marks the location of the permanent spring. At the time of photograph (August 2002) some flow from recent rain can be seen along creek bed in distance. All land surface seen in photo is outcrop of Hermannsburg Sandstone.



Plate 4-7 Oasis Spring (bottom water), Palm Valley.

A lone Palm (*Livistona mariae*) grows at this part of the spring system. Fish are recorded here. A distinct joint plane forms one boundary of the water pool. This accessible pool of water was sampled for chemistry and stable isotope analyses.



Plate 4-8 Oasis Spring, main area.

This heavily vegetated area is the main Oasis Spring area. No readily accessible pools of water were found for groundwater sampling during visits to the area. The vibrant vegetation, however, suggests a significant resource of groundwater.

5. Hydrochemistry

5.1. *Introduction*

Many factors influence the make up of groundwater chemistry. At the ground surface ionic concentration can be increased by evaporation of rain or stream water and/or by dissolving surface evaporites. From the time rain or stream water enters the soil, the chemical reactivity of water ensures a rapid change in the original water composition. The chemistry of a host rock aquifer then influences subsequent developments of water chemistry, with additional variables of rock surface area, water residence times, solute transport rate away from reaction sites and temperature all further influencing water chemistry (Freeze and Cherry, 1979).

Evaporation of shallow groundwater can influence groundwater chemistry by increasing ionic concentration. However, direct evaporation of groundwater is restricted to a theoretical maximum depth below ground surface of 4 m (De Weist, 1965), and is usually only a factor when groundwater is less than 2 m below ground surface (Schoeller, 1959).

Transpiration by plant root uptake of water can also be expected to concentrate soil moisture at the root zone (Allison, 1988), which can then be flushed or dissolved into groundwater, thereby increasing ionic concentration. Transpiration by direct water uptake from the saturated zone by tree roots, as postulated by Pidsley et al. (1994) may also concentrate groundwater.

The chemical equilibrium reactions possible with dissolved soil gases and various host aquifer compositions and the change of individual constituent solubilities as a result of various combinations of these chemical factors are extensively examined in texts such as Hem (1985), Lloyd and Heathcote (1985) Freeze and Cherry (1979), Stumm and Morgan (1996). Schoeller (1959) gives a comprehensive overview of groundwater chemistry, especially in relation to arid zone conditions where respiration by plants is noted to produce significant soil CO₂ gas which plays an important part in arid zone groundwater chemistry.

The most obvious result of these chemical reactions between water and the subsurface is the amount of dissolved solids within the water, which controls salinity and therefore the quality of groundwater. Apart from the health considerations of individual ions that may be present in groundwater, hydrochemical evaluation of groundwater is usually based on six major inorganic ions: sodium (Na^+) magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}). The total concentration of these six major ions normally comprises more than 90% of the total dissolved solids in water regardless of whether the water is dilute or has salinity greater than seawater (Freeze and Cherry, 1979). Standard chemical analyses conducted by the Northern Territory Government often also include potassium (K^+), fluoride (F^-), nitrate (NO_3^-), iron (Fe^{2+}) and silica (SiO_2) determinations in addition to the six major inorganic ions.

5.2. Previous work

The hydrochemistry of the Hermannsburg Sandstone in the Missionary Plain area near Hermannsburg community (12 bores) was briefly examined by McQueen and Knott, (1982). Groundwater was noted, based on classification of water types according to the domain in which they plotted on the major anion and cation triangles of a Piper Diagram (see Fig. 5.1), to range between a magnesium bicarbonate chemical type and to a lesser extent calcium bicarbonate type. On a Piper trilinear diagram the Hermannsburg Sandstone analyses generally plotted near the middle of the cation triangle with some plots showing Mg^{2+} as the dominant cation. Anions plotted as bicarbonate water with 25 - 50 % chloride. Sulphate concentration showed only a slight increase with chloride content. The Hermannsburg Sandstone data were noted to be a distinct group compared to the Mereenie Sandstone (Deep Well area) where sodium and chloride were more dominant. Jacobson et al. (1989) also present chemical data from 11 bores thought to tap the Hermannsburg Sandstone in the folded rock belt of the Amadeus Basin. No chemical distinction was drawn between these bores and the four other Mereenie Sandstone bores and one Bitter Springs Formation bore that made up their folded rock belt data group. Cation chemistry showed variation in that calcium, sodium or magnesium could be the dominant cation in this sample set. Anion data showed low relative sulphate and either bicarbonate or chloride to be dominant.

5.3. *Palm Valley area*

5.3.1. Major ion chemistry

The major ion chemistry of sites sampled for this study is shown in Table 5.1. The Northern Territory Government Water Laboratory in Darwin conducted all these analyses. The Standard methods of the American Public Health Association are used at this laboratory (APHA, 1998). All groundwater is, by central Australian standards, low salinity with TDS less than 800 mg/L.

Figure 5.1 shows a piper plot of data in Table 5.1. From this figure, it can be seen that apart from Injarrtnama (RN 14952) these waters have no dominant cation discernable when using this graphical technique. There is, however, a trend from bicarbonate dominant to no dominant anion type water. This limited range of graphically classified water type can then be taken to indicate only slight variation in evaporation concentration and/or water – rock reaction histories has occurred. For example, Oasis Spring plots nearest to chloride type water ($\text{Cl}^- > \text{HCO}_3^-$ Table 5.1), probably a result of evaporation from this spring pool (see Chapter 6).

The fact that Areyonga, Injarrtnama and Hermannsburg groundwater (RNs 10774, 14952, 14616 respectively) all plot in a similar position to the Palm Valley samples indicates that no distinct spatial trend in Hermannsburg Sandstone groundwater chemistry is seen along the regional outcrop (Fig. 4.7). By contrast many previous studies chart the evolution of anion chemistry from HCO_3^- dominant to either Cl^- or SO_4^{2-} dominant along flow path, particularly in large sedimentary basins (Freeze and Cherry, 1979; Schoeller, 1959; Jankowski and Jacobson, 1989). These results suggest comparisons based on anion chemistry may not be helpful here.

Table 5.1 Groundwater chemical data, Palm Valley study

Location	SampleID	TYPE ^a	pH	Temp (°C)	EC (µS/cm)	(mg/L)										(mass)			Date
						TDS	Mg	Na	Ca	K	Fe	HCO ₃	Cl	SO ₄	NO ₃	F	SiO ₂	Cl/Br ^b	
Palm Valley	RN004508	Mg-Ca-Na-HCO ₃ -Cl	7.1	27	1190	748	56	90	90	13	0.1	406	150	77	1	0.2	13	160	Jan-88
Palm Valley	ROAD Sp	Mg-Ca-Na-HCO ₃ -Cl	7.7	20	774	429	37	54	51	5		243	97	45				158	Sep-94
Hermannsburg	RN014165	Mg-Ca-Na-HCO ₃ -Cl	7.9	28	1075	607	52	67	75	7	0.2	408	113	87	3	0.4	14		Aug-98
Palm Valley	OASIS Sp	Mg-Na-Ca-Cl-HCO ₃	7.9	27	892	522	43	76	37	7	0.1	227	152	39	2	0.4	14		Feb-93
Palm Valley	RN012024	Mg-Na-Ca-HCO ₃ -Cl	7.5	28	971	559	54	84	71	7	4	361	135	75	12	0.6	33	147	Sep-94
Injartnama	RN014952	Mg-Na-HCO ₃ -Cl	8.4		704	414	49	52	15	7	0.3	218	83	46	26	0.5	22		Oct-94
Palm Valley	WEST Sp	Mg-Na-HCO ₃ -Cl	8.4	19	802	436	42	71	20	13		217	121	53					Sep-94
Palm Valley	RN014616	Ca-Mg-Na-HCO ₃ -Cl	8.1	25	802	438	34	52	73	7	0.2	321	77	42	18	0.4	18	160	Aug-94
Areyonga	RN010774	Ca-Mg-HCO ₃ -Cl	7.5	27	809	458	38	40	79	7	21.5	354	70	47	1	0.3	15		Mar-94
Palm Valley	PV04/200	Na-Mg-HCO ₃ -Cl	8.4	23	811	462	25	93	32	15		243	106	48	19	0.4	19		Oct-94
Palm Valley	L PALM Sp	Na-Ca-Mg-HCO ₃ -Cl	7.5	21	444	255	14	37	29	6	0.3	155	55	18	1	0.5	18		Feb-93

^a Water type classification is derived from the program Aquachem (1999) where major cations and anions are listed only when concentration in milli equivalents exceeds 10% of the molar concentration of the solution. ^b Cl/Br ratio determined by UNSW University Analytical Lab using standard ion chromatography to determine the chloride level and by ICP/mass spectrometry technique for the determination of bromide from samples taken in 2002. Depth of boreholes sampled shown in Table 4.2. All samples, apart from RN004508, collected by John Wischusen.

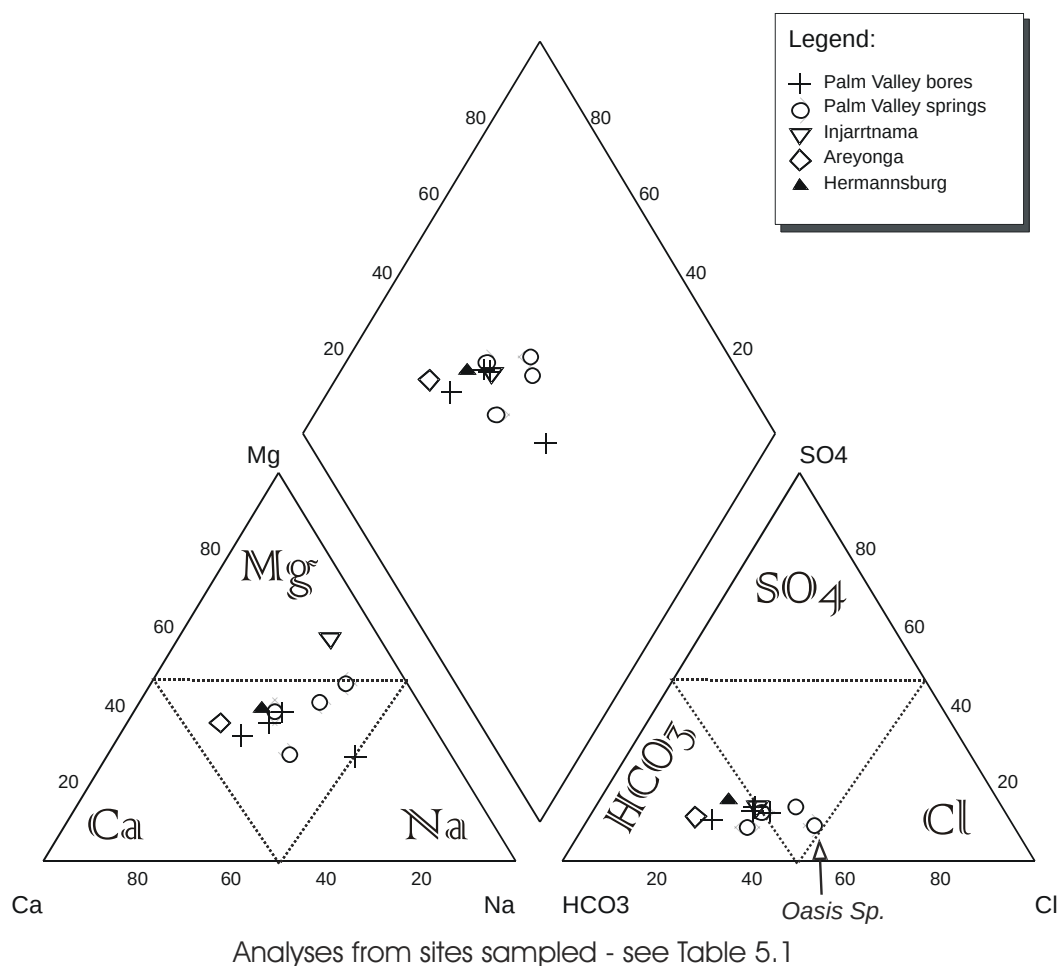


Figure 5-1 Piper plot of major cation chemistry.
Samples taken from the Hermannsburg Sandstone at Palm Valley and selected communities (See Table 5.1).

Given the similarity in relative major cation concentrations seen in Figure 5.1, it is likely that some commonly used water type classification schemes, such as the Szczukariew and Priklonski scheme (Alekin, 1970) where water type classification is based on listing only the ions that occur in concentrations above 20 % of the molar concentration of the solution, are not suitable for examining the subtle differences in cation chemistry seen for this aquifer. Consequently, the more sensitive water type classification scheme derived from the computer program Aquachem (1999), where major anions and cations are listed only when concentration in milli equivalents exceeds 10% of the molar concentration of solution is used throughout this study.

Examination of the water types classified in Table 5.1 shows all sites analysed for this study (apart from Oasis Spring discussed above) are bicarbonate dominant type waters. This is typical of low salinity arid zone groundwaters where recharge through vadose zones enriched in CO₂ gas from heavy plant respiration, is expected (Mazor, 1997). Water type classification based on cation chemistry, however, is seen to vary for these samples. Variation in major cation chemistry is common in groundwater flow systems; however, detailed consideration of specific hydrochemical processes is often needed for observed concentrations to be accounted for. A simple examination of cation chemistry below outlines some of the hydrochemical processes that may occur within the Hermannsburg Sandstone.

5.3.2. Hydrochemical processes

5.3.2.1. Saturation Indices

Figure 5.2a shows the saturation indices (SI) with respect to calcite and dolomite for each sample. Only Little Palm Spring water plots as undersaturated, though it is still close to the range where equilibrium to one or both of these phases might reasonably be expected (e.g. $SI \pm 0.3$). Saturation indices were calculated using the PHREEQC model (Parkhurst and Appelo, 1999). As no field HCO₃⁻ determinations were made and field pH measurements were not recorded at all sites, laboratory results were used to calculate the SI data shown in Figure 5.2a. While field pH and HCO₃⁻ measurements are desirable for accurate SI calculation (Hem 1985) it is believed that these data still give a reasonable indication of SI. This is because field pH, when recorded at 8 sites, is never

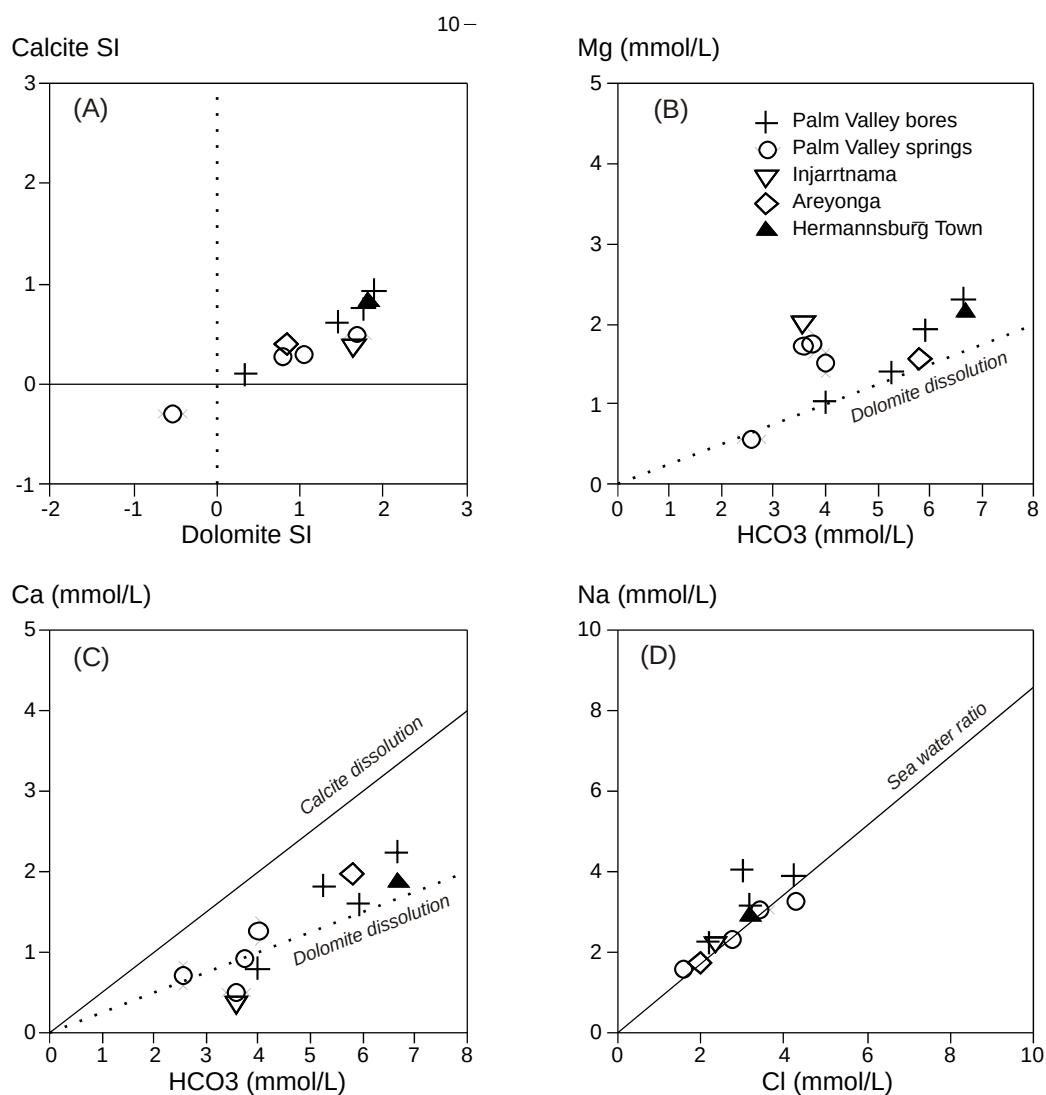


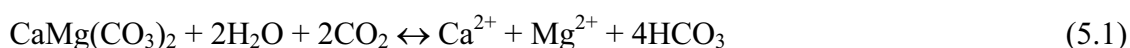
Figure 5-2 (a-d), aspects of groundwater chemistry sampled for this study in the Palm Valley area. Plot of (A); saturation indices of calcite and dolomite (B); magnesium against bicarbonate (C); calcium against bicarbonate (D); sodium against chloride.

less than 90% (usually >95%) of the laboratory determined pH. Given the similarity of field and laboratory pH and the fact that field HCO_3^- is often higher than laboratory HCO_3^- (Hem, 1985), using laboratory parameters to determine SI most likely gives a fair approximation here.

Given this saturation with respect to carbonates, variations of Ca^{2+} , Mg^{2+} and HCO_3^- concentration in groundwater, should not be further influenced by aquifer carbonate dissolution as equilibrium conditions are indicated. Freeze and Cherry (1979) note that $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio can vary widely due to a number of different processes in calcite and dolomite terrains, even without cation exchange reactions. It should be noted that a positive SI does not necessarily mean that phase exists within the system.

5.3.2.2. Dissolution / Precipitation reactions

The majority of samples show magnesium to be the dominant cation (Table 5.1). When magnesium is plotted against bicarbonate (Fig.5.2b) and compared to a 1:2 ratio line (representing dissolution of pure dolomite), it can be seen that a simple dissolution of dolomite;



cannot account for all the magnesium concentration in this aquifer. While many different processes may produce magnesium in excess of that expected from dolomite dissolution, the make up of the Hermannsburg Sandstone gives a clue to possible processes. Chlorite and micas are noted secondary minerals in the Hermannsburg Sandstone (Lau and Jacobson, 1991), thus the high Mg^{2+} content of groundwater could be a result of the weathering of detrital magnesium rich chlorites. For example chlorite in its most simple form (Drever, 1988) may react as:

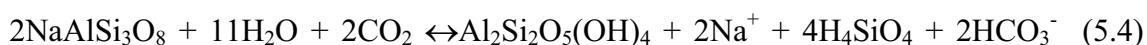


Groundwater calcium is commonly derived from dissolution of calcium rich carbonates (e.g. calcite):



Figure 5.2c shows the expected 1:2 calcite and 1:4 dolomite (Eqs. 5.1& 5.3) ratio lines, based on the stoichiometry if calcium were derived from dissolution of calcite or dolomite respectively. This plot shows dissolution of calcium carbonates could account for most of the calcium in solution.

Figure 5.2d shows a sodium against chloride plot. While a positive correlation consistent with evapo-concentration of recharge water is observed, two points plot off the linear trend. This may indicate some other reactions can interfere with the Na/Cl ratio of recharge water once it enters the aquifer. As chloride is typically conservative, reactions with sodium rich feldspars within the feldspathic Hermannsburg Sandstone may well account for slight anomalies in Na/Cl ratio. For example dissolution of sodium feldspars would increase Na^+ relative to Cl^- by way of the reaction:



Similar reactions of calcium rich plagioclase feldspars and/or back reactions with weathering products may account for the slight variation of calcium concentration from the calcite dissolution line (Fig. 5.2c). For example;



Cation chemistry may also be influenced by the change of conditions experienced once groundwater discharges at a spring or seep. Degassing of dissolved CO_2 and or temperature rise can be expected to lower the solubility of carbonates, which may then precipitate. As calcite precipitates more readily than dolomite (Hem, 1985), a decrease in the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio in spring water when compared to nearby groundwater might be expected. No such pattern, however, is discernible when spring and bore chemistry is

compared (Table 5.1). The fact that all sites are saturated with respect to carbonates (Fig. 5.2a) also means observed variation in $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios cannot be readily attributed to preferential precipitation of calcite. The one site not supersaturated with respect to calcite and dolomite, Little Palm Spring, has Ca^{2+} in excess of Mg^{2+} (Table 5.1). Despite these data, the readily observed calcrete stains and deposits throughout the area indicate carbonates are precipitated at Palm Valley.

5.4. Regional data set

5.4.1. Description

To further examine groundwater chemistry of the Hermannsburg Sandstone, chemistry data from the regional data set of bores used to examine the aquifer characteristics in the folded rock belt of the Amadeus Basin, presented in Table 4.1, were gathered. Chemistry data from these bores is presented in Table 5.2. These major ion data are from the Northern Territory Government database.

Figure 5.3, compares the chemistry of water at Palm Valley with around 40 other bores (data from Tables 5.1 and 5.2) drilled elsewhere in the Hermannsburg Sandstone within the folded rock province of the Amadeus Basin. This plot, which also shows the data from Palm Valley discussed above, confirms that the groundwater at Palm Valley is chemically typical of the Hermannsburg Sandstone. There is a slightly wider range of anion chemistry than that discussed above for the Palm Valley data set. For instance one bore RN 13652 plots (see also Table 5.2) showing chloride to comprise more than 50% of anion chemistry, while another RN 6949 shows bicarbonate to comprise 80% of anion chemistry. Apart from these anion outliers, the chemistry represented by this graphical technique is much the same as shown for the Palm Valley data set above. Cations are again seen to exist in roughly equal proportions.

Table 5.2 Groundwater chemical data, Hermannsburg Sandstone regional data set

SampleID	Depth (m)	Date	pH	TDS (mg/L)	Charge balance %	TYPE* (>10% meq)	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	K (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	NO ₃ (mg/L)	SiO ₂ (mg/L)	Alkali- nity (mg/L)	DIC (mg/L)
Kaporija Sp.	0	26/08/1984	7.6	500	0.21	Mg-Na-Ca-HCO ₃ -Cl	62	39	51	8	0.2	261	114	50	4	19	214	54
<i>Lt. Palm Sp.</i>	0	4/02/1993	7.5	255	-1.54	Na-Ca-Mg-HCO ₃ -Cl	37	14	29	6	0.3	155	55	18	1	18	127	32
<i>Oasis (sth) Sp.</i>	0	4/02/1993	7.9	522	-0.01	Mg-Na-Ca-Cl-HCO ₃	76	43	37	7	0.1	227	152	39	2	14	186	45
<i>PV 4/200</i>	8	7/10/1994	8.4	462	-1.33	Na-Mg-HCO ₃ -Cl	93	25	32	15		243	106	48	19	19	206	47
<i>PV 1/608</i>	8	27/09/1994			-100	Cl							212					0
<i>Road Sp.</i>	0	19/09/1994	7.7	429	2.61	Mg-Ca-Na-HCO ₃ -Cl	54	37	51	5		243	97	45			199	49
<i>West Sp.</i>	0	20/09/1994	8.4	436	-1.25	Mg-Na-HCO ₃ -Cl	71	42	20	13		217	121	53			178	42
RN000052	56	25/09/1986	7.5	555	-1.37	Na-Mg-Ca-HCO ₃ -Cl	73	38	59	10	2.0	275	135	67	6	12	225	57
RN000291	137	21/10/1981	7.7	460	-2.37	Ca-Mg-Na-HCO ₃ -Cl	51	39	66	13	0.1	360	90	49	1	15	295	73
RN002830	109	10/03/1994	7.1	469	2.41	Ca-Mg-HCO ₃ -Cl	39	37	84	11	0.4	334	70	63	1	15	274	76
RN002934	98	12/08/1998	8	498	-1.97	Mg-Ca-Na-HCO ₃ -Cl	64	36	57	7	0.1	275	110	72			226	54
RN003280	55	7/06/1971	7.3	640	-0.84	Mg-Ca-HCO ₃ -Cl	55	65	85	7	0.1	434	141	54	8	19	356	93
RN003618	193	21/12/1982	7.5	970	0.38	Na-Ca-Mg-Cl-HCO ₃ -SO ₄	189	48	92	13		307	260	216	5	12	252	64
RN004508	92	19/01/1988	7.1	748	3.22	Mg-Ca-Na-HCO ₃ -Cl	90	56	90	13	0.1	406	150	77	1	13	333	92
RN005740	37	17/07/1970	8.1	610	-0.92	Mg-Ca-Na-HCO ₃ -Cl	59	62	75	7	0.2	381	144	64	9	19	312	74
RN006949	85	11/11/1997	6.8	417	-3.82	Ca-Mg-HCO ₃	20	29	84	6	0.1	407	34	25			334	105
RN007175	171	21/12/1982	7.7	670	-2.66	Mg-Ca-Na-HCO ₃ -Cl-SO ₄	84	57	76	11	0.1	384	140	132	5	13	315	78
RN007291	165	12/08/1971	7.4	620	-0.69	Mg-Ca-Na-HCO ₃ -Cl	59	59	63	9	2.1	351	134	66	5	15	288	74
RN007292	141	12/08/1998	7.8	419	-1.51	Mg-Ca-Na-HCO ₃ -Cl	50	31	50	7	0.4	236	97	49			194	47
RN010209	244	1/05/1998	6.6	581	-1.94	Na-Mg-Ca-HCO ₃ -Cl	97	41	52	7	0.1	319	134	81			262	94
RN010774	182	10/03/1994	7.5	458	6.01	Ca-Mg-HCO ₃ -Cl	40	38	79	13	21.5	354	70	47	1	15	290	70
RN011338	122	10/10/1988	7.9	1010	-0.16	Mg-Na-Ca-Cl-HCO ₃	158	88	88	9	0.8	390	327	138	19	23	320	77
RN011341	129	17/03/1986	7.6	650	-0.57	Mg-Na-Ca-HCO ₃ -Cl	80	70	52	5	0.5	387	135	56	47	19	318	79
RN011342	129	10/10/1988	7.8	930	0.22	Mg-Na-Ca-Cl-HCO ₃	128	90	90	6	0.4	392	287	109	45	16	321	78
RN011343	61	15/08/1994	7.6	729	2.26	Ca-Na-Mg-HCO ₃ -Cl	90	39	117	7	0.2	389	163	75			319	80
RN011439	61	11/10/1988	7.8	475	-0.76	Ca-Mg-HCO ₃ -Cl	41	40	71	8	0.8	361	77	41	1	9	296	72
RN011440	84	7/12/1976	7.5	792	-0.97	Ca-Na-Mg-HCO ₃ -Cl	72	38	86	8	0.4	371	119	64	11	22	304	77
RN011446	137	10/10/1988	7.7	665	2.91	Mg-Ca-Na-HCO ₃ -Cl	78	70	70	5	0.4	413	124	52	42	22	339	84
RN011447	153	10/10/1988	7.7	1030	-0.58	Na-Mg-Ca-Cl-SO ₄ -HCO ₃	184	56	92	8	10.7	305	278	245	2	10	250	60
RN011448	122	25/08/1988	7.6	645	-0.32	Mg-Ca-Na-HCO ₃ -Cl	56	63	57	8	0.1	347	110	58	45	30	285	71

NOTE: Data from NTG database, ions and SiO₂ and DIC all measured in mg/L. .

pH is Laboratory measure. Site refers to location area. Bore locations shown on Fig. 4.6. All sites interpreted to tap the Hermannsburg Sandstone.

Highlighted sample IDs represent sites used for Palm Valley study (see Table 5.1). Additional site data shown in Table 4.1.

* Water type classification is derived from the program Aquachem (1999) where major cations and anions are listed only when concentration in meq/L exceeds 10% of total.

Table 5.2 Groundwater chemical data, Hermannsburg Sandstone regional data set

SampleID	Depth (m)	Date	pH	TDS (mg/L)	Charge balance %	TYPE* (>10% meq)	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	K (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	NO ₃ (mg/L)	SiO ₂ (mg/L)	Alkali-nity (mg/L)	DIC (mg/L)
RN011831	433	5/10/1986	7.5	770	2.6	Na-Mg-Ca-Cl-HCO ₃	135	58	71	15	1.0	369	230	61	3	16	303	77
RN012022	200	2/11/1978	7.6	570	0.63	Ca-Mg-Na-HCO ₃ -Cl	54	43	75	16	0.6	348	99	51	22	22	285	71
RN012023	100	3/11/1978	7.4	710	0.14	Na-Mg-Ca-HCO ₃ -Cl	105	47	67	14	0.3	320	176	88	3	18	262	67
RN012024	67	1/12/1994	7.8	559	-0.33	Mg-Ca-Na-HCO ₃ -Cl	73	47	64	6	0.3	361	113	64			296	72
RN012025	200	15/11/1978	7.8	758	0	Mg-Ca-Na-HCO ₃ -Cl	51	64	54	12	3.8	397	92	57	19	11	326	79
RN012026	168	10/10/1988	7.8	695	-0.44	Mg-Na-Ca-HCO ₃ -Cl	77	75	62	5	1.3	431	134	58	51	20	353	86
RN012549	150	18/08/1994	8.3	743	3.08	Mg-Na-Ca-HCO ₃ -Cl	105	76	72	7	0.1	424	182	77			348	81
RN012650	152	12/11/1997	7.6	568	-4.36	Mg-Ca-Na-HCO ₃ -Cl	55	50	63	8	0.1	370	118	63			303	76
RN013652	110	30/04/1998	6.6	783	-1.98	Na-Mg-Ca-Cl-SO ₄	94	46	65	16	0.1	138	243	138			113	44
RN013653	330	12/04/1983	7.5	270	1.63	Mg-Ca-HCO ₃	24	25	41	7	1.2	218	36	22	7	12	179	45
RN014164	128	1/08/1997	7.2	475	0.77	Ca-Na-Mg-HCO ₃ -Cl-SO ₄	71	34	68	9	1.9	301	91	92			247	66
RN014165	166	12/08/1998	7.9	607	-2.57	Mg-Ca-Na-HCO ₃ -Cl	67	52	75	7	0.2	408	113	87			335	81
RN014166	220	6/12/1995	7.4	614	-0.95	Na-Ca-Mg-HCO ₃ -Cl	110	29	64	10	1.9	287	152	89			235	60
RN014616	121	10/08/1994	8.1	438	3.25	Ca-Mg-Na-HCO ₃ -Cl	52	34	73	7	0.2	321	77	42			263	63
RN014952	195	6/10/1994	8.4	414	2.36	Mg-Na-HCO ₃ -Cl	52	49	15	7	0.3	218	83	46			185	42
RN014956	79	15/08/1994	7.8	657	-0.73	Mg-Ca-Na-HCO ₃ -Cl	81	50	80	9	0.8	338	165	89			277	68
RN014957	112	16/08/1994	7.5	471	-0.6	Ca-Mg-Na-HCO ₃ -Cl	53	33	71	10	1.3	297	97	65			244	62
RN015006	250	3/03/1994	7.6	747	2.48	Na-Ca-Mg-Cl-HCO ₃ -SO ₄	123	41	92	11	0.4	279	178	160	1	15	229	57
RN015007	220	12/08/1998	7.6	631	-2.59	Mg-Ca-Na-HCO ₃ -Cl	75	48	75	7	3.9	393	115	104			322	80
RN016359	193	16/02/1994	7.2	491	0.61	Mg-Ca-Na-HCO ₃ -Cl	44	48	68	8	0.6	357	73	47	28	25	293	79

NOTE: Data from NTG database, ions and SiO₂ and DIC all measured in mg/L.

pH is Laboratory measure. Site refers to location area. Bore locations shown on Fig.4.6. All sites interpreted to tap the Hermannsburg Sandstone.

Highlighted sample IDs represent sites used for Palm Valley study (see Table 5.1). Additional site data shown in Table 4.1.

* Water type classification is derived from the program Aquachem (1999) where major cations and anions are listed only when concentration in meq/L exceeds 10% of total.

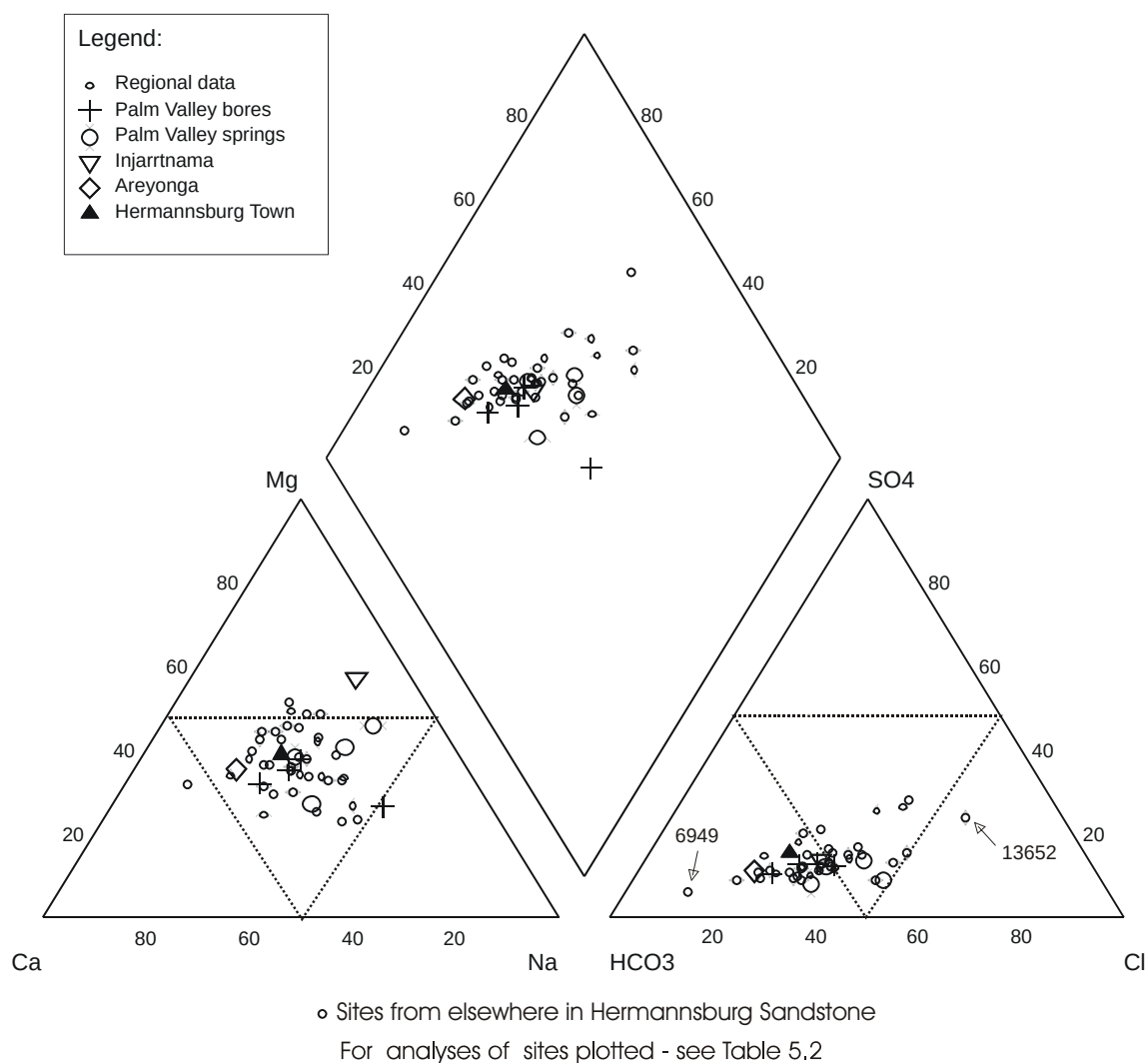


Figure 5-3 Piper plot of major cation chemistry from samples taken from the Hermannsburg Sandstone. Plot shows the Palm Valley area data from Table 5.1 (Fig. 5.1) compared with the Hermannsburg Sandstone regional data set compiled from the NTG database and presented in Table 4.2.

5.4.2. Major Ion chemistry

Figure 5.4 shows plots of some major ions against chloride concentration. Again, the analyses from Palm Valley are seen to be typical of Hermannsburg sandstone. No distinct correlation between chloride (commonly assumed to behave conservatively in groundwater) and the major ions, as would be expected if water chemistry were derived solely from the concentration of rainfall, is shown in Figure 5.4. The plot of sulphate against chloride (Fig. 5.4c) does, however, show a positive correlation trend. This may indicate that redox conditions are roughly similar throughout the Hermannsburg Sandstone. Such relationships are commonly observed in groundwater from central Australia (e.g. Harrington, 1999; Jankowski and Jacobson, 1989; Wischusen, 1995b, 1998) and other arid regions (e.g., Schoeller, 1959; Mazor, 1991) and are taken to reflect the influence of water-rock interactions on groundwater chemistry.

5.4.3. Hydrochemical processes

5.4.3.1. Dissolution / Precipitation reactions

As previously discussed, (Section 5.3.1.), the uptake of CO_2 in the vadose zone and dissolution of carbonates and silicates also adequately accounts for the chemical variations seen in Figure 5.4. This point is illustrated in Figure 5.5a-d where the plots of Figure 5.2a-d previously discussed are shown with the additional regional data from Table 5.2. From this Figure it can be seen that saturation with respect to dolomite and calcite (Fig. 5.5a), magnesium to carbonate ratio in excess of dolomite dissolution stoichiometry (Fig. 5.5b), calcium to carbonate ratio within that expected from calcite dissolution stoichiometry (Fig. 5.5c), and sodium to chloride correlation roughly along a concentration of seawater trend (Fig. 5.5d), are regional phenomena within the Hermannsburg Sandstone.

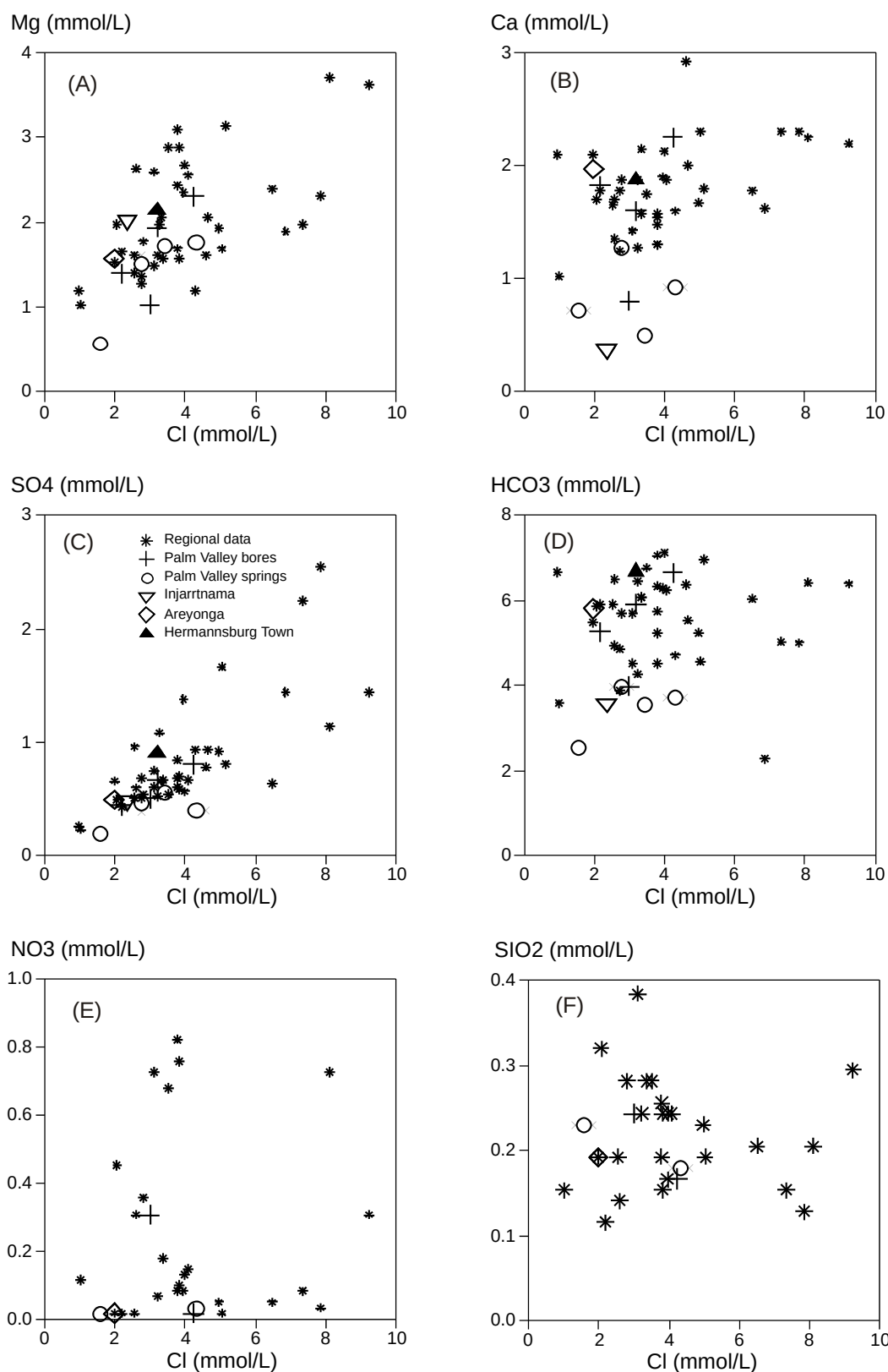


Figure 5-4 (a-f) Hermannsburg Sandstone (Table 5.2) major ion versus chloride plots. (A); Mg²⁺ v. Cl⁻ (B); Ca²⁺ v Cl⁻ (C); SO₄²⁻ v Cl⁻ (D); HCO₃⁻ v Cl⁻ (E); NO₃⁻ v Cl⁻ (F); SiO₂ v Cl⁻. (note Na⁺ v Cl⁻ shown in Fig. 5.5d).

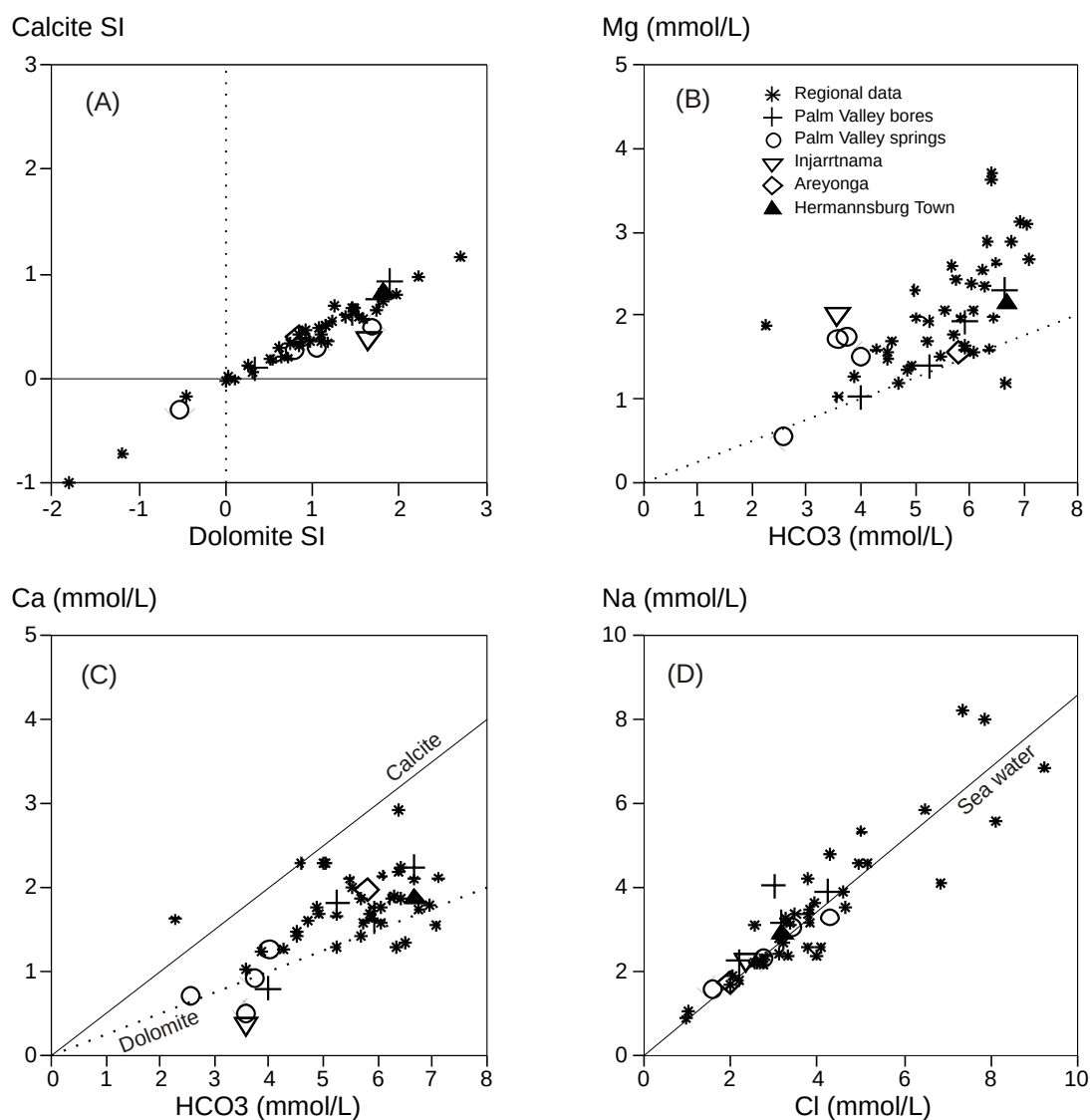


Figure 5-5 (a-d) aspects of groundwater chemistry from the regional Hermannsburg Sandstone data set plotted with Palm Valley area data. Plot of (A); saturation indices of calcite and dolomite (B); magnesium against bicarbonate (C); calcium against bicarbonate (D); sodium against chloride. Compare with Fig. 5.2.

There is a slight anomaly in Figure 5.5a where it can be seen that in contrast to the consistent regional trends, three bores plot as being under saturated with respect to calcite and dolomite. These bores, RN 13652, 10209, 6949 are unusual in that they alone record acidic water ($\text{pH} < 7$) in this data set, Table 5.2. The relationship to pH and carbonate saturation is shown in Figure 5.6a where these three bores are readily identified. As these bores have all been sampled relatively recently (Table 5.2) and all occur on Owen Springs Station (around 60km east of Palm Valley), this under saturation probably reflects variation in chemical conditions rather than incorrect pH being entered in the database. The reason for these anomalous lower pH readings is not readily apparent from examination of Table 5.2, however, as noted above, two of these bores (RN 13652, 6949) plot as outliers at either end of the $\text{HCO}_3^- / \text{Cl}^-$ range on the piper diagram (Fig. 5.3). Given this atypical chemistry and pH, a detailed site and bore lithology investigation may be needed to confirm that these bores do indeed tap the Hermannsburg sandstone and not some other Amadeus Basin sequence.

5.4.3.2. Factors affecting pH

It is also possible that poor sampling protocol has caused a problem in pH calculation for the three Owen Springs Station bores, RN 13652, 10209, 6949. In most instances, water samples collected in the Northern Territory for standard major ion analyses are not filtered and acidified and rarely are field parameters recorded. While this system allows non-specialists to collect water so that the groundwater's suitability for stock or human consumption can readily be determined, such a sampling protocol may limit the accuracy of chemical information. For instance, iron is common in central Australian groundwater; levels of total iron are routinely assessed for water quality purposes (e.g. high iron can cause staining of washing or unsightly clouding etc.) in samples submitted to the laboratory, but virtually never at the time of sampling.

Hem (1985) notes the oxidation of ferrous iron to precipitate ferric hydroxide post sampling can lower pH prior to laboratory analyses. Thus, it is possible that some peculiarity of aquifer chemistry produces a more reducing environment with a consequent anomalous amount of dissolved ferrous iron in this region. Such an environment may have resulted in Ferric hydroxide precipitation post sampling. If so, this would lower pH and influence saturation calculations based on carbonate equilibria.

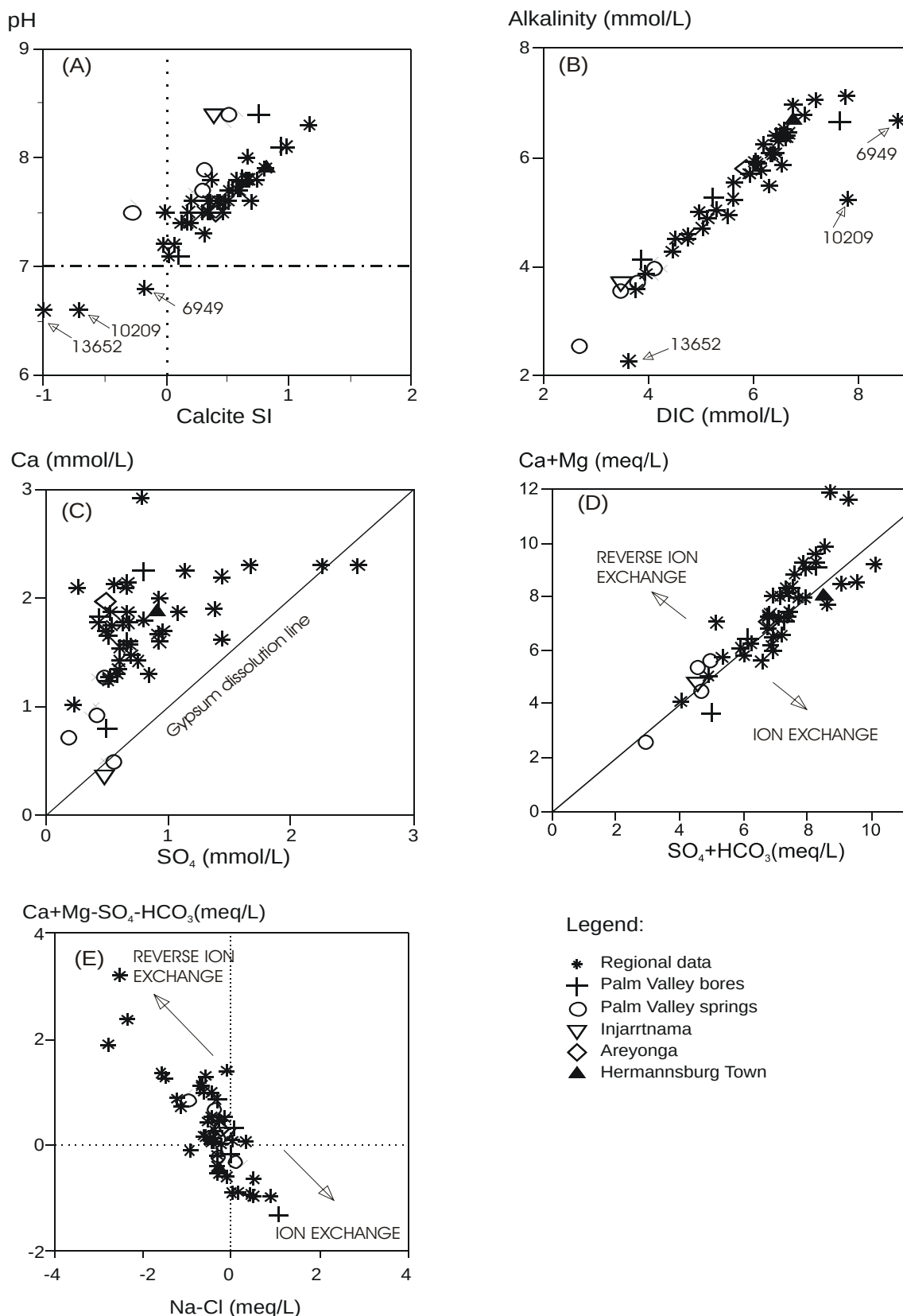


Figure 5-6 (a-e) Plots highlighting some possible hydrochemical processes in the Hermannsburg Sandstone. Plot (A); pH v calcite saturation indices (B); Alkalinity v dissolved inorganic carbon, a Deffeyes type plot (C); calcium v sulphate (D); divalent cations v sulphate plus bicarbonate plot, potential ion exchange trends annotated (E) plot $\text{Na}^+ - \text{Cl}^-$ of against $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-$.

For example, a plot (Fig. 5.6b) of DIC against alkalinity shows most of the Hermannsburg Sandstone data to follow a linear trend. Such a tight grouping is expected for samples within the pH range above 7 – 8.5 (Deffeyes, 1965). The Hermannsburg Sandstone data set (excluding the anomalous Owen Springs bores) has mean pH of 7.7, standard deviation of 0.31 and a range of 7.1 to 8.4 (derived from pH data Table 5.2). If the three anomalous bores are taken to be vertically displaced from the main Hermannsburg Sandstone group (Fig. 5.6b), this may indicate that a reduction in alkalinity due to a proton yielding reaction such as nitrification or sulphide oxidation has occurred (Stumm and Morgan, 1996).

Alternatively, it is also possible that this displacement is caused by addition of CO₂ and these three anomalous bores have been shifted horizontally from the main group due to an increase in DIC content (Deffeyes, 1965). As no ready source of CO₂ in addition to atmospheric flux is known for this area, it seems more likely that if these anomalous bores do represent a deviation from the main group, then some form of pH changing reaction is the likely cause.

5.4.3.3. Redox potential

Investigation of redox potential of these waters is not possible due to a lack of data; furthermore, proxy indicators of redox conditions such as nitrate concentration (e.g. Edmunds, 1995) are also not available. One potential indicator of a more reducing environment is water depth (i.e. the greater the depth the less connection with atmospheric oxygen). From Table 4.2 it can be seen that these three Owen Springs bores have deeper water levels than the mean of 34m below ground level, in fact bore RN 10209 has the deepest water level recorded at 120+ m. Thus, careful re-sampling and analysis of chemical parameters may also help explain why these three bores are anomalous compared to the rest of the Hermannsburg Sandstone data set.

5.4.3.4. Saturation indices

Saturation indices determined by the chemical modelling program PHREEQC (Parkhurst and Appelo, 1999) are shown in Table 5.3 for all the samples from the Hermannsburg Sandstone. These saturation indices are shown plotted against TDS in

Figure 5.7. Apart from the generally positive carbonate (Fig. 5.7a) and dolomite (Fig. 5.7b) saturation indices discussed above it can be seen that all samples are under saturated in respect to both gypsum (Fig. 5.7c) and anhydrite (Fig. 5.7d). There is, however, a trend of increase in saturation indices with increase in TDS for these sulphate rich phases, which probably reflects the rough positive correlation between chloride and sulphate observed in Figure 5.7c above. Figure 5.7e shows that a small minority of bores in the Hermannsburg Sandstone are saturated with respect to siderite. The reason for this saturation is not known, however it is interesting to note that the bore at Areyonga RN 10774 (shown to be saturated with respect to siderite on Fig. 5.7e) was identified to have an iron fouling problem due to unfavourable well hydraulic characteristics allowing iron compounds to be precipitated in response to pumping (Wischusen, 1994b). Thus these siderite saturated bores may reflect disturbance of chemical equilibrium due to excessive pumping rates rather than natural variations in the chemical characteristics of the Hermannsburg Sandstone.

Figures 5.7f and 5.7g show the saturation indices of chalcedony and quartz respectively where it can be seen that while most samples are saturated in respect to quartz they are under saturated in respect to the amorphous chalcedony silica form, a situation that is not unusual for groundwater (Hem, 1985). While the source of silica is not known reactions such as the breakdown of feldspar shown in equation 5.4 are among the likely sources of silica input to groundwater (Hem, 1985).

Table 5.3 Selected saturation indices and available $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values, Hermannsburg Sandstone regional data set

SITE	CALCITE	DOLOMITE	SIDERITE	SATURATION INDEX					QUARTZ	$\delta^{18}\text{O}_{\text{‰}}$ $\delta^2\text{H}_{\text{‰}}$		$\delta^{13}\text{C}_{\text{‰}}$	PDB
				GYPSUM	ANHYDRITE	CHALCEDONY		VSMOW					
Kaporilja Sp.	0.21	0.65	-1.08	-2.10	-2.32	-0.06		0.37					
<i>Lt. Palm Sp.</i>	-0.28	-0.53	-0.94	-2.64	-2.86	-0.09		0.34	-3.75	-28.9		-9.2	
<i>Oasis (sth) Sp.</i>	0.31	1.03	-1.98	-2.34	-2.56	-0.20		0.23	-3.59	0.6			
<i>PV 4/200</i>	0.76	1.76		-2.28	-2.50	-0.08		0.35	-7.25	-45.8			
<i>PV 1/608</i>									-6.72	-46.7			
<i>Road Sp.</i>	0.29	0.79		-2.13	-2.35				-6.89	-44		-11.8	
<i>West Sp.</i>	0.50	1.68		-2.46	-2.68				-4.29	-36.2		-11	
RN000052	0.18	0.52	0.09	-1.93	-2.15	-0.26		0.17	-7	-47.7		-9.9	
RN000291	0.55	1.22	-1.41	-2.02	-2.24	-0.17		0.26					
RN002830	0.02	0.04	-0.30	-1.81	-2.03	-0.16		0.26	-6.7	-52.5		-10.1	
RN002934	0.66	1.47	-2.10	-1.91	-2.13								
RN003280	0.31	0.85	-0.85	-1.95	-2.17	-0.06		0.37					
RN003618	0.34	0.74		-1.36	-1.58	-0.26		0.17					
RN004508	0.10	0.34	-0.85	-1.77	-1.99	-0.23		0.20	-7.51	-49		-10.8	
RN005740	0.98	2.23	-1.87	-1.92	-2.14	-0.07		0.36					
RN006949	-0.17	-0.45	-0.99	-2.18	-2.40				-7.94	-52.2			
RN007175	0.58	1.39	-1.40	-1.61	-1.83	-0.23		0.20				-10.6	
RN007291	0.20	0.72	0.32	-1.95	-2.17	-0.16		0.26					
RN007292	0.37	0.88	-1.17	-2.09	-2.31							-9.3	
RN010209	-0.71	-1.18	-1.27	-1.91	-2.13				-6.39	-44.1		-7.9	
RN010774	0.40	0.84	1.21	-1.96	-2.18	-0.17		0.26					
RN011338	0.81	1.96	-0.87	-1.61	-1.83	0.02		0.45					
RN011341	0.35	1.18	-0.52	-2.13	-2.35	-0.06		0.37					
RN011342	0.73	1.82	-0.98	-1.69	-1.91	-0.14		0.29					
RN011343	0.69	1.25	-0.92	-1.66	-1.88								
RN011439	0.68	1.46	-0.69	-2.07	-2.29	-0.39		0.04					
RN011440	0.46	0.91	-0.49	-1.82	-2.04	0.00		0.43					

Table 5.3 Selected saturation indices and available $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values, Hermannsburg Sandstone regional data set

SITE	CALCITE	DOLOMITE	SIDERITE	SATURATION INDEX				QUARTZ	VSMOW		PDB
				GYPSUM	ANHYDRITE	CHALCEDONY	$\delta^{18}\text{O}\%$		$\delta^2\text{H}\%$		
RN011446	0.60	1.54	-0.76	-2.05	-2.27	0.00	0.43				
RN011447	0.51	1.14	0.51	-1.32	-1.54	-0.34	0.09				
RN011448	0.35	1.10	-1.27	-2.05	-2.27	0.14	0.56				
RN011831	0.35	0.96	-0.10	-1.97	-2.19	-0.14	0.29		-7.48	-52	-6.9
RN012022	0.48	1.07	-0.48	-1.97	-2.19	0.00	0.43				
RN012023	0.18	0.55	-0.56	-1.80	-2.02	-0.09	0.34				
RN012024	0.62	1.45	-1.12	-1.94	-2.16				-7.7	-51.3	-9.4
RN012025	0.58	1.58	0.02	-2.08	-2.30	-0.30	0.13				
RN012026	0.65	1.74	-0.42	-2.06	-2.28	-0.04	0.39				
RN012549	1.17	2.71	-2.56	-1.90	-2.12						
RN012650	0.43	1.10	-1.24	-1.96	-2.18				-7.8	-54.3	-9.17
RN013652	-1.00	-1.80	-1.60	-1.62	-1.84				-7.32	-53.3	-7.9
RN013653	-0.01	0.11	-0.21	-2.46	-2.68	-0.26	0.17		-7.31	-52.1	-7.31
RN014164	-0.02	0.00	0.34	-1.74	-1.96						
RN014165	0.82	1.83	-1.44	-1.77	-1.99						
RN014166	0.12	0.25	0.20	-1.78	-2.00				-7.24	-48	-8.74
RN014616	0.93	1.89	-1.94	-2.04	-2.25				-7.16	-45.8	-9
RN014952	0.39	1.64	-2.56	-2.64	-2.86						
RN014956	0.67	1.48	-0.73	-1.74	-1.96						
RN014957	0.30	0.62	-0.06	-1.86	-2.08						
RN015006	0.43	0.85	-0.76	-1.44	-1.66	-0.17	0.26				
RN015007	0.50	1.16	0.37	-1.69	-1.91						
RN016359	0.06	0.32	-0.09	-2.04	-2.26	0.06	0.49				

Highlighted site IDs represent sites used for Palm Valley study. Additional stable isotope data from Jacobson et al., 1989. Saturation indices determined by model PHREEQC (Parkhurst and Appelo, 1999)

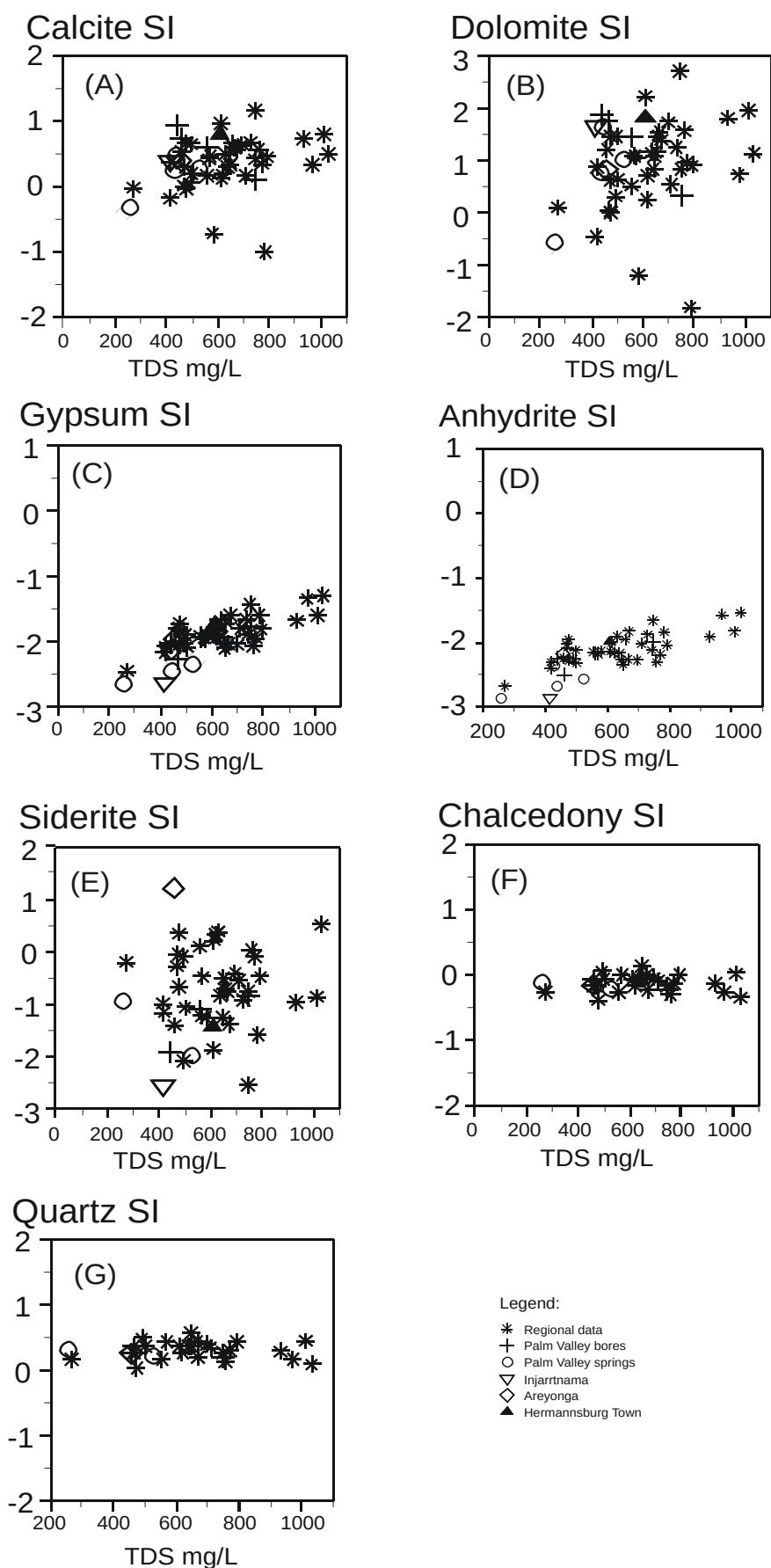


Figure 5-7 (a-g) Saturation indices versus TDS: A) calcite SI; B) dolomite SI; C) gypsum SI; D) anhydrite SI; E) siderite SI; F) chalcedony SI; F) quartz SI.

5.4.3.5. Sulphate

Further chemical characteristics are discernible from these regional data shown in Table 5.3. While lack of field based measurement as discussed above may limit the accuracy of these data some regional trends are still apparent. For instance, all samples are under saturated with respect to gypsum. Given the low sulphate concentration in this aquifer (Table 5.2) and the fact that gypsum is more soluble than carbonates (Freeze and Cherry, 1979), it seems that dissolution of gypsum plays less of a role than carbonates in the hydrochemistry of the Hermannsburg Sandstone.

For instance, Figure 5.6c shows the relationship between calcium and sulphate. Nearly all analyses show that calcium exists in greater concentrations than would be expected were dissolution of gypsum the sole source of calcium to the system:



As mentioned above, dissolution of carbonates and silicates is a potential source of calcium in this aquifer. If gypsum and or anhydrite are not major salts in this system then additional sources of sulphate may also be a factor.

Sulphate forms a significant portion, often in excess of chloride, of inland rainfall composition (Hem, 1985). Indeed in central Australia Hutton (1983) and Keywood (1995) found sulphate to be in excess of chloride in rainfall analysed from Alice Springs. Furthermore, both these studies considered suspended dust provided a significant proportion of ions to rainfall and the land surface as dry fallout. Therefore, concentration of rainfall by evapotranspiration and dissolution of dry fall and root zone salts in the vadose zone could also provide a source of sulphate to this aquifer. Other sources are also feasible, for example, oxidation of pyrite can also produce SO_4^{2-} in groundwater.

5.4.3.6. Ion exchange

Another possible influence on cation chemistry is ion exchange between ions in solution and cation receptors such as clays. Figure 5.6d shows a composite ion plot of the divalent cations against carbonate and sulphate. The divalent cations are plotted as these ions are nearly always exchanged for monovalent cations like sodium or potassium held on ion absorbers such as clays (Freeze and Cherry, 1979, Hem, 1985). Cerling et al. (1989) have previously used this graphical method to investigate ion exchange processes. A 1:1 relationship is evident if dissolution of gypsum, dolomite and calcite are the dominant processes. If data plots below the 1:1 line an excess of alkalinity from silicate weathering (e.g. alkali feldspar weathering in the presence of CO_2 can also produce bicarbonate) reactions and/or a reaction that consumes Ca^{2+} and Mg^{2+} (e.g. ion exchange) is implied (Cerling et al., 1989). As Figure 5.5d shows Na^+ is not in excess of Cl^- there is no ready indicator of silicate weathering producing significant excess alkalinity.

Another method for examining ionic exchange processes is to plot $\text{Na}^+ - \text{Cl}^-$ against $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-$ where $\text{Na}^+ - \text{Cl}^-$ represents the amount of Na gained or lost relative to halite dissolution and $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-$ represents the amount of Mg^{2+} and Ca^{2+} lost or gained relative to dissolution of calcite, gypsum and dolomite (Fisher and Mullican, 1997). If the relationship between these two ionic balance values is linear along a slope of -1 away from the origin then Fisher and Mullican (1997) note that cation exchange (e.g. Na^+ for Ca^{2+} and Mg^{2+}) may be important in controlling groundwater mineral composition. Such a plot, displayed as Figure 5.6e, shows the Hermannsburg Sandstone data to plot mainly about the origin (X,Y = 0,0) though points are generally distributed along the line of -1 slope annotated on this diagram. Although some cation exchange may be indicated from this figure, the spread of data points does not extend very far from the origin like the data shown (origin to -40 along a -1 slope) by Fisher and Mullican (1997) as evidence for ion exchange in the USA. Thus while this plot shows some ion exchange may occur in the Hermannsburg Sandstone the cluster of data points about the origin suggests this process may not be significant. On examination of Figure 5.6d, it can be seen that ion exchange processes are also indicated to be unlikely to be a significant influence on cation chemistry as a rough 1:1 relationship is observed.

These plots (Fig. 5.6 e and d) do not imply, however, that other chemical processes such as dissolution of chlorite etc discussed above are not also influencing groundwater chemistry. Indeed the fairly consistent SiO_2 levels (see Table 5.2 & Fig. 5.5f) and saturation with respect to quartz (Table 5.3) is a possible indication that dissolution of silicates (e.g. Eq. 5.4) does occur in the Hermannsburg Sandstone.

5.4.3.7. Discussion

No matter what processes cause these observed variations in cation ratios, it is apparent that distinct water type groups can be recognised on the basis of cation signature. Examination of the analyses from the whole Hermannsburg Sandstone data set (Table 5.2) shows that all six types of water based on relative dominance of major cations exist. Frequency of these “cation” water type ranges are roughly 37% Mg-Ca-Na, 18% Mg-Na-Ca, 16% Ca-Mg-Na, 14% Na-Mg-Ca, 8% Na-Ca-Mg and 6% Ca-Na-Mg. Based on these cation ratio groups, five “cation” water types are represented in the data set used for study at Palm Valley (Table 5.1). From this grouping it is clear that the majority (55%) of sites sampled in the Hermannsburg Sandstone have Mg^{2+} as the dominant cation with Na^+ and Ca^{2+} being equally distributed, each being the dominant cation at around 22% of sites.

In the absence of evidence to the contrary, it is possible that these observed differences in cation chemistry are the result of variation in chemical conditions experienced along differing groundwater flow paths through the Hermannsburg Sandstone. Evidence of differing conditions along various flow paths may be helpful in understanding the isotope chemistry of sites sampled in the Palm Valley region discussed below (Chapter 6 and 7).

It should be noted that the use of cation ratios to identify different flow paths is not without precedent. For instance, Edmunds et al. (2003) distinguish convergence of different flow lines with separate geochemical evolution in the Chotts area of Tunisia on the basis of observed differences in cation ratios between some bores sampled in the region.

5.5. Conclusion

Groundwater at Palm Valley and in the surrounding Hermannsburg Sandstone is generally of low salinity (<1000 mg/L) and bicarbonate rich. Comparisons with a regional data set shows groundwater at Palm Valley to be typical of the Hermannsburg Sandstone from the folded rock province (Lloyd and Jacobson, 1987) of the Amadeus Basin. A lack of field measured chemical parameters limits the chemical interpretations possible from the available chemical data. Nevertheless, it is apparent that apart from a few exceptions groundwater is saturated with respect to calcite and dolomite. Magnesium is usually the dominant cation, which apart from a credible carbonate dissolution origin, may also reflect reactions with magnesium rich accessory minerals such as chlorite and micas. Cation ratios are, however, variable throughout this aquifer. Possible processes that explain these differences can be readily identified. The actual processes that control cation chemistry variation are yet to be determined. The variations in cation chemistry recorded are taken as evidence that different flow paths with separate geochemical histories have been sampled. This compilation of chemical data provides the basis for studying the stable isotope and radiocarbon hydrology of the Hermannsburg Sandstone at Palm Valley discussed in the following Chapter.

6. Stable Isotope and Radiocarbon Hydrology

6.1. Oxygen-18 and deuterium

6.1.1. Introduction

The isotope ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ in a groundwater sample are measured as the relative difference in ratios to a reference sample by mass spectrometry. The ratios measured are expressed as delta (δ), which is the difference from an arbitrary standard known as the Vienna standard mean ocean water (VSMOW) in units of parts per thousand (‰) (Clark and Fritz, 1997).

Delta units (δ) for the isotope ratio (R) are expressed by the equation

$$\delta \text{ (‰)} = \left(\frac{R \text{ sample} - R \text{ standard}}{R \text{ standard}} \right) \times 1000 \quad (6.1)$$

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for VSMOW are by definition equal to 0‰.

Changes in water isotope concentration (fractionation) occur when water undergoes phase changes, due to the differing behaviour of different isotopes of water. Thus when water moves through the hydrologic cycle from the sea, changes in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values occur. For instance when clouds are formed by evaporation of sea water the more common lighter molecules of water (e.g. H_2^{16}O) are slightly easier to evaporate, thus clouds are depleted in ^{18}O and ^2H when compared to VSMOW (Gat, 1980). This fractionation affect is also influenced by temperature, thus rainwater (evaporated sea water) $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition also varies with latitude, (cold) high latitude rainfall is noted to be more depleted than (warm) tropical rainfall when compared to VSMOW (Gat, 1980). As movement of water vapour over continental land masses can experience cooler temperatures than at the coast (e.g cooler land surface or elevation change over mountains) inland rainfall $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition can be more depleted than coastal rainfall (Gat, 1980). However, as first noted by studying fresh water compositions by

Craig (1961), and later slightly modified after world wide analyses of rain water composition (Rozanski et al., 1993) most rainwaters in the world are observed to have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions that plot approximately along a straight-line relationship characterised by the equation:

$$\delta^2\text{H} = 8.13 \delta^{18}\text{O} + 10.8 \quad (6.2)$$

which, when plotted on charts such as Figure 6.1, is known as the world meteoric water line (WMWL). Clark and Fritz (1979) note that while the meteoric relationships between ^{18}O and ^2H such as the meteoric water lines plotted on Figure 6.1 are due to fractionation due to condensation, it is a Rayleigh distillation process that causes the difference in warm and cold region rainfall isotopic composition. While the WMWL gives an approximation to rainfall in most regions, detailed studies can benefit from the construction of a local meteoric water line (LMWL), if data are available.

The comparison of groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values to these meteoric water lines has various applications for the interpretation of groundwater (Allison, 1981). For example as fractionation of ^{18}O and ^2H is not known to occur within an aquifer under normal processes such as flow and plant root uptake, deviation from a meteoric line may indicate that some form of fractionation process such as evaporation or isotope exchange with mineral phases has occurred. The inset chart shown in Figure 6.1 outlines some of the processes that may cause deviation away from a meteoric water line (Fontes, 1980).

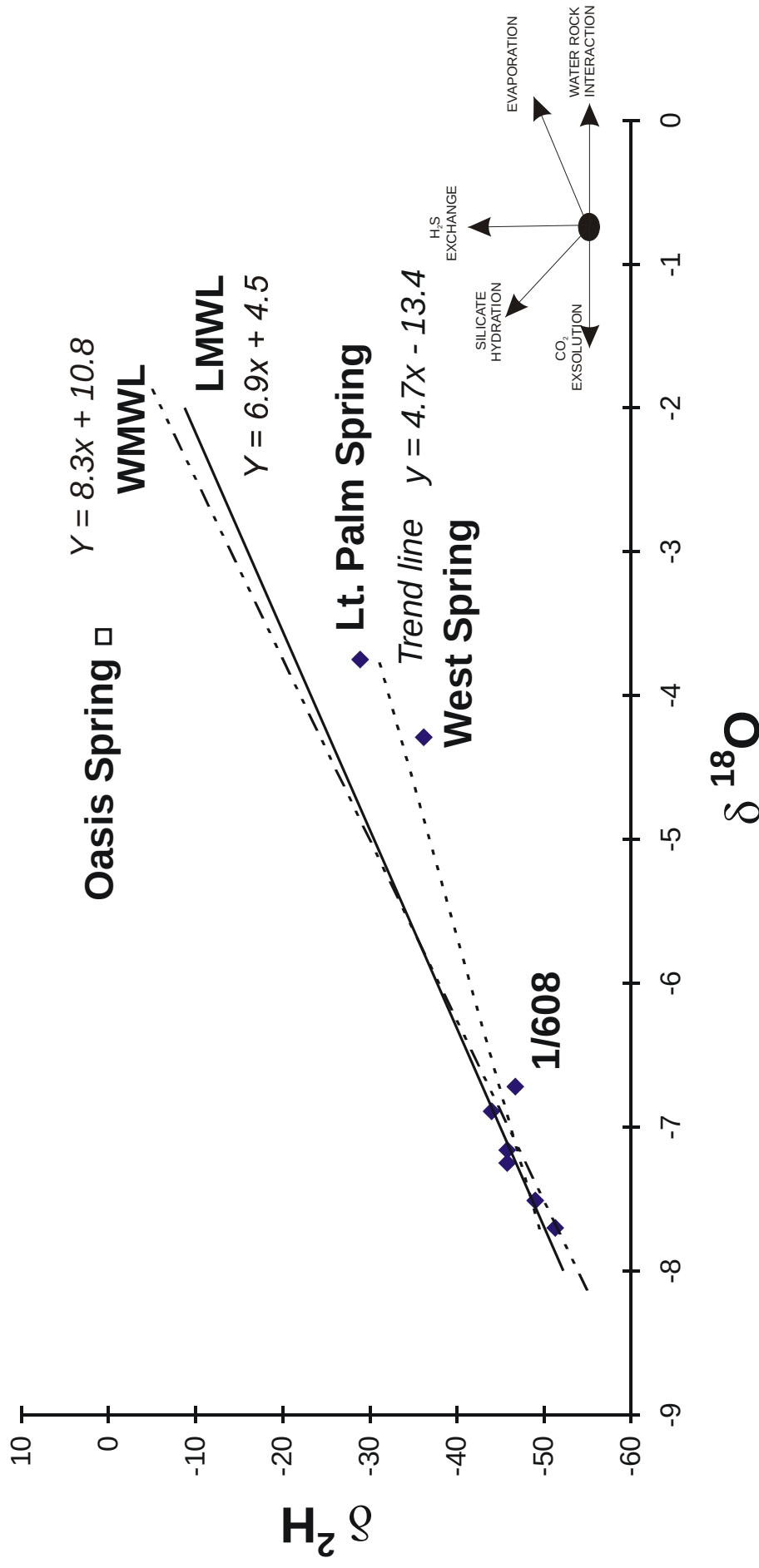


Figure 6-1 Stable isotope data – groundwater samples, Palm Valley. Relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for samples from the Hermannsburg Sandstone in the Palm Valley area. The local meteoric water line (LMWL) is obtained from the Alice Springs station (IAEA/WMO, 2001). While evaporation affects seem to influence isotope ratios at West and Little Palm Spring, the reason for Deuterium enrichment at Oasis Spring is not known (The likely influence of various processes shown as inset after Fontes, 1980).

6.1.2. Results

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values presented for this study were determined by standard mass spectrometry at the CSIRO Isotope Laboratory in Adelaide, South Australia. These results, a LMWL for Alice Springs and the WMWL are shown drawn on Figure 6.1. The LMWL;

$$\delta^2\text{H} = 6.9\delta^{18}\text{O} + 4.5 \quad (6.3)$$

is constructed from the Alice Springs (150 km east of Palm Valley, Fig. 1.1) station of the global network of isotopes in precipitation station (IAEA/WMO 2001). Most of the groundwater samples plot on or near the LMWL. In the main cluster of data points (around $\delta^{18}\text{O} = -7\text{‰}$) one sample plots slightly to the right of the LMWL. This point, seismic shot hole 1/608, which has an electrical conductivity 1470 $\mu\text{S}/\text{cm}$, may have been more affected by evaporation during recharge than other sites and is thus slightly more enriched in ^{18}O and ^2H .

Oasis Spring plots above the LMWL. The reason for this is not known, though localised condensation affects are attributed to cause the shift of ^{18}O and ^2H above a LMWL on some water condensed on vegetation in Kenya (Ingraham and Matthews, 1988) and in some water condensed in Arctic caves (Lauriol and Clark, 1993). Clark and Fritz (1997) note that in low humidity regions re-evaporation of precipitation from local surface waters creates vapour masses with isotopic signatures that plot above local meteoric water lines. If such vapour recondenses before mixing with other atmospherically derived isotope reservoirs, the resulting water will also plot above the LMWL. It is feasible that such a situation may have occurred at this spring prior to sampling. The different anion ratio noted previously for this site also indicates evaporation processes have probably affected the nature of water at this spring when sampled.

Two data points, Little Palm Spring and West Spring, plot out of the main cluster and are significantly enriched in ^{18}O and ^2H when compared to the other samples. Given these samples are from free standing pools of water, enrichment due to evaporation can be expected.

Allison (1982) showed that when a free body of water is evaporated, subsequent enrichment of stable isotopes results in the evaporated water samples plotting to the right of the starting water stable isotope composition, when displayed on a $\delta^{18}\text{O}$ against $\delta^2\text{H}$ diagram similar to Figure 6.1. The slope of the trend away from the initial isotope composition can be a function of humidity, salinity and temperature (Gat, 1981). Allison (1982) also showed that the maximum slope away from the meteoric water line that could occur for free standing evaporated water samples was along a slope of 5 (i.e. $\delta^2\text{H} = 5\delta^{18}\text{O}$) from the starting isotope composition. Thus, if a slope of five was projected through the West and Little Palm Spring plot points to intersect the LMWL, an estimate of the starting composition of the water prior to evaporation could be made. When a trend line between these two springs and the main cluster of data points is constructed, a line with a slope of around 5 (i.e. slope 4.7, Fig. 6.1) connects the two sets of data points.

As this line has a slope no greater than five it can be taken as evidence that spring and groundwater may share a common origin, that is, Little Palm and West Springs at the time of sampling contained evaporated Hermannsburg Sandstone groundwater and were not ponds of recent rainfall. The sample from Road Spring, which plots near the LMWL, may also indicate a groundwater origin of water at this spring. Thus, apart from Oasis Spring, it is concluded that stable isotope data confirms that the waters sampled in the Palm Valley area share a similar origin.

The fact that groundwater plots on or near the LMWL suggests little evaporation during the recharge process, which in turn suggests a rapid indirect recharge mechanism. Jacobson et al. (1989) have previously postulated that rapid recharge through fissures may be the dominant process in the folded rock province sandstones in the Amadeus Basin. If recharge were rapid into the Hermannsburg Sandstone, this would probably influence groundwater chemistry in that dissolution and weathering rather than precipitation would be expected in the vadose zone.

Figure 6.2 compares some oxygen/deuterium data that has been previously sampled from within the regional data sets of bores. These data, presented in Table 5.3, were sourced from the NTG database and originally published by Jacobson et al. (1989).

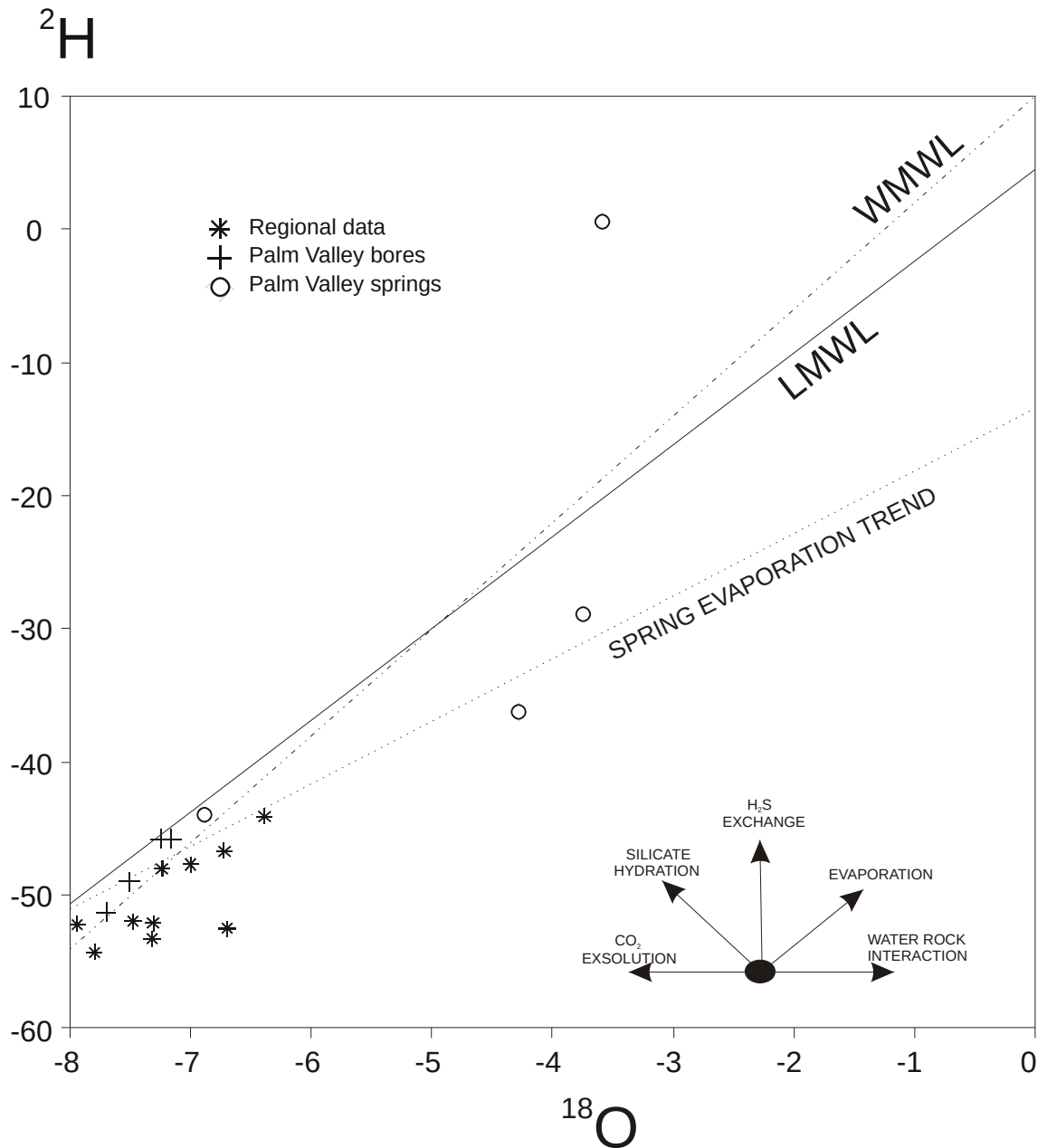


Figure 6-2 Relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for samples from the regional Hermannsburg Sandstone data set (Table 5.3) and the Palm Valley area (Fig. 6.1). The LMWL is obtained from the Alice Springs station (IAEA/WMO, 2001). $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (apart from some springs) from the Palm Valley area are seen to be similar to other Hermannsburg Sandstone sites.

This plot shows that the Palm Valley study samples plot in similar position to other bores sampled from the regional Hermannsburg Sandstone data set and that given little evidence of evaporation (deviation from LMWL) the postulated rapid recharge mechanism of Jacobson et al. (1989) seems likely for Hermannsburg Sandstone at Palm Valley and elsewhere in the region.

Figures 6.3a and 6.3b show the relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ against chloride respectively. From these figures it can be seen that stable isotopes do not vary with chloride content which also suggests that evaporation is not responsible for the stable isotope composition except at some springs sampled at Palm Valley. These Figures also suggest that chloride content variations within the Hermannsburg Sandstone may result from differing amounts of surface or vadose zone chloride entering the aquifer at the time of recharge at different locations and/or times, rather than differing amounts evaporation. Alternatively it may be that evaporation concentration of chloride is an active process at recharge but its affect is not sufficient to noticeably influence stable isotope composition.

6.1.3. Stable isotopes: a proxy for groundwater age?

It should also be noted that the stable isotope data from the Hermannsburg Sandstone give no hint as to time of recharge as $^2\text{H} / ^{18}\text{O}$ depletion is similar in magnitude to that found in aquifers known to contain modern water elsewhere in central Australia (e.g. Wischusen, 1994a). Elsewhere in the world stable isotopes can be used to draw inferences on groundwater age. For instance, Guendouz et al. (2003) note that groundwater believed to have been derived from Pleistocene rainfall in northern Africa is often distinguished from that derived from modern and Holocene rainfall as stable isotopes were more depleted during the Pleistocene. Zuppi and Sacchi (2004) note this phenomenon is widespread in the large sedimentary basins of Europe (e.g. Edmunds and Smedley, 2000) as well as northern Africa (e.g. Guendouz et al., 2003; Rozanski et al., 1993). This depletion of ^{18}O compared to modern rainfall is attributed to lower temperatures during the recharge processes during humid periods of the Quaternary.

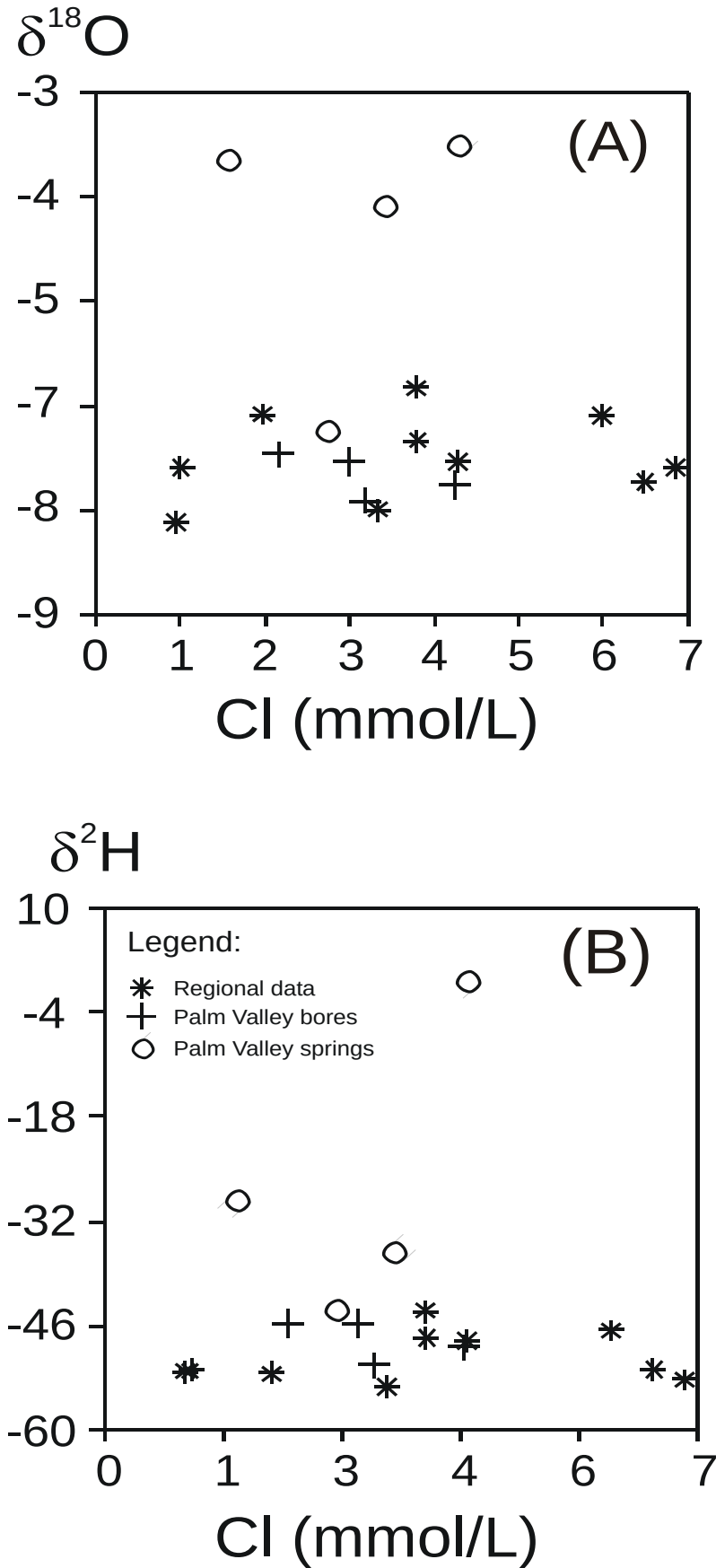


Figure 6-3 Relationship between stable water isotopes and chloride. Plot (A); $\delta^{18}\text{O}$ versus chloride, (B); $\delta^2\text{H}$ versus chloride.

They then note that stable isotopes may be used as a proxy to identify palaeo waters over the last 70 ka in this location.

In contrast, Plummer (1993), while noting the widespread correlation of cooler temperatures and depletion of ^{18}O and ^2H values for Pleistocene recharged groundwater, presents data from southern U.S.A. where this depletion phenomenon may be masked by associated changes in the season of recharge during the Pleistocene.

While temperature dependant amino-acid racemization reactions have been studied in fossil emu egg shells at Lake Eyre to interpret temperatures were some 9 degrees colder during the last glacial maximum in the arid interior of Australia (Miller et al. 1997), relations of ^{18}O depletion to temperature and hence age of groundwater are not usually drawn in central Australia. This is because precipitation is so variable in the region that the amount effect (Dansgaard, 1964) is thought to dominate stable isotope composition. Rozanski et al. (1993), show that amount of precipitation and not temperature variation is the dominant influence on stable isotope composition at various locations (e.g. Guam and India) affected by monsoon rain events. Given the monsoon (Section 3.2) also affects rainfall in central Australia it is not surprising an amount effect is thought to dominate in central Australia. This is certainly the case at Alice Springs where the ^{18}O depletion of rainfall is seen to vary from a mean of -2.5‰ for light rainfall months ($< 50\text{mm}$) to $> -13.0\text{‰}$ for heavy rainfall (200mm) months (calculated from International Atomic Energy Agency/World Meteorological Organization data by Harrington et al. 2002.) This correlation of $\delta^{18}\text{O}$ to monthly rainfall amount has been used to study the character of modern recharge rain in several previous studies in central Australia (e.g. Wischusen, 1994a, Calf et al. 1991).

While the amount effect limits a ready characterization of age of groundwater based on stable isotopes in the Hermannsburg Sandstone, it is not evidence that this groundwater is derived from modern rainfall. The fact that groundwater plots on or near the LMWL suggests little evaporation during the recharge process, which in turn suggests a rapid indirect recharge mechanism. Jacobson et al. (1989) have previously postulated that rapid recharge through fissures may be the dominant process in the folded rock province sandstones in the Amadeus Basin and speculate that this may have occurred during some previous climatic regime. If recharge were rapid into the Hermannsburg

Sandstone, this would probably influence groundwater chemistry in that dissolution, rather than precipitation, would be expected in the vadose zone.

6.2. Radiocarbon (^{14}C)

6.2.1. Background

Radioactive carbon-14 (^{14}C) is formed naturally in the earth's atmosphere by the bombardment of nitrogen-14 by cosmic rays. Carbon-14 has a half-life of 5730 years. Its activity decays exponentially, the law of radioactive decay describes the rate at which the activity of radiocarbon decreases with time. This is expressed by the decay equation:

$$A_t = A_0 e^{-\lambda t} \quad (6.4)$$

where: A_t = Activity at time t , A_0 = Activity at time 0 (recharge), λ = decay constant for radio isotope ($^{14}\text{C} = 1.2097 \times 10^{-04} \text{ yr}^{-1}$).

Under natural conditions new carbon-14 forms as older (around 40 ka) ^{14}C atoms lose their radioactivity (become radioactively dead). Therefore, given a sufficient sample of carbon atoms, the mix of carbon-14 atoms in various states of decay should remain constant, thus atmospheric carbon has a constant carbon-14 activity. This atmospheric (modern) carbon activity is used as the benchmark for radiocarbon analyses with measured activity expressed as percent modern carbon (pmc).

Due to the changes in the atmosphere since the industrial revolution (i.e. release of old dead carbon with use of fossil fuels and increase in natural levels of ^{14}C following surface nuclear testing in the 1950's and 1960's) the benchmark modern carbon activity is taken to be that of atmospheric carbon prior to the Industrial Revolution. Current atmospheric levels are now well above 100 pmc (Kalin, 2000).

Radiocarbon dating of groundwater operates on the assumption that once water enters an aquifer having picked up atmospheric carbon from soil CO₂ etc, no further addition of radiocarbon from the atmosphere is expected, thus carbon-14 activity of a groundwater sample should be related to the amount of time elapsed since recharge occurred

6.2.2. Carbon 13

Carbon 13 isotope content of groundwater used to be expressed as parts per thousand from the Pee Dee Belemnite (PDB) standard of $\delta^{13}\text{C} = 0\text{‰}$, (measured from CO₂ prepared from Belemnites collected from the upper Cretaceous Pee Dee Formation of South Carolina, USA; Bates and Jackson. (1987). Due to a decline in the reserves of this standard Belemnite the International Atomic Energy Agency in Vienna have set a hypothetical standard (VPDB, virtually identical to PDB) beside which $\delta^{13}\text{C}$ determinations are reported (Clark and Fritz, 1997). One of the common uses of carbon-13 data is to give an indication of the behaviour of ¹⁴C in groundwater. For example as ¹⁴C and ¹³C behave very similarly, if a groundwater sample has a lower than expected $\delta^{13}\text{C}$ content, then some dilution of radiocarbon activity can be suspected.

The δ shift of ¹³C from the standard can, like ¹⁸O and ²H, be caused by fractionation processes. The change of gaseous CO₂ to aqueous carbonate species when rainwater passes through the soil to an aquifer can theoretically cause around + 8 ‰ fractionation of the soil $\delta^{13}\text{C}$ value (e.g. Hendy, 1971; Carothers and Kharaka, 1980; Mook et al., 1974; Salomons and Mook, 1986). Reaction of soil CO₂ with aquifer carbonates (e.g. Eqs. 5.1 & 5.3) also enriches the $\delta^{13}\text{C}$ content of dissolved inorganic carbon (DIC) in groundwater as non marine carbonates are expected to have $\delta^{13}\text{C}$ values near 0‰ (Herczeg et al., 1991). The extent of this enrichment depends on the availability of mineral carbonate, the partial pressure of soil CO₂ and whether the system is open to the atmosphere (Clark and Fritz, 1979). Thus the $\delta^{13}\text{C}$ of DIC in groundwater is influenced by several factors including the extent of aquifer carbonate dissolution which influences radiocarbon interpretations (see below). In studies of carbonate behaviour in groundwater it is common to plot the relationship between $\delta^{13}\text{C}$ and DIC (e.g. Schofield and Jankowski, 2004). For instance if $\delta^{13}\text{C}$ values become more enriched as DIC

content increases this may be evidence of an increased component of rock carbonate derived carbon entering the groundwater system.

Figure 6.4a shows a plot of $\delta^{13}\text{C}$ against DIC for the available analyses from the Hermannsburg Sandstone data set (Table 5.3) where it can be seen that no strong correlation exists. Thus these data allow no obvious conclusion as to the effect of rock or matrix carbonate dissolution on the stable carbon isotope content and hence also no readily apparent potential dilution of radiocarbon activity.

In some other Australian studies (e.g. Calf, 1978 and 1979) the method of plotting $\delta^{13}\text{C}$ against $1/\text{total carbonate}$ outlined by Pearson and Swarzenki (1974) has been used to estimate soil and mineral $\delta^{13}\text{C}$ content by extrapolating trends to intersect the $\delta^{13}\text{C}$ axis at zero reciprocal carbonate and also to derive estimates of soil gas $\delta^{13}\text{C}$ from the slope of the line of best fit. When $\delta^{13}\text{C}$ is plotted against $1/\text{DIC}$ as shown in Figure 6.4b it can be seen that the spread of plot points (as noted above in Fig. 6.4a) does not allow a distinct trend to be drawn, hence the use of the Pearson and Swarzenki (1974) technique is not readily applied here.

Furthermore, Allison (1981) gives some examples on the use of $\delta^{13}\text{C}$ data to correct age determination with ^{14}C activity data, and also notes that the amount of fractionation of ^{13}C can vary in response to water pH and temperature changes, therefore the accuracy of corrections based on ^{13}C may be limited.

6.2.3. Corrections

The major complication in determining radiocarbon age is adequately allowing for dissolved groundwater carbon reactions with soil and aquifer carbon reservoirs, such as aquifer and soil carbonates and soil CO_2 gas. Interaction between water and subsurface carbon reservoirs has the potential to significantly lower the initial ^{14}C activity (A_0). For example, recharging water reacting with CO_2 gas and CaCO_3 in the subsurface as shown in Eq. 5.3 would produce groundwater bicarbonate with both solid carbonate and CO_2 derived carbon atoms. As subsurface carbonate minerals usually contain old “dead” carbon (^{14}C activity = 0 pmc), then, depending on the amount of carbonate dissolution,

groundwater ^{14}C activity can be expected to be less than atmospheric carbon ^{14}C activity, even at the time of recharge.

Various methods exist that attempt to account for carbon exchange processes so as to estimate the initial groundwater activity A_0 at the time of recharge. Some of the commonly used methods to estimate A_0 for this study have been applied; the empirical approach of Vogel (1967), Tamers' chemical mass balance model (Tamers, 1967), Pearson's isotope mass balance model (Ingerson and Pearson, 1964) and the Fontes and Garnier (F-G) chemical mass- balance with isotope exchange model (Fontes and Garnier, 1979).

Due to a lack of data, several commonly used assumptions are necessary to apply these models; the atmospheric and mineral carbon activities were taken to be 100% and 0% (pmc) respectively, $\delta^{13}\text{C}$ composition of soil gas CO_2 and matrix carbon was taken to be -20‰ , and -1.5‰ PDB respectively. The matrix carbon $\delta^{13}\text{C}$ composition is taken from measurements made of calcite veins within the Hermannsburg Sandstone by Jacobson et al. (1989). No soil gas CO_2 measurements are available in this region so a value representing a possible mix of carbon fixing mechanisms expected for arid regions (Clark and Fritz, 1997) was adopted. This value is considered a reasonable estimate as a soil gas CO_2 value of around -20‰ was also assumed by Love et al. (2000) in the arid north of South Australia.

Reported measured soil gas CO_2 values from other arid areas (e.g. Murray Basin, Australia, -18‰ , Leaney and Allison 1986; Karmel mountains, Israel, -22‰ Bajjali and Abu-Jaber, 2001; Continental Terminal aquifer, Niger, -14 to 21‰ , Le Gal La Salle et al. 1995; Continental Terminal aquifer, Niger, -20‰ in soil under native vegetation, Le Gal La Salle et al., 2001; West Texas, -17‰ and Russia, -18‰ , cited by Calf, 1979) also indicate -20‰ is a reasonable assumption.

Furthermore, as enrichment of soil CO_2 gas $\delta^{13}\text{C}$ values occur during hydration of CO_2 and also with increasing carbonate dissolution towards calcite saturation (Clark and Fritz, 1997), it seems reasonable to assume a soil CO_2 gas $\delta^{13}\text{C}$ value significantly depleted compared to measured groundwater values (Table 6.1) here.

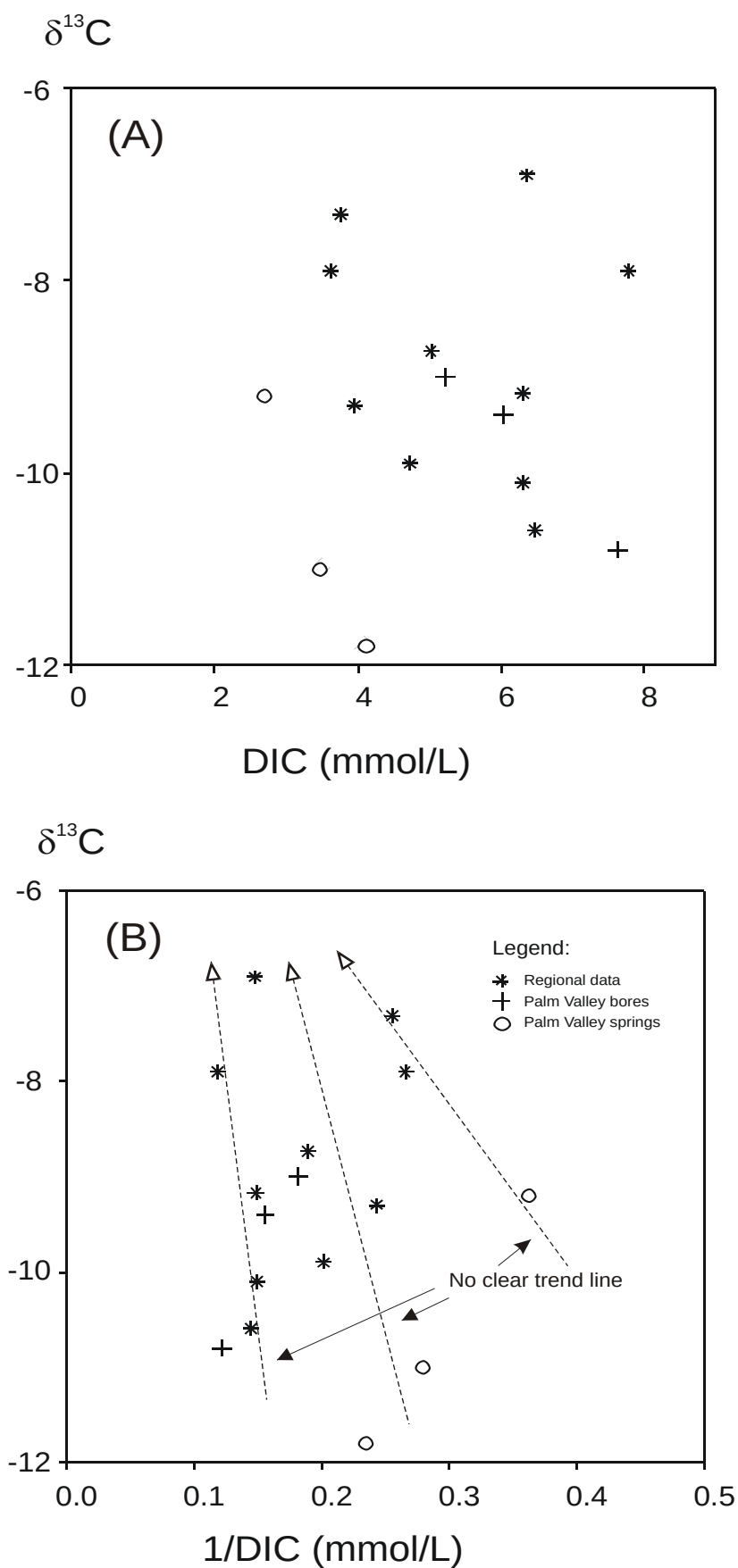


Figure 6-4 Relationship between $\delta^{13}\text{C}$ and dissolved inorganic carbon DIC. Plot (A); $\delta^{13}\text{C}$ versus DIC, (B); $\delta^{13}\text{C}$ versus 1/DIC.

The speciation capabilities of the PHREEQC (Parkhurst and Appelo, 1999) model were used to compute the dissolved inorganic carbon (DIC) carbon content of samples.

6.2.4. Results - Radiocarbon age

The results of carbon-14 and carbon-13 analyses from water samples taken from the Hermannsburg Sandstone at Palm Valley are shown in Table 6.1. The age of groundwater, as calculated using the different models discussed above, is also presented for comparison in Table 6.1. As assumptions have been used to calculate these results, the reliability of absolute ages determined is questionable. Nevertheless, comparison of relative ages is interesting in that a significant reduction in initial ^{14}C activity is indicated, particularly by the F-G model. The chemical mass balance component of the F-G model uses cation concentrations to determine the amount of matrix (^{14}C dead) derived carbonate in solution. The greater the proportion of matrix derived carbonate, the lower A_0 . Given, however, that Mg^{2+} (Eq. 5.2) and Ca^{2+} (Eq. 5.5) maybe derived from sources other than carbonate dissolution (Section 5.4), the portion of matrix-derived carbonate may be overestimated, and hence the F-G model may underestimate groundwater ages.

Furthermore, Harrington (1999) and Harrington and Herczeg, (2000, 2003) note in a study of groundwater in the Cainozoic Ti Tree sedimentary Basin (250 km north East of Palm Valley) that existing ^{14}C correction schemes may not be applicable in some arid settings. This was considered because comparison of strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) ratios in groundwater with those of local carbonate and silicate minerals indicated that a significant proportion of groundwater HCO_3^- may be derived from silicate weathering (e.g. Eqs. 5.4 and 5.5). As such a source of dead carbon is not adequately accounted for by the standard correction models, groundwater ^{14}C ages may be younger than calculated using the standard correction methods if silicate hydrolysis is significant. Given that dissolution of silicates has been identified as a possible process (Section 5.3.2.2) it may be that corrected ^{14}C ages are similarly affected in the Hermannsburg Sandstone.

Table 6.1 Radiocarbon results and corrections, Palm Valley study

SampleID	¹⁴ C (pmc)	δ ¹³ C‰ (PDB)	DIC* (mmol/L)	Uncorrected age (years)	Tamers (1967) age	Ingerson & Pearson (1964) age	Vogel (1967) age	Fontes & Garnier (1979) age
RN004508	3.1	-10.8	7.65	28716	24008	23009	27373	22819
RN010774			6.57					
RN012024	22.5	-9.4	5.84	12331	7080	5267	10987	5656
RN014165			6.73					
RN014616	4.2	-9	5.22	26206	20597	18709	24862	16966
RN014952			3.61					
PV04/200			4.01					
ROAD Sp	42.4	-11.8	4.10	7093	1667	2234	5749	modern
L PALM Sp	87.2	-9.2	2.69	1132	modern	modern	modern	modern
OASIS			3.76					
WEST Sp	79	-11	3.47	1949	modern	modern	605	modern

* DIC Dissolved inorganic Carbon calculated using PHREEQC (Pankhurst and Appelo, 1999)

Another potential complication to the results shown in Table 6.1 is the fact three of the samples are from surface water pools at springs, this may mean gaseous exchange between DIC and atmospheric CO₂ has occurred. This could then elevate the ¹⁴C activity of any “old” groundwater discharging at these springs. The fact that ¹⁴C activities at these springs are well below the current atmospheric ¹⁴C activity of > 100 pmc (Kalin, 2000) suggests at least that these springs are groundwater derived rather than ponds of recent rainfall.

It should also be noted that the two bores RN 4508 and RN14616 are at or near background ¹⁴C activities, for instance Love et al. (2000) note that < 4% (pmc) is considered the limit of detection for the direct adsorption method. Given that significant drawdown can be expected from low k aquifers (e.g. Theis, 1940), it is possible that aeration during pumping (production pumps used for sampling) has resulted in slight gaseous exchange with atmospheric CO₂. Furthermore, Walker and Cook (1991) have also noted that vertical diffusion of atmospheric ¹⁴C may increase radiocarbon activity in low recharge arid zone aquifers. Geyh (2000) also notes that diffusion of modern carbon is significant when old groundwater rises towards the surface, so much so that Pleistocene groundwater may erroneously carry a Holocene ¹⁴C signature in some instances. Thus, it may well be that groundwater at these bores is in fact older than the detectable limit of radiocarbon (>30 ka).

Given these potential shortfalls in estimating groundwater ¹⁴C ages and lack of knowledge of the exact chemical composition and process occurring, it may be better to think of the radiocarbon technique as only a semi quantitative indicator of groundwater age in the Hermannsburg Sandstone.

Apart from these considerations of absolute radiocarbon age determination, results in Table 6.1 show groundwater age may vary across, or even exceed, the whole radiocarbon detection range. Consequently, it was decided to further examine the age of groundwater using a radionuclide with a longer half-life than ¹⁴C.

7. Chlorine-36

7.1. Chlorine – 36 in the environment

7.1.1. Introduction

Chlorine-36 is an unstable isotope, production in the atmosphere is by cosmic-ray interaction, mainly with argon in the stratosphere and fallout shows a strong latitudinal dependence. The greatest atmospheric fallout occurs at mid-latitudes. The atmosphere also contains stable chloride (^{35}Cl and ^{37}Cl) derived from sea-spray, and from remobilised terrestrial salts. Chlorine-36 mixes with stable chloride in the atmosphere and this mixture of isotopes then travels the hydrologic cycle as the chloride ion. Chlorine-36 is also produced by cosmic ray interaction with near-surface rocks (epigene production) and hence may be released by weathering. Chlorine-36 is also produced in the deep subsurface (hypogene production) through neutron-capture on ^{35}Cl (the neutron flux arising from the decay of natural radioactivity), producing a low and roughly constant level of background chlorine-36 to groundwater systems (Bentley, et al., 1986a). Figure 7.1 shows a schematic of ^{36}Cl and Cl^- in the hydrological cycle which illustrates some of these processes.

The ratio of chlorine-36 to stable chloride ($^{36}\text{Cl}/\text{Cl}$) can be measured readily using accelerator mass spectrometry on a few milligrams of chloride precipitated from groundwater as silver chloride (Elmore et al., 1979) and varies in natural systems from around a thousand parts in 10^{15} of total chloride, down to a background of a few parts in 10^{15} . The fact that ^{36}Cl is radioactive and has a half life of around 300 ka means that this radio isotope offers the potential to date groundwater to over a million years (Bentley et al., 1986a). The conservative nature of the chloride ion chemistry, hence also ^{36}Cl , in groundwater suggests use of this isotope for dating old groundwater should be widely applicable (Fontes and Andrews, 1994).

Age dating groundwater with radioisotopes is based on the principle that once water reaches the saturated zone it is closed off from the atmosphere. Thus any measured radioisotope activity in groundwater that is less than atmospheric activity at the time of

recharge, can be taken to indicate radioactive decay, and can then be used to estimate groundwater age or residence time. The law of radioactive decay (as previously described in Eq. 6.4) describes the rate at which the activity of a radioisotope decreases with time. For radio chlorine this is expressed by the decay equation:

$$A_t = A_0 e^{-\lambda t} \quad (7.1)$$

where: A_t = Activity at time t , A_0 = Activity at time 0 (recharge), λ = decay constant for $^{36}\text{Cl} = 2.3028 \times 10^{-06}$.

Thus, if activity at the time of recharge (A_0) is known, measured groundwater activity can be used to compute age by rearranging the standard decay equation as;

$$t = \frac{-1}{\lambda} \left(\ln \frac{A_t}{A_0} \right) \quad (7.2)$$

where A_t is the activity for the groundwater sample, A_0 is the radioisotope activity at time of recharge, t is the period of radioactive decay in years and $1/\lambda$ is the mean life of the radioisotope ($^{36}\text{Cl} = 434,251$ yrs).

The direct application of equating groundwater age with observed radioactivity is not, however, necessarily straightforward. Some of the considerations and pitfalls of applying radioactive tracer techniques are discussed in detail in specialist texts such as Fritz and Fontes, (1986), Clark and Fritz, (1997), Mazor, (1997) and Cook and Herczeg, (2000).

For groundwater age studies using chloride-36, the amount of ^{36}Cl in the atmosphere in relation to stable chloride needs to be established at the time of recharge. Commonly the ratio of ^{36}Cl to stable chloride in rainfall ($^{36}\text{Cl}/\text{Cl}$) is assumed to represent the initial or input radioactivity of chloride-36. The determination of the natural (input) rainfall $^{36}\text{Cl}/\text{Cl}$ ratios is a major undertaking in its own right and is not yet clearly defined in all parts of the world (Phillips, 2000).

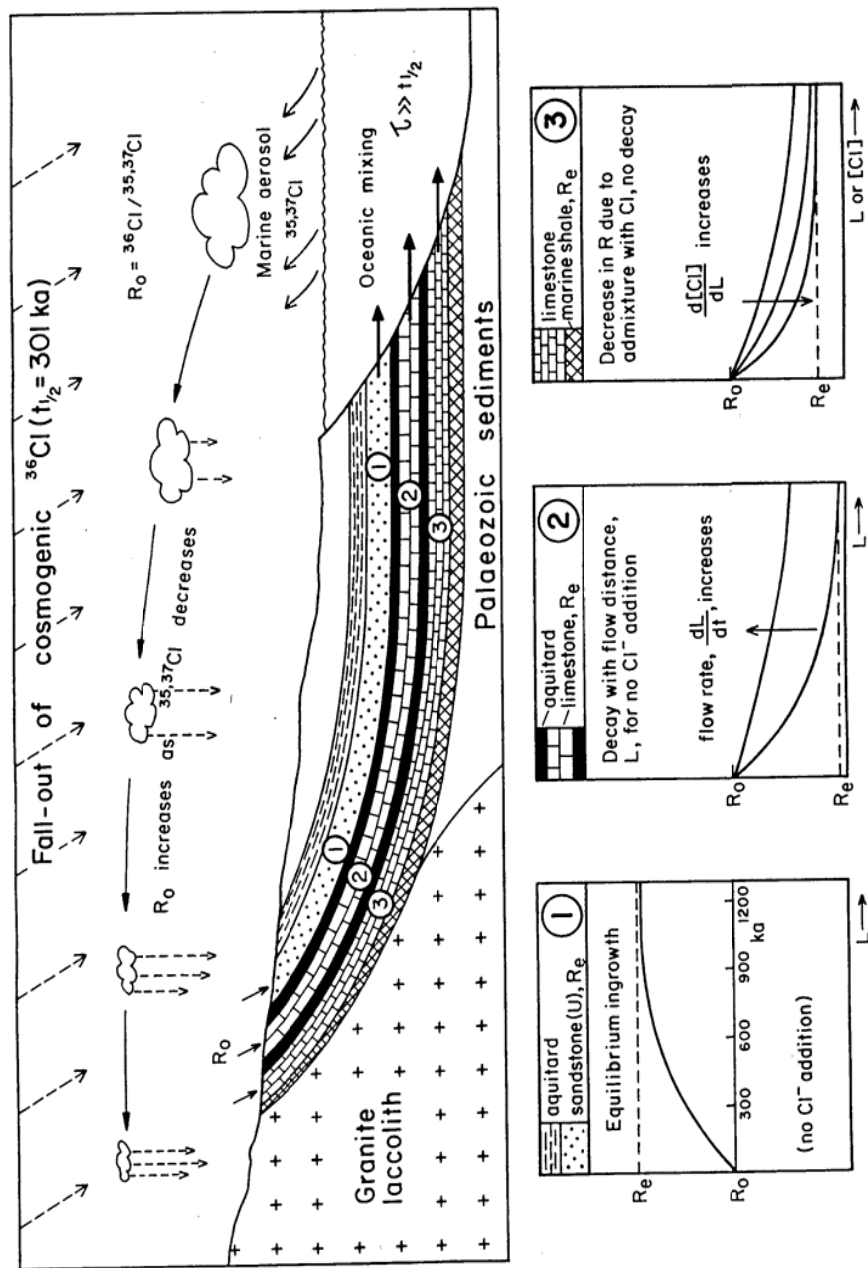


Figure 7-1 A schematic of ^{36}Cl in the hydrological cycle. Marine Cl^- is depleted in ^{36}Cl as the residence time of Cl^- in the oceans greatly exceeds the 301 ka half life of ^{36}Cl . Dilution of cosmogenic ^{36}Cl by ^{35}Cl and ^{37}Cl derived from marine aerosols decreases with distance from the coast and also varies with weather patterns. The evolution of ^{36}Cl is illustrated in 3 cases where R_0 is the input and R_e is the secular equilibrium ratio of $^{36}\text{Cl}/\text{Cl}$. Case 1 shows in situ activation of ^{36}Cl in U rich environments from neutron flux. Case 2 shows decay of the input ratio along flow paths without Cl^- addition in low U sediments. Case 3 shows the affect of subsurface addition of Cl^- on $^{36}\text{Cl}/\text{Cl}$ ratio. Note a) similarity of response in case 2 and 3 and b) Cosmogenic ^{36}Cl fallout varies with latitude and possibly hemisphere. Reprinted from Nuclear Instruments and Methods in Physics Research B, vol 92, Fontes and Andrews 1994 "Accelerator mass spectrometry in hydrology" p 367-375 © 1994 with permission from Elsevier.

Three further complexities also exist: this input ratio may have varied in response to changes in the earth's magnetic field in the past (Plummer et al., 1997). Atmospheric testing of nuclear weapons in the 1950 and 1960 produced a short lived “bomb” peak of ^{36}Cl many orders of magnitude above natural ^{36}Cl levels (Suter et al., 1987). Chlorine-36 can also be produced by subsurface nuclear reactions associated with neutron production from uranium-thorium decay; when this production is significant compared to decay concentrations of atmospheric derived Cl, interpretation of groundwater age is difficult.

Many previous ^{36}Cl groundwater studies have found evidence that chloride additions post recharge have complicated interpretation of measured $^{36}\text{Cl}/\text{Cl}$ ratios. For example dissolution of old chloride with no ^{36}Cl can lower the $^{36}\text{Cl}/\text{Cl}$ ratio of groundwater, and indicate an age greater than that derived from radioactive decay of ^{36}Cl . Given the potential complexities in calculating which mechanism is responsible for measured $^{36}\text{Cl}/\text{Cl}$ ratios, it is apparent that all sources and sinks of chloride to an aquifer should be determined and allowed for when estimating groundwater age using the ^{36}Cl decay method.

A background to the processes affecting ^{36}Cl distribution in the environment is presented below.

7.1.2. Measurement

The abundance of ^{36}Cl in the environment is very rare with activity in natural samples ranging from 1 by 10^{-16} to 1 by 10^{-10} $^{36}\text{Cl}/\text{Cl}$. Most samples, however, record $^{36}\text{Cl}/\text{Cl}$ ratios near the lower end of this range (Bentley et al., 1986a). Indeed chemical data reference texts reflect this rarity as they only list the abundances of ^{35}Cl and ^{37}Cl (at 75.5% and 24.5% respectively). The measurement of the ratio $^{36}\text{Cl}/\text{Cl}$ only became readily feasible with the advent of Accelerator Mass Spectrometry (AMS) techniques in the late 1970s (Elmore et al., 1979). The $^{36}\text{Cl}/\text{Cl}$ ratio is commonly measured in natural groundwater systems from a background level of 1 to over 1000 parts in 10^{15} of total chloride. However, fallout from atmospheric nuclear testing may result in $^{36}\text{Cl}/\text{Cl}$ ratios of over 5000 parts in 10^{15} being measured in some systems (e.g. Davis et al., 2001).

Most ^{36}Cl analyses conducted for studies in Australia are run at the Australian National University (ANU) in Canberra. This is one of the four centres in the world which routinely determine ^{36}Cl on water samples, (Phillips, 2000). Fifield et al. (1987, 1990, 1994) describe the 14 million-volt 14UD accelerator AMS system used at the ANU, Canberra, Australia. The technique involves converting a small sample (of only a few milligrams) into ions, and then accelerating these ions in the 14UD particle accelerator. As the ions emerge from the accelerator, they are separated by magnetic and electrical fields according to their mass, and then counted by various detectors (Fifield et al., 1987). Analysis of ^{36}Cl from water samples requires chloride to be precipitated out as a pure silver chloride, low in sulphur. This solid is then subjected to a beam of Cs ions which then provides the source of Cl^- ions for acceleration through the AMS, and subsequent analysis of ^{36}Cl isotope content. The ratio of chlorine-36 to total chloride is derived from the observed currents of stable Cl ion beams and the counting rate of ^{36}Cl ions measured at a detector (Fifield et al., 1987).

By convention, this ratio is reported as $^{36}\text{Cl}/\text{Cl}$ by 10^{-15} which give values from 0 to several thousand for the amount of ^{36}Cl typically found in the environment. Fifield et al. (1994) note that repeat measurements on reference standards show system variations contribute at most a 2% standard deviation to $^{36}\text{Cl}/\text{Cl}$ ratios determined at the Australian National University AMS. When total chloride content of the water sample is determined separately by standard analytical techniques such as titration by silver nitrate with potassium chromate indicator (APHA, 1998) or ion chromatography, the number of ^{36}Cl atoms per litre can also be calculated:

$$\frac{^{36}\text{Cl}}{\text{Cl}} \times m\text{Cl} \times A^o = ^{36}\text{Cl atoms per litre} \quad (7.3)$$

where; $^{36}\text{Cl}/\text{Cl}$ is the ratio determined by AMS, $m\text{Cl}$ is the number of moles of Cl^- determined by standard analytical techniques, A^o is Avogadro's number i.e. around 6.022×10^{23} . This concentration of ^{36}Cl is often multiplied by a factor of 10^7 to give values between 0 and 100 (Clark and Fritz, 1997).

It is common practice to report results as both the $^{36}\text{Cl}/\text{Cl}$ ratio measured by AMS and as the number of ^{36}Cl atoms per litre calculated. This is because different processes can

be examined by each result. For example when comparing waters that have undergone differing amounts of evaporation the $^{36}\text{Cl}/\text{Cl}$ ratio does not change during concentration by evaporation whereas the concentration of ^{36}Cl atoms will (Clark and Fritz, 1997).

The relationship between ^{36}Cl atoms, $^{36}\text{Cl}/\text{Cl}$ and total Cl varies for different processes that may affect groundwater. The effect of various processes on ^{36}Cl and Cl levels is shown for various combinations of these parameters on the charts presented in Figure 7.2. Many ^{36}Cl decay dating studies report results in a similar format to one or more of these charts.

7.1.3. ^{36}Cl production

7.1.3.1. Atmospheric fallout

Chlorine-36 is formed in the atmosphere by spallation reactions of atmospheric gases with cosmic radiation. The spallation reaction of ^{40}Ar is the most important reaction;



Where: p = proton, n = neutron and α = alpha particle.

The neutron activation reaction of ^{36}Ar to produce ^{36}Cl was once thought to contribute around 33% of ^{36}Cl production in the atmosphere (Bentley et al., 1986a). However, subsequent studies cited by Andrews and Fontes (1992) have since shown negligible ^{36}Cl is produced by this reaction;



Where n = neutron; p = proton.

Most (>60%) of the atmospheric ^{36}Cl is produced by spallation in the stratosphere (i.e. the layer of atmosphere above about 12 km from the surface of the Earth at mid latitudes) with the rest produced by spallation in the underlying troposphere layer.

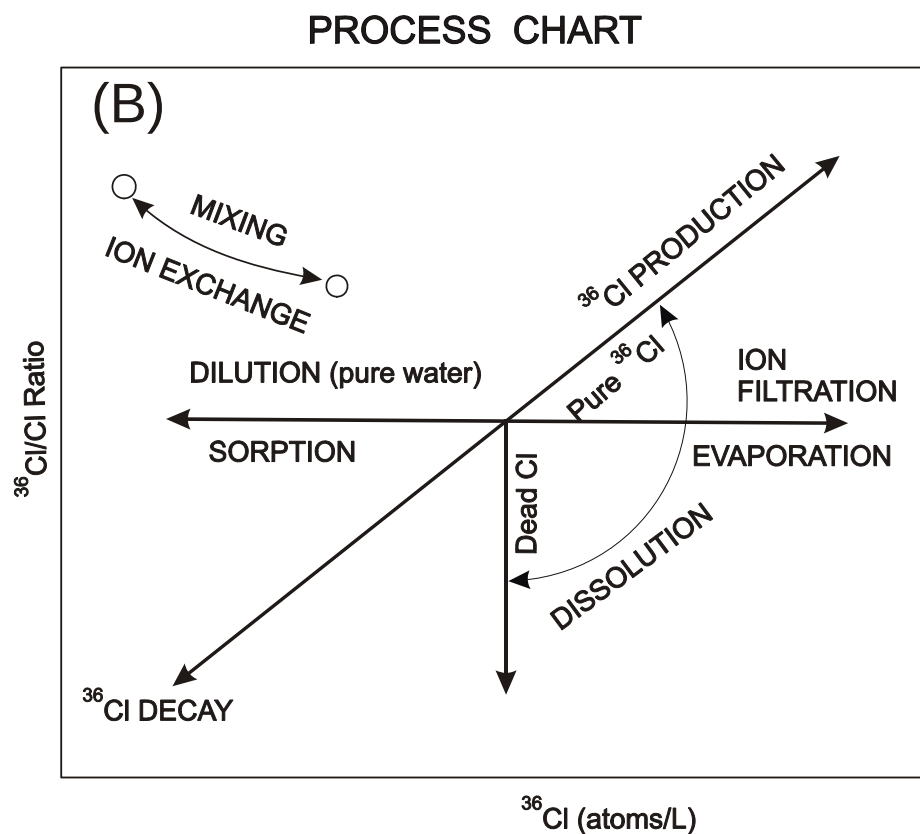
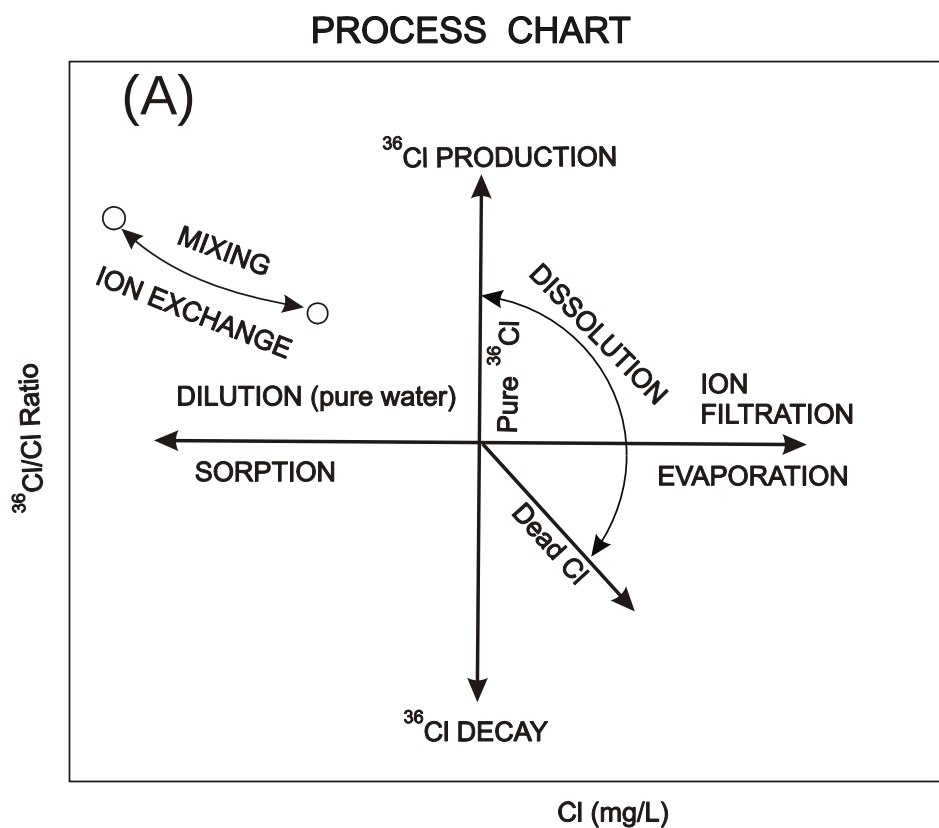


Figure 7-2 The affect of various processes on ^{36}Cl and Cl^- levels illustrated by a) $^{36}\text{Cl}/\text{Cl}$ versus Cl^- and b) $^{36}\text{Cl}/\text{Cl}$ versus ^{36}Cl atoms. After Bird et al., 1991.

Variability in the Earth's magnetic field, hence also variability in cosmic radiation shielding efficiency, means spallation production of ^{36}Cl varies in relation to geomagnetic latitude within the stratosphere (Fontes and Andrews, 1994).

Due to various atmospheric circulation processes and seasonal adjustments of troposphere thickness, much of the air mass in the stratosphere transfers to the troposphere at mid ($35\text{--}40^\circ$) latitudes (Keywood, 1995; Hainsworth et al., 1994). As a result, the ^{36}Cl formed in the stratosphere mixes with aerosols comprised of marine (and terrestrial) derived Cl along with ^{36}Cl produced in the troposphere. These aerosols only survive in the atmosphere for about a week (Andrews and Fontes, 1992) and then fall out as either dry or wet (rain) deposition to the surface of the Earth.

Consideration of these factors of spallation rate, latitude dependence and likely atmospheric circulation, has allowed charts showing expected ^{36}Cl fallout in $\text{atoms m}^{-2} \text{ s}^{-1}$ to be plotted against latitude. The initial latitude dependence of ^{36}Cl fallout was determined by Lal and Peters (1967). This estimate was then altered (Bentley et al., 1986a) to incorporate possible additional ^{36}Cl production in the atmosphere. Andrews and Fontes (1992), on consideration of subsequent research showing a lack of evidence for ^{36}Ar neutron activation reactions (Eq. 7.5) in the atmosphere, reinstated the Lal and Peters model.

Andrews and Fontes (1992) show ^{36}Cl fallout latitude dependency as symmetrical for both hemispheres – ranging from a maximum of $20 \text{ atoms m}^{-2} \text{ s}^{-1}$ at mid latitudes to less than $5 \text{ atoms m}^{-2} \text{ s}^{-1}$ at the poles and equator. The mean ^{36}Cl fallout is computed as $11 \text{ atoms m}^{-2} \text{ s}^{-1}$.

As marine Cl has negligible ^{36}Cl activity (Fontes and Andrews, 1994) and terrestrially derived Cl usually has low ^{36}Cl activity, the ratio of ^{36}Cl ions to stable Cl ions in precipitation is largely determined by the ratio of cosmogenic ^{36}Cl to marine and terrestrial derived Cl (Davie et al., 1989). Near the coast, precipitation contains a large amount of marine Cl; however, because of fallout (dry and wet) with some modification due to prevailing wind and orographic effects (Bentley et al., 1986a), the amount of chloride in rain decreases markedly with distance inland (Hutton, 1976). The fallout of ^{36}Cl is superimposed on this pattern (see Fig. 7.1) with only a latitude effect (Bentley et

al., 1986a). Consequently, at a given latitude, a lower rain $^{36}\text{Cl}/\text{Cl}$ is expected at continental margins than in continental interiors. By combining an estimate of latitude dependant ^{36}Cl fallout with records of stable chloride content of rainfall, Bentley et al. (1986a) predicted the long-term average $^{36}\text{Cl}/\text{Cl}$ in atmospheric fallout across the USA.

Later studies of ^{36}Cl in rainfall in the USA and Australia (Hainsworth et al, 1994; Keywood, 1995; Keywood et al., 1998) found that the predictions of Lal and Peters (1967) underestimated recorded ^{36}Cl fallout to the Earth. Consequently, Hainsworth et al. (1994) note the initial prediction of $^{36}\text{Cl}/\text{Cl}$ fallout variation across the USA by Bentley et al. (1986a) based on Lal and Peters (1967) work is also likely an underestimate of ^{36}Cl fallout in some regions. Keywood (1995) proposed that the estimates of Lal and Peters should be multiplied by a factor 1.47 in the southern hemisphere. Phillips (2000) synthesised data from the USA and Australia (Keywood's 1998 data) to produce a new estimate of ^{36}Cl latitude dependent fallout. In contrast to previous studies, Phillips (2000) estimates ^{36}Cl fallout latitude dependency to range from a maximum of about $50 \text{ atoms m}^{-2} \text{ s}^{-1}$ at mid latitudes down to around $10 \text{ atoms m}^{-2} \text{ s}^{-1}$ at the poles. Phillips (2000) and Keywood (1995) both estimate the mean fallout to the surface of the earth to be around $30 \text{ atoms m}^{-2} \text{ s}^{-1}$. The reasons for ^{36}Cl fallout being higher than the earlier estimates is unknown, though various explanations such as the existence of unidentified additional ^{36}Cl atmospheric production reactions are speculated upon by Phillips (2000) and Keywood, (1995).

Keywood et al. (1998), on comparing the smaller fallout rates recorded in Australia than those in published USA data sets, note that fallout of ^{36}Cl may well be asymmetric about the two hemispheres, as was the case for ^{90}Sr fallout from surface weapons testing. Unfortunately, direct comparison between hemispheres is not possible, as very little overlap of sample collection latitude exists. The possibility that, if bomb derived ^{36}Cl is still retained in the biosphere (e.g. Milton et al., 1997; Cornett et al., 1997), it is more likely to occur in the northern hemisphere, is another feasible reason proposed by Keywood et al. (1998) to explain the observed skewness of ^{36}Cl fallout between hemispheres. Moreover, analyses of rain and dry Cl fallout from composite annual samples collected from 28 meteorological stations around the world (Blinov et al (2000); Scheffel et al., 1999) have also shown ^{36}Cl fallout to be higher than predicted.

The possibility that bomb derived ^{36}Cl is still circulating in the atmosphere is the explanation of elevated ^{36}Cl fallout preferred by these authors.

While these calculations of ^{36}Cl fallout infer a constant rate at a given latitude, actual results of methodical rainfall monitoring undertaken in Australia (Keywood, 1995, 1998) and USA (Kniess et al., 1994; Hainsworth et al., 1994) have shown significant seasonal variations in fallout at any one field site. Furthermore, Kniess et al. (1994) record ^{36}Cl concentrations to vary even during the one rainfall event. Keywood et al. (1998) noted only a weak correlation between ^{36}Cl fallout and rainfall amount in Australia in contrast to stronger correlation noted by Kniess et al (1994) in the wetter less variable rainfall climate of Indiana, USA.

The fallout rate is an important parameter to measure for hydrological studies. For instance, in the absence of nearby rainfall monitoring of ^{36}Cl content (as is usually the case) estimates of ^{36}Cl fallout are combined with best knowledge of total stable chloride fallout (estimate of dry fallout and Cl content of rainfall) to calculate the likely input $^{36}\text{Cl}/\text{Cl}$ ratio of any groundwater recharge. Dry fallout, which in general terms can be expected to mix with subsequent rain and contribute to recharge, is estimated to represent < 50% of Cl fallout by Keywood (1995), and < 30% by Hainsworth et al. (1994).

Other local studies of ^{36}Cl in precipitation have been conducted in some other parts of the world. Herut et al. (1992) report that ^{36}Cl determinations from high Cl rainfall events in Israel indicate a significant terrestrial derived Cl source for these events. Magaritz et al. (1990) use a $^{36}\text{Cl}/\text{Cl}$ determination from snow on a mountain in Jordan to determine likely precipitation ^{36}Cl content in this region. Finkel et al. (1980) report on ^{36}Cl determinations from Antarctic surface ice.

Phillips (2000), notwithstanding the documented variations in ^{36}Cl fallout observed between hemispheres, seasons and rain events, has used selected northern hemisphere data sets to derive a precipitation ^{36}Cl deposition correlation, normalised for latitude and a mean latitude precipitation rate. This correlation is used to update the work of Bentley et al. (1986a) and construct a new map of $^{36}\text{Cl}/\text{Cl}$ ratio of meteoric deposition across the USA. Interestingly, when data typical of Alice Springs, central Australia (chloride

concentration of rain $0.6 \mu\text{eq/l}$, mean rain of 250 mm yr^{-1} , latitude of 22° S ; Keywood et al., 1997, 1998) are used in Phillips (2000) correlation equation, the meteoric deposition $^{36}\text{Cl}/\text{Cl}$ ratio calculated is about $300 \text{ by } 10^{-15}$. This is comparable to the mean $^{36}\text{Cl}/\text{Cl}$ ratios calculated from two years of rain and dry fallout observations in this region by Keywood (1995).

The use of annual average assumptions commonly applied for hydrologic assessments in temperate zones should only be employed with caution in arid areas, given the spatial and temporal variation of rainfall in arid areas (e.g. Lerner et al., 1990). This implies a long term assessment (decades) of atmospheric fallout may be necessary to delineate the possible range of $^{36}\text{Cl}/\text{Cl}$ ratios in rainfall. For instance Ambroggi (1977) postulates unusually heavy rain events may only be expected once every fifteen years in arid regions. Such events may be crucial sources of replenishment to arid zone aquifers. Thus, unless a considerable period of monitoring is undertaken, the $^{36}\text{Cl}/\text{Cl}$ ratios of some significant hydrologic events may go unrecorded. This dilemma is demonstrated by Keywood's (1995) work where the period of sample collection in central Australia (1992 – 1994) was unremarkable in that annual rainfall was within 150 mm of the mean. By contrast during the “big” wet years of 1974 and 2000 annual rainfall was more than five times the mean (www.bom.gov.au). Due to the likelihood of significant recharge for some arid area aquifers during these unusually wet years, it is probable that a more accurate determination of likely groundwater input $^{36}\text{Cl}/\text{Cl}$ ratios would have been obtained if assessment of atmospheric ^{36}Cl fallout had occurred during “big” wet years. Such considerations are common to all aspects of hydrological assessment in arid areas (Lerner et al., 1990), hence the need to heed the caution of using average annual assumptions (unfortunately often the only available data) when assessing hydrological data in arid zones.

Natural fallout of ^{36}Cl is still being defined. Recent data collected from both hemispheres seems to indicate that the rate of ^{36}Cl fallout to Earth is higher than predicted by Lal and Peters (1967). The reasons for this disparity between theoretical and recorded fallout rates are yet to be determined.

7.1.3.2. Changes in fallout rate in the past

Bird et al. (1991) note that because of the long half life, changes in the past affecting ^{36}Cl concentrations such as unknown variation in cosmic ray flux or climate could affect the accuracy of any radio chlorine determined age. Earlier ^{36}Cl groundwater studies (e.g. Bentley et al., 1986b) did not consider past variation in ^{36}Cl atmospheric production. More recently Plummer et al. (1997) calibrated ^{36}Cl data from fossil pack rat middens with ^{14}C data and concluded that atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios dropped markedly at the start of the Holocene in semi arid inland U.S.A. This variation is thought to arise from recorded changes in the earth's magnetic field strength. When the earth's magnetic field is stronger, more cosmogenic energy is deflected and ^{36}Cl production is less (i.e. atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios are likely to be less during periods of higher magnetic field strength). At the around start of the Holocene, field strength rose to around current levels after a long period (>10 ka) of lower mean field strength (Tric et al., 1991; Guyodo and Valet, 1999). Thus, pre Holocene atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios are expected to have been up to 50% higher than present levels at mid latitudes (Plummer et al., 1997).

While Plummer et al. (1997) also postulate that one possible cause of this past atmospheric $^{36}\text{Cl}/\text{Cl}$ variation is climate change affecting atmospheric circulation and hence latitude dependence of ^{36}Cl fallout rate (Section 7.1.3.1), both Davis et al. (1998a) and Phillips (2000) consider that past variation in the earth's magnetic field to be the most significant influence on cosmogenic ^{36}Cl production. This conclusion is partly based on the fact that detailed independently dated ^{14}C measurements show radiocarbon activity (which is not latitude dependent) in the atmosphere 25 ka was almost double that of modern times and that the pattern of ^{14}C variation with time seems to correlate with reconstructions of past magnetic field variation (Phillips, 2000). However, a detailed study of ^{14}C concentration calibrated against a ^{230}Th chronology in a stalagmite by Beck et al. (2001) concluded that the variation in the ^{14}C record cannot be accounted for by modulations of the earth's magnetic field alone, and suggest that substantial fluctuations in the carbon cycle must also have occurred over the last 45 ka.

Given this evidence for a climate change effect, in addition to the geomagnetic influence on cosmogenic nucleide production, exact reconstruction of past fluctuations

of ^{36}Cl production in the atmosphere may be difficult. Nevertheless Davis et al. (1998a) use the geomagnetic palaeo-intensity data of Tric et al. (1991) to construct a diagram showing relative production rate of atmospheric ^{36}Cl over the last 80 ka. This diagram is reproduced in Figure 7.3 where it can be seen that the major past deviations from current conditions have been periods of increased atmospheric ^{36}Cl production rates. In keeping with this pattern Guyodo and Valet (1999), in a study of the relative intensity of the earth's magnetic field, note that many intensity lows have occurred over the last 800 ka. Modern magnetic intensity is then apparently at around the maximum field intensity recorded for this period, as seen in Figure 7.4 which shows Guyodo and Valet's (1999) work. Given the above data, and relying on earth's magnetic field intensity as the major control on ^{36}Cl production, it would seem unlikely that atmospheric ^{36}Cl levels were ever significantly lower than current levels during the Pleistocene. Thus, ^{36}Cl decay dating of groundwater is only likely to underestimate groundwater age if past fluctuations in atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios at the time of recharge are unknown. Given these past fluctuations, however, there is a potential discrepancy where two groundwater samples, recharged 10 ka apart, may have markedly different $^{36}\text{Cl}/\text{Cl}$ ratios. In recognition of this and other potential complications such as bomb pulse ^{36}Cl contamination Davis et al. (1998a) recommend a suite of complementary analyses when assessing shallow groundwater ^{36}Cl values. These and other considerations are discussed in Section 7.1.4 below.

7.1.3.3. Epigene production

Production of ^{36}Cl by cosmogenic reactions also occurs in the upper few metres of the earth's crust and oceans. As argon is not abundant here, the main production reactions (Phillips et al., 1986a) are from spallation of K and Ca by energetic secondary neutrons and thermal neutron activation of ^{35}Cl :



Where n = neutron; p = proton; α = alpha particle; γ = gamma radiation, (Clark and Fritz, 1997).

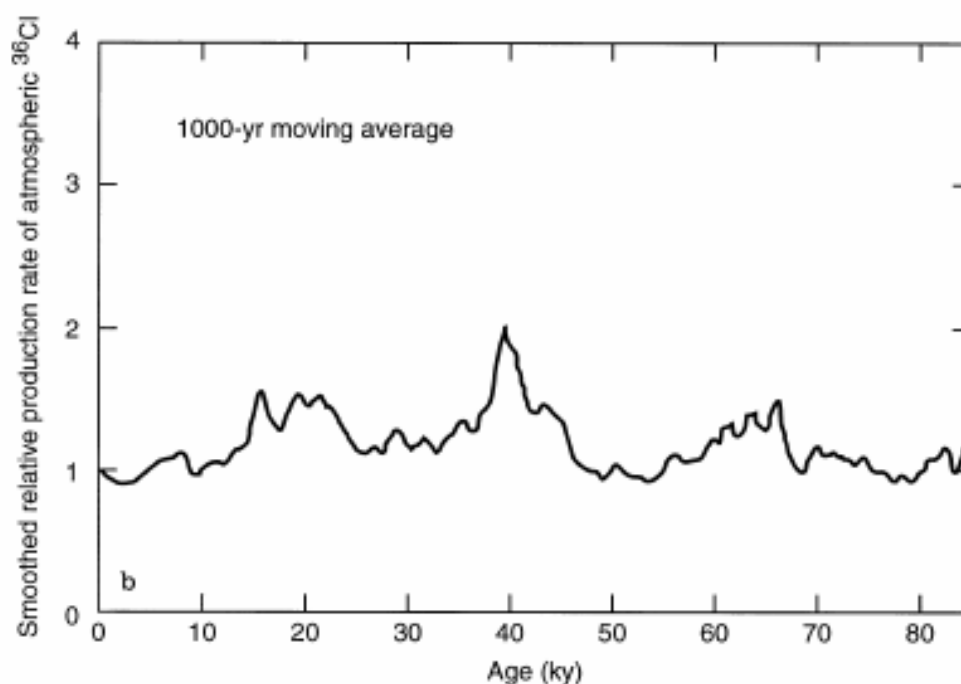


Figure 7-3 Relative production rate of atmospheric ^{36}Cl over the last 80 ka. Reproduced from Davis et al., 1998a with kind permission of Springer Science and Business Media. Original data from Tric et al., 1991.

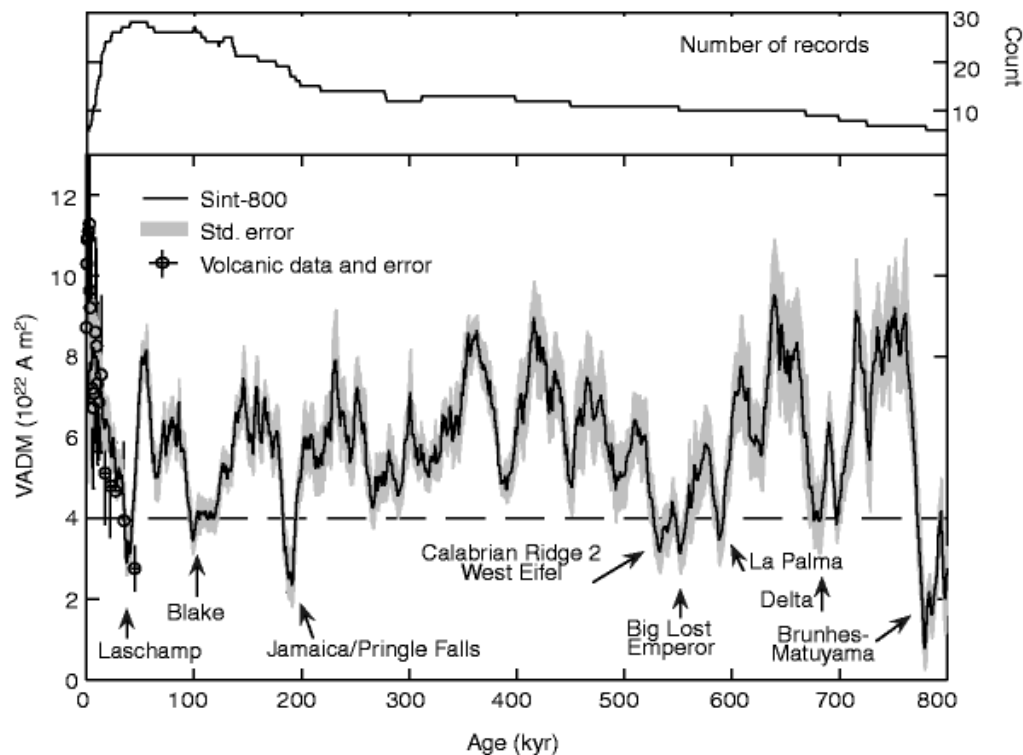


Figure 7-4 Variation of Earth's Magnetic field strength over last 800 ka. Note magnetic field (VADM) has never been higher than at present – hence atmospheric fallout ^{36}Cl is unlikely to have been lower than at present during the last 800 ka. Reprinted by permission from Macmillan Publishers Ltd: Nature, Guyodo and Valet, 1999. © 1999.

Andrews and Fontes (1992) calculated the equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio in the topmost metres of the ocean from epigene production would be 1300×10^{-15} , however, with the oceanic circulation of ^{36}Cl dead chloride from deep old waters continuously mixing with near surface chloride, the $^{36}\text{Cl}/\text{Cl}$ ratio of the oceans is actually $< 4.2 \times 10^{-15}$. Fallout of atmospherically produced ^{36}Cl to the oceans is similarly diluted.

On the land, ^{36}Cl from cosmic ray processes builds up as soon as a rock is exposed at the surface. Eventually the $^{36}\text{Cl}/\text{Cl}$ ratio will attain a secular equilibrium with the production rate and the ^{36}Cl half-life (i.e. the exposed rock accumulates ^{36}Cl until the rate of ^{36}Cl decay, which increases with the number of ^{36}Cl atoms, equals the rate of production, Phillips et al., 1986a). If the chemical composition of the rock and its altitude are known, it is possible to calculate the secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio (Bentley et al., 1986a). If a rock were suddenly exposed at the surface (eg. basalt) secular equilibrium is not reached until around 1 Ma, thus ^{36}Cl accretion information can be useful as geological dating tool in the 1 to 500 ka range (Bentley et al., 1986a). As most rocks are exposed at the surface by erosion and epigene ^{36}Cl production is rapidly attenuated with depth, most rocks do not reach a secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio. If the erosion rate is fairly constant, it is possible calculate erosion rates from the amount of cosmic-ray produced ^{36}Cl build-up (Bentley et al., 1986a). Gosse and Phillips (2001) give a detailed account of surface exposure dating methods using multi terrestrial in situ cosmogenic nucleides and Phillips et al. (2001) present improved methods for calculating neutron flux in the epigene.

The potential effect of ^{36}Cl epigene production on groundwater $^{36}\text{Cl}/\text{Cl}$ ratios has been considered by a number of workers. Andrews et al. (1991) note the theoretical epigene secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio at 1m depth for the sandstone at Milk River, Canada to be in the order of $16,000 \times 10^{-15}$, and speculate that epigene produced ^{36}Cl may explain high $^{36}\text{Cl}/\text{Cl}$ found in this aquifer. Andrews and Fontes (1992) note that in arid zones much chloride may exist at shallow depths due to evapotranspiration processes and thus a potential source of mobile epigene ^{36}Cl may complicate hydrological applications of ^{36}Cl in these regions. Fontes and Andrews (1993) calculated a 0.3 m deep brine with $\text{Cl} = 60,000 \text{ mg/l}$ and stream water with 7 mg/l of Cl at 0.3 m to have theoretical epigene secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratios of 105 and 7800×10^{-15} respectively. Interestingly the rates of increase in $^{36}\text{Cl}/\text{Cl}$ ratios as a result of epigene production were calculated to be

modest at only 0.24 ka for the brine and 18 ka for the stream water. As epigene ^{36}Cl production takes many thousands of years to build up, and water flux through the upper few metres of subsurface is comparatively usually much more rapid, it seems unlikely that epigene ^{36}Cl production would affect many shallow groundwater systems. Furthermore, bomb peak ^{36}Cl horizons are found in the unsaturated zone in many localities (Section 7.1.3.5) including arid zones (e.g. Liu et al., 1995). This suggests that epigene production, which theoretically produces more ^{36}Cl than bomb peak fallout given sufficient time (Andrews et al., 1991), is not readily discernible at many locations.

Phillips et al. (1986a) note that as epigene ^{36}Cl is created by cosmic ray reactions largely within mineral grains that must be released by weathering before entering groundwater, epigene production is rarely likely to affect groundwater $^{36}\text{Cl}/\text{Cl}$ ratios. Furthermore, Phillips (2000) calculates the annual release of in situ cosmogenic produced ^{36}Cl from most rock types, under high and moderate weathering rates, to be extremely small. Carbonate rocks, due to greater susceptibility to weathering, are likely to release the most ^{36}Cl . As cosmogenic ^{36}Cl production increases with altitude, all rock types other than sandstone were shown to begin to have appreciable release when above 2 km in altitude. Based on these calculations Phillips (2000) concludes that except at high mountain elevations ^{36}Cl released by weathering from most rock types will be insignificant in comparison to meteoric input. Davis et al. (1998a) also doubt that epigene production would normally affect to any significant degree the input ratio of $^{36}\text{Cl}/\text{Cl}$ in groundwater systems.

Given these considerations, it seems that while epigene production can theoretically produce high $^{36}\text{Cl}/\text{Cl}$ ratios in shallow subsurface rocks and water, the rate of build-up and release is so slow when compared to the flux of water that the effects of epigene ^{36}Cl production can usually be disregarded for groundwater studies.

7.1.3.4. Hypogene production

Chlorine-36 is also produced in the deep subsurface through neutron-capture on ^{35}Cl , the neutron flux arising from the decay of natural radioactivity producing a low, and roughly constant level of background chlorine-36 to groundwater systems (Bentley, et al., 1986a).

Fontes and Andrews, (1994) note that α particle emissions by U and Th and their decay products in rocks produces ^{36}Cl by way of the reactions:



Of these two reactions the thermal neutron activation of ^{35}Cl is by far the most significant. Consequently, subsurface production rate of ^{36}Cl is usually proportional to Cl^- concentration. Therefore, hypogene ^{36}Cl production is usually expressed as the $^{36}\text{Cl}/\text{Cl}$ ratio at secular equilibrium (R_{se}) with subsurface neutron flux, and not as the number of ^{36}Cl atoms produced per unit volume per unit time (Phillips, 2000).

Hypogene production reaches 97% of equilibrium after 5 half-lives of ^{36}Cl , about 1.5 Ma (Fontes and Andrews, 1994). The equilibrium rate is usually much less than atmospheric rates unless a very high source of radioactivity, such as a uranium ore body, is present. .

Generally, at depths below the influence of cosmogenic radiation, the maximum R_{se} expected is about 50×10^{-15} (Phillips, 2000). Bentley et al. (1986a) outline a method of calculation for R_{se} and note that apart from needing to know the rock density, porosity and chloride concentration of groundwater, the calculation of the neutron flux derived from natural radioactivity is difficult. The method presented by Feige et al. (1968) is commonly used to estimate neutron flux (e.g. Phillips, 2000, Andrews and Fontes, 1992, Bentley et al., 1986a). Bentley et al., (1986b) note that hypogene production is a factor to consider if determining absolute groundwater age by way of the equation:

$$t = \frac{-1}{\lambda_{36}} \ln \frac{R - R_{\text{se}}}{R_0 - R_{\text{se}}} \quad (7.11)$$

where t is time, λ_{36} is the decay constant of ^{36}Cl , R is the measured $^{36}\text{Cl}/\text{Cl}$ ratio, R_0 the initial $^{36}\text{Cl}/\text{Cl}$ ratio, and R_{se} the secular equilibrium due to hypogene production.

From this equation, hypogene production can be seen to be an important factor for determining groundwater ages, particularly in very old groundwater where hypogene production of ^{36}Cl may approach the level of ^{36}Cl activity left after decay of initial atmospheric ^{36}Cl .

Fontes and Andrews (1994) tabulated the hypogene production R_{se} for various rock types, as calculated from published average US rock analyses. R_{se} for common rock types; basalt, granite, sandstone, limestone and clay/shale are calculated as 6.9, 28.3, 2.1, 8.8 and 2.1 by 10^{-15} respectively. Bentley et al., (1986a) give guideline averages of 30×10^{-15} for granites, 10×10^{-15} for shales and limestones and 5×10^{-15} for sandstones and basalts. These values give an indication of the groundwater $^{36}\text{Cl}/\text{Cl}$ ratio in various systems that can be approached before ^{36}Cl groundwater dating is implausible. Addition of chloride along flow lines in an aquifer by leakage from aquitards, subsurface brines or mixing with another groundwater of unknown Cl^- concentration can complicate interpretation of hypogene content and hence also groundwater dating. Such situations seem common as outlined in Chapter 8 below.

Conversely, in high U and Th host rocks such as uranium ores or some granites the R_{se} can be very high. For example Fabryka-Martin et al. (1987) report very high $^{36}\text{Cl}/\text{Cl}$ ratios in some groundwaters (up to > 1700 by 10^{-15}) around the Alligator River Uranium Ore Province in the Northern Territory (NT) of Australia. Songsheng et al. (1994) also report on high $^{36}\text{Cl}/\text{Cl}$ ratios in groundwater (up to 1200 by 10^{-15}) around a uranium ore body in China.

High levels of ^{36}Cl production associated with granites are reported from Sweden (Andrews et al., 1986; Mahara et al., 2001) and Canada (Gascoyne et al., 1994). Lehman and Loosli (1990) report on hypogene production from various lithology types in northern Switzerland. In these instances hypogene production is greater than atmospheric sources of ^{36}Cl and groundwater dating by way of ^{36}Cl decay is not possible. Fontes and Andrews (1994) and Andrews and Fontes (1992) note, however, that dating may sometimes be possible by determining the amount of ^{36}Cl ingrowth before secular equilibrium is obtained. This situation, with no Cl^- addition, is illustrated in Figure 7.1.

The use of discordance between calculated subsurface equilibrium ratios and measured values in samples to calculate water residence time (ingrowth method of Fontes and Andrews, 1994) is the usual method of dating geothermal systems (Phillips, 2000). For example, Aquilina et al. (2002), in a study on the origin of thermal springs in southern France, make a rough (order of magnitude) estimate of geothermal groundwater age (200 ka) by assuming that the ingrowth of hypogene ^{36}Cl (assumed secular equilibrium of 11×10^{-15}) has raised the deep aquifer $^{36}\text{Cl}/\text{Cl}$ ratio above the input sea water ratio (i.e. $\approx 0 \times 10^{-15}$). Fehn et al. (1994) make preliminary age estimates of very deep (> 1.8 km) groundwater in Germany and California, USA by considering the amount of likely subsurface production of ^{36}Cl in each region.

Lippmann et al. (2003) consider the high ^{36}Cl concentrations of groundwater sampled in ultra deep mines (>0.7 km) in South Africa to indicate subsurface ^{36}Cl production is at secular equilibrium and thus groundwater is assumed to be at least 1.5 Ma (5 times λ ^{36}Cl). This conclusion is confirmed by complementary noble gas data that show groundwater to be very old (range 1 – 100 Ma).

Phillips (2000) notes ^{36}Cl is also useful to distinguish the source of the Cl in geothermal systems. For example Balderer and Synal (1996), on the basis of ^{36}Cl results and complementary geological data, speculate that at the Tulza geothermal area of Turkey tectonic processes are squeezing brine from Aegean Basin sediments through crystalline basement faults, where the brines are heated before rising and mixing with low salinity shallow groundwater in overlying volcanics. A similarly complex source of chlorides is derived from ^{36}Cl data for the hydrothermal fluids in the Valles caldera in New Mexico, USA by Rao et al. (1996). They propose that brines are derived from meteoric waters that travelled through Precambrian basement and Palaeozoic strata leaching chloride before reaching the intra-caldera volcanic suite via convective up-welling. Some low chloride, high $^{36}\text{Cl}/\text{Cl}$ groundwaters of recent meteoric origin are also distinguishable at this caldera.

Recent work by Chimiel et al. (2003) has shown rocks such as carbonaceous shales, coals, phosphorites and granites/pegmatites can concentrate high levels of uranium and may consequently have significant in situ ^{36}Cl production when compared to atmospheric sources of ^{36}Cl .

Consequently, on the basis of the above discussion, it appears that unless measured $^{36}\text{Cl}/\text{Cl}$ approaches expected R_{se} values and/or exceptionally high rock U and Th values are suspected, ^{36}Cl groundwater dating should be possible in systems with consistent chloride concentrations. If R_{se} is unknown then an approximation of age may be made, assuming R_{se} to be small or negligible.

7.1.3.5. Anthropogenic sources

7.1.3.5.1. Bomb Peak

The advent of nuclear technology has resulted in an anthropogenic component of radioactive nuclides now being present in the environment. Surface testing of thermonuclear weapons in the 1950s and 60s released many radioactive nuclides into the environment (Bentley et al., 1982). The production of ^{36}Cl occurred during these events because ^{35}Cl has a large thermal neutron capture cross section and free neutrons are easily absorbed (see Eq. 7.6). Consequently, the nuclear testing on barges in the sea (i.e. irradiation of seawater ^{35}Cl) near Bikini and Eniwetok atolls in the Pacific between 1952 and 1958 resulted in a large amount of ^{36}Cl being released into the atmosphere (Phillips, 2000).

The actual amounts of ^{36}Cl released from these tests have been calculated by Synal et al. (1990). Fallout of ^{36}Cl from these tests was recorded in precipitation by Schaeffer et al. (1960). Measurement of ^{36}Cl in shallow ice cores from Dye-3 in Greenland has provided a record of this “bomb peak” or pulse (Elmore et al., 1982; Suter et al., 1987; Synal et al., 1990). The results from three separate cores near Dye-3 show a peak in the late 1950s of 500 to 1000 times the expected cosmogenic ^{36}Cl production. (Synal et al., 1990). These data are interpreted to show that ^{36}Cl fallout had returned to natural levels by around 1985. In keeping with this interpretation, Vogt et al. (1994) concluded no bomb ^{36}Cl was present in precipitation samples they analysed from Indiana in the USA.

The distribution of the bomb peak ^{36}Cl fallout from these tests near the equator was assumed by Bentley et al. (1986a) to be equally dispersed about the hemispheres. This

interpretation was backed up by cited data (Lockhart, 1959), which shows ^{185}W fallout from some of these tests to be equally distributed in northern and southern hemispheres.

Conversely, Keywood et al. (1998) cite ^{90}Sr fallout data (Machta and List, 1959) that shows fallout from these tests was four times greater in the northern hemisphere than the southern. This asymmetry is also noted to apply to aerosols and ozone and is attributed to the different topography of the northern hemisphere land masses causing a much more turbulent troposphere, which then results in greater troposphere – stratosphere transfer in the northern hemisphere (Keywood et al., 1998).

The worldwide peak of ^{36}Cl injected into the atmosphere from the thermonuclear weapons testing programs of the 1950s and 1960s is of potential benefit to hydrological studies as it provides a readily detectable tracer (Bentley et al., 1986a). This is particularly so as bomb peak tritium (half life of only 12.4 years) has largely decayed to modern rain levels in the subsurface, which has virtually rendered bomb tritium an ineffective tracer in the southern and most of the northern hemisphere (Hendrickx and Walker, 1997). Phillips (2000) notes that the advent of chlorofluorocarbon (CFC) and tritium/helium 3 techniques to study modern water has probably resulted in bomb ^{36}Cl being under utilised as a tracer. Nevertheless, Bomb Peak ^{36}Cl has been used as a tracer for various hydrological applications in many parts of the world.

Inferences on recharge have been attempted, using bomb peak ^{36}Cl . For example; Liu et al., (1995) in shallow vadose zone in the desert of Arizona, USA; Cook et al. (1994) in the vadose zone of the Murray Basin, South Australia; Scanlon et al. (1990) in Texas, USA; and Norris et al. (1987) in Nevada, USA. Phillips et al. (2000) note that the use of bomb ^{36}Cl in the vadose zone to study recharge has been largely inconclusive in many arid zones as slow recharge rates have resulted in the bomb ^{36}Cl being concentrated near the root zone.

Another application of bomb ^{36}Cl is as an indicator for the presence of a component of modern (post nuclear testing) recharge in groundwater. Samples that show $^{36}\text{Cl}/\text{Cl}$ ratios above expected atmospheric levels can indicate the presence of bomb ^{36}Cl . For example Campbell et al. (2003) present some data from the Yucca Mountain proposed nuclear waste repository in Nevada. High ^{36}Cl levels at 200m below ground surface indicate

water containing bomb ^{36}Cl has travelled via preferred pathways to this depth in the vadose zone. Murad and Krishnamurthy (2004) interpret the ^{36}Cl data from eastern United Arab Emirates aquifers to indicate a component of bomb ^{36}Cl , and hence post 1950 recharge, has reached these aquifers. Although no comparison to expected atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios is made, the evidence of anthropogenic contamination from other chemical data confirm the presence of bomb peak ^{36}Cl . A study in Zimbabwe by Larsen et al. (2002) attempted to look at recharge rates by tracing bomb peak ^{36}Cl in the Karoo Formation but preliminary results proved inconclusive.

Davis et al. (1998a) discuss criteria to identify groundwater that may have a component of bomb ^{36}Cl so that such samples can be disregarded in ^{36}Cl decay age dating studies.

7.1.3.5.2. *Recirculation of bomb ^{36}Cl*

While surface nuclear testing has ceased and atmospheric ^{36}Cl levels are now back to pre-testing levels (Suter et al., 1987) some recent studies (Blinov et al., 2000; Corcho Alvarado et al., 2005; Cornett et al., 1997; Herczeg et al., 1997; Milton et al., 2003; Scheffel et al., 1999) note that some bomb ^{36}Cl may still be circulating in the environment with the potential to complicate hydrological studies using ^{36}Cl . In North America due the fact that chloride is known to be an essential micronutrient for higher plants (e.g. White and Broadley, 2001), this effect is thought to be related to the entrapment, and subsequent slow release, of bomb ^{36}Cl in the vegetation rich biomass associated with conifer forests (Milton et al., 2003; Cornett et al., 1997.) Production by plants is now recognised as a significant source of methyl chloride in the atmosphere (Rhew et al., 2000, 2003) so, depending on the halide retention time within plants and availability of bomb ^{36}Cl , some bomb ^{36}Cl may well be currently released to the atmosphere. The magnitude of this effect on atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios is difficult to estimate. The evidence from the Dye-3 ice core analyses discussed above suggests this effect may be only subtle on a global scale. This point is reinforced by Yokouchi et al. (2000) who suggest only 12% of estimated global CH_3Cl flux cannot be accounted for by oceanic fluxes.

In south-eastern Australia Herczeg et al. (1997) noted that groundwater $^{36}\text{Cl}/\text{Cl}$ values are greater than predicted atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios and speculate that bomb ^{36}Cl may be recirculating back to the environment in the vicinity of sinkholes and thereby affecting groundwater $^{36}\text{Cl}/\text{Cl}$ ratios. However, as the predicted atmospheric ratios $^{36}\text{Cl}/\text{Cl}$ ratios are based on the Lal and Peters (1967) ^{36}Cl fallout rate which has since been found to underestimate natural fallout (Keywood, 1998; Phillips, 2000), it may be that no evidence of bomb ^{36}Cl exists. Indeed Herczeg et al. (1997) note an alternative explanation is that a component of continental-derived Cl in rainfall from dust containing some bomb ^{36}Cl , as discussed by Simpson and Herczeg (1994), results in groundwater $^{36}\text{Cl}/\text{Cl}$ ratios being above expected atmospheric levels. In the Yass Valley of New South Wales Turner et al. (1992) also explain recorded $^{36}\text{Cl}/\text{Cl}$ ratios from shallow groundwater slightly above the expected Lal and Peters (1967) predictions as being the result of bomb ^{36}Cl . Again it is possible that a reappraisal of atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios in this region may diminish the perceived effect of bomb ^{36}Cl .

Scheffel et al. (1999) and Blinov et al. (2000) suggest recycling of bomb ^{36}Cl may be occurring. This is on the basis of ^{36}Cl analyses of composite annual rainfall from various sites around the world showing elevated $^{36}\text{Cl}/\text{Cl}$ compared with predictions of an atmospheric transport model they had developed. However, it should be noted that samples from various years between 1989 and 1996 were used and only two sites from the southern hemisphere in New Zealand were sampled. Thus, other factors such as rainfall intensity and alternative atmospheric circulation models as proposed for the southern hemisphere by Keywood et al. (1998) may also influence these results. By contrast Vogt et al. (1994) from results at Indiana, USA concluded no bomb ^{36}Cl was circulating in the atmosphere. A recent study of groundwater $^{36}\text{Cl}/\text{Cl}$ ratios from 38 sites across the United States and previously published data by Moysey et al. (2003) attributes observed differences in $^{36}\text{Cl}/\text{Cl}$ to natural variation expected in the atmosphere (e.g. variation in Cl fallout in rainfall) across a continental land mass. The possibility of bomb ^{36}Cl still circulating in the environment was not invoked to explain $^{36}\text{Cl}/\text{Cl}$ variation across the continent. Thus it may be that recycling of bomb ^{36}Cl in the environment is only a localised phenomenon.

Hence, given there is still some uncertainty that recirculating bomb ^{36}Cl is ubiquitous in the environment, it may be that further studies of atmospheric ^{36}Cl fallout need to be undertaken to clarify this matter.

7.1.3.5.3. *Localised anthropogenic ^{36}Cl sources*

Apart from the worldwide distribution of bomb ^{36}Cl resulting from nuclear testing in the Pacific, other anthropogenic activities produce ^{36}Cl in the environment which may be used as a tracer at a local scale. For example, Milton et al. (1994) and Beasley et al. (1993) trace reactor-produced ^{36}Cl in the vicinity of nuclear power plants at Ontario, Canada and Idaho, USA respectively.

Local nuclear testing may also provide useful radioisotope tracers. Cresswell et al. (2002) speculate that British onshore nuclear weapons testing at Maralinga in central South Australia between 1952 and 1963 has resulted in a ^{36}Cl bomb peak in some shallow aquifers further north in the Anangu Pitjantjatjarra Lands of South Australia. British weapons' testing is considered to be the source because this bomb peak is recorded only in a narrow band to the north east of the test site. Bird et al. (1991) note $^{36}\text{Cl}/\text{Cl}$ ratios at up to 10^{-11} at the surface near Maralinga, which is the same as recorded (non-hazardous) contamination around the Lucas Heights research reactor in southern Sydney. Although onshore tests are not thought to produce significant ^{36}Cl (Phillips, 2000) due to a lack of nearby ^{35}Cl , this pattern might indeed represent the remnants of localised windblown radioactive contamination following the weapons testing.

7.1.4. **Inputs**

To measure the ^{36}Cl decay in groundwater it is necessary to have an idea of the initial or input $^{36}\text{Cl}/\text{Cl}$ ratio to use the decay equation (Eq. 7.2). When local ^{36}Cl fallout data are not available, as is often the case, other strategies are needed to estimate input $^{36}\text{Cl}/\text{Cl}$ ratio. Davis et al. (1998a) give a review of the considerations necessary to best predict this ratio. One method is to use the theoretical fallout of ^{36}Cl and the expected amount of chloride in precipitation for a given area to calculate atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios. Another more empirical approach is to measure $^{36}\text{Cl}/\text{Cl}$ ratios in groundwater at

locations perceived to lie in recharge areas and assume these ratios represent pre-anthropogenic atmospheric input ratios. Consideration of changes in past fallout ratios due to variations (discussed Section 7.1.3.2) in the earth's magnetic field are also recommended by Davis et al. (1998a).

Given the problems in accurately predicting atmospheric ^{36}Cl fallout discussed above (Section 7.1.3.1) and inherent uncertainties associated with identifying recharge zones Davis et al. (1998a) note these methods may have serious weaknesses.

Previous Australian studies or discussions have relied on measured $^{36}\text{Cl}/\text{Cl}$ ratios of shallow groundwater in assumed recharge zones to provide an estimate of input ratio (e.g. Kellett et al., 1990; Torgersen et al., 1991; Mazor, 1992; Love et al., 2000; Cresswell et al., 1999a). While such an approach has, on first impressions, the potential to provide a true input ratio as natural variations in atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios may all be integrated into a representative sample, care must be taken because many factors may potentially affect the $^{36}\text{Cl}/\text{Cl}$ of shallow groundwater.

Davis (1998a) propose that when no actual atmospheric $^{36}\text{Cl}/\text{Cl}$ measurements are available, shallow groundwaters need to be screened to assess that no bomb ^{36}Cl or dead chloride additions have affected the $^{36}\text{Cl}/\text{Cl}$ ratio. Screening of samples usually involves measuring for other radio isotopes (tritium or ^{14}C) to ensure that no bomb ^{36}Cl contamination is indicated and that the sample is in fact young enough to provide an estimate of modern atmospheric ^{36}Cl input.

While unravelling the provenance of all chloride content in groundwater to check for addition of dead chloride or other potential complications is acknowledged to be difficult, much weight is given to the insights offered from studying the Cl/Br ratios of groundwater. Like chloride, bromide is also considered to act conservatively in groundwater (Hem, 1985) and therefore the Cl/Br ratio of recharge water should remain constant through an aquifer unless addition or a loss of halides occurs. In simple terms, the use of the Cl/Br ratio is based on the premise that halides in rainfall or recharge water are of oceanic origin. Given the high solubility of halides, losses of chloride or bromide via precipitation of salts from solution are not expected in any but hyper-saline groundwaters. Hence, as the Cl/Br mass ratio of seawater is around 290 (Hem, 1985),

any measured groundwater Cl/Br ratio in excess of 290 can indicate chloride content may have a component derived from other sources. If other sources of chloride are indicated use of the decay equations (Eq.7.2) for ^{36}Cl decay dating becomes problematical. Given this utility, the use of Cl/Br ratios has been recommended as part of routine assessment of ^{36}Cl groundwater data sets by Mazor (1992) and Fontes and Andrews (1994).

There is an exception to this general trend that should be considered for studies of hyper saline groundwater. For instance Penny et al. (2003) note groundwaters derived from remnant evaporated brines beyond halite saturation can exhibit Cl/Br ratios less than seawater. Davis et al. (1998b) cite several studies of hyper saline (TDS > 100,000 mg/L) groundwaters which have very low Cl/Br ratios apparently as a result of this phenomenon. Davis et al. (1998b) give a review of the use of Cl/Br mass ratios in groundwater studies and recommend bromide concentrations to be determined as a matter of course in groundwater investigations.

The use of Cl/Br (or Br/Cl) ratios as a tool to trace subsurface chloride origins has been widely reported in many studies. For example: Edmunds (1996) uses Br/Cl ratios to examine origins of salinity in several British aquifers; Fabryka- Martin et al. (1991) use halide ratios to study the origins of subsurface chlorides in the Milk River aquifer in Canada; Herczeg et al. (1991) use Cl/Br ratios to study the behaviour of chloride in the Great Artesian Basin; Andrews et al. (1994) and Edmunds and Smedley (2000) use Br/Cl ratios to examine the Midlands aquifer of England; Cartwright et al. (2004) make much use of Cl/Br ratios when tracing the origins of salinity in the Murray Basin of south eastern Australia.

In recognition of the usefulness of shallow groundwater analyses to determine $^{36}\text{Cl}/\text{Cl}$ input ratios, a large project to assess ^{36}Cl distribution across the USA has focussed on shallow groundwater $^{36}\text{Cl}/\text{Cl}$ ratios. Results from this project are reported in a series of publications (Davis et al., 1998a, 2000, 2001, 2003; Moysey et al., 2003). At the culmination of this study Davis et al. (2003) set criteria to evaluate groundwater samples for anthropogenic affects or chloride contamination (e.g addition of subsurface brine) to ensure useful $^{36}\text{Cl}/\text{Cl}$ data are determined. These criteria are: Chloride concentration < 10 mg/L, Tritium < 2 units, ^{14}C < 86% (pmc), $^{36}\text{Cl}/\text{Cl} < 2000 \times 10^{-15}$,

Cl/Br mass ratio < 260 , $\text{NO}_3 < 5$ mg/L. In other parts of the world, some of these criteria may not be suitable as indicators of anthropogenic contamination. For example in central Australia, where virtually no agriculture or pollution is expected in this sparsely populated region, high NO_3 levels are endemic with natural levels often in excess of 50 mg/L (Murray and Seibert, 1962). Various natural biological factors are considered responsible for generating these high nitrates in central Australia (Barnes et al., 1992). Groundwater salinity, hence also chlorinity, is also high in central Australia. Tickell (1997) maps groundwater salinity to be at least above 500 mg/L TDS in this region. Another study in this region, which included data from over 800 bores, recorded only one analysis where chloride was less than 10 mg/L (Wischusen, 1998).

Consequently, it seems that radioactive evidence of anthropogenic contamination (Tritium, ^{14}C , high $^{36}\text{Cl}/\text{Cl}$ ratio) and deviation from expected atmospheric Cl/Br ratios to highlight subsurface brine contamination etc. (Davis et al. (1998b, 2001), are the only criteria that may be applicable to determining integrity of shallow groundwater ^{36}Cl data in central Australia (and most likely other sparsely populated arid regions).

7.1.5. Conclusions

Natural fallout of ^{36}Cl to the earth is yet to be categorically determined. The theoretical fallout calculated by Lal and Peters (1967) seems to underestimate fallout when compared to the available, but limited, empirical data sets. The amount of ^{36}Cl fallout in precipitation is shown to vary with seasons at any particular field site, so an average annual assumption is used to estimate ^{36}Cl fallout. More routine collection of ^{36}Cl in rainfall across continents is needed to better estimate the spatial distribution of atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios.

Studies of the palaeo intensity of the earth's magnetic field over the last 800 ka indicate intensity has never been significantly higher than at present. Consequently, atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios are unlikely to have ever been lower over the same period.

The effects of epigene ^{36}Cl production can usually be ignored on groundwater studies as the rate of epigene ^{36}Cl production is very slow compared to the flux of water in the subsurface.

Hypogene production is usually only small (<10 by 10^{-15}) when compared to atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios. Only when exceptionally high rock U and Th contents are suspected, or measured groundwater ratios approach hypogene production levels, is it an important consideration in ^{36}Cl decay dating. Geothermal systems can sometimes be dated by comparing the amount of ^{36}Cl ingrowth with a known secular equilibrium ratio. More often age is difficult to quantify. Use of ^{36}Cl has proved useful as a tracer to help identify origins of chloride in some geothermal systems.

Bomb peak ^{36}Cl is a useful hydrological tracer. There is some evidence that bomb produced ^{36}Cl is still being released into the environment via methyl chloride production from plants. Based on known global methyl halide budgets the significance of this effect seems slight. It may be that in some heavily vegetated areas the effect is more pronounced.

Determination of an initial input $^{36}\text{Cl}/\text{Cl}$ ratio when atmospheric data are absent is necessary to determine ^{36}Cl decay age. Evidence of anthropogenic radioactive contamination and deviation from expected atmospheric Cl/Br ratios are the most appropriate criteria against which to test shallow water samples for ^{36}Cl integrity in sparsely populated arid regions.

7.2. Results

7.2.1. Introduction

Chlorine-36 (^{36}Cl) is a radioactive isotope with a half-life of 301 000 years. As chloride is hydrophilic, study of this isotope has the potential to be used as a groundwater dating tool for waters some millions of years old. Thus, this isotope also has the potential to determine whether measured ^{14}C activity is truly representative of groundwater residence time or merely the signature of the mixing of older water with modern carbon-

14 bearing water. Bethke and Johnson (2002) illustrate how only slight contamination of a very old water by a modern water can result in an apparent isotope age very much younger than the actual mix ratio of vintages would suggest.

Once all the factors that can affect ^{36}Cl decay dating are accounted for (see review of ^{36}Cl in the environment in Section 7.1 above), $^{36}\text{Cl}/\text{Cl}$ ratios can be used to estimate age of groundwater if four assumptions are made (e.g. Andrews and Fontes, 1992):

- the only sink for ^{36}Cl in the aquifer is radioactive decay;
- the only source for additional ^{36}Cl is normal deep subsurface production;
- additional ^{36}Cl sources can be identified and quantified;
- production rate for ^{36}Cl is the same now as at the time of recharge.

The groundwater may then be dated using the standard decay equation (Eq. 7.2) where A_t is the $^{36}\text{Cl}/\text{Cl}$ ratio for the groundwater sample, A_o is the $^{36}\text{Cl}/\text{Cl}$ ratio for the recharge (or input function), and $1/\lambda$ is the mean life of ^{36}Cl (434,251 years).

7.2.2. ^{36}Cl analyses

The results of ^{36}Cl analyses of samples taken from Palm Valley and at several other sites along strike in the vast Hermannsburg Sandstone outcrop are shown in Table 7.1.

Plots of these data using one of the standard graphical presentations outlined by Bird et al. (1991) are shown in Figures 7.5 and 7.6. When the data are plotted as shown on Figure 7.5 it can be seen most data points fall along the ^{36}Cl decay line centred on a chloride content of around 100 mg/L. One point (shot hole 1/608) plots along the evaporation line, another, RN 14952, seems to plot on a dilution line, when these results are compared to the processes chart included in Figure 7.5. Figure 7.6 shows a distinct decay trend when data are compared to the included processes chart. It seems that evaporation effects could account for all deviations off the decay line seen in Figure 7.6.

Table 7.1 Isotope data, Palm Valley study

SITE	LOCATION	$\delta^{18}\text{O}$ ‰ SMOW	$\delta^2\text{H}$ ‰ SMOW	^{14}C ‰ MC	$\delta^{13}\text{C}$ ‰ PDB	Cl mg/L	^{36}Cl atoms/L by 10^6	$^{36}\text{Cl}/\text{Cl}$ by 10^{-15}	ERROR $^{36}\text{Cl}/\text{Cl}$ analysis	^{36}Cl age, years	Depth of sample (m)	Water level (m)
RN 4508	Palm Valley	-7.51	-49	3.1	-10.8	118	290	130	8	397900	-70	-1.5
RN 10074	Areyonga					76	220	175	10	268818	-100	-3.0
RN 12024	Palm Valley	-7.7	-51.3	22.5	-9.4	132	545	245	10	122705	-18	-8.4
RN 14165	Hermannsburg					114	350	190	10	233106	-161	-0.5
RN 14616	Palm Valley	-7.16	-45.8	4.2	-9	81	310	220	15	169444	-95	-0.8
RN 14952	Intjartrnama					83	390	290	15	49480	-180	-41.0
PV04/200	Palm Valley	-7.25	-45.8			100	220	160	10	307733	-8	-6.0
PV01/608	Palm Valley	-6.72	-46.7			212	520	205	10	200109	-5	-3.0
Road Sp.	Palm Valley	-6.89	-44	42.4	-11.8	96	260	190	15	233106	-0.5	surface
Lt. Palm Sp.	Palm Valley	-3.75	-28.9	87.2	-9.2						-0.5	surface
Oasis Sp.	Palm Valley	-3.59	0.6									surface
West Sp.	Palm Valley	-4.29	-36.2	79	-11	114	360	265	15	88629	-1	surface

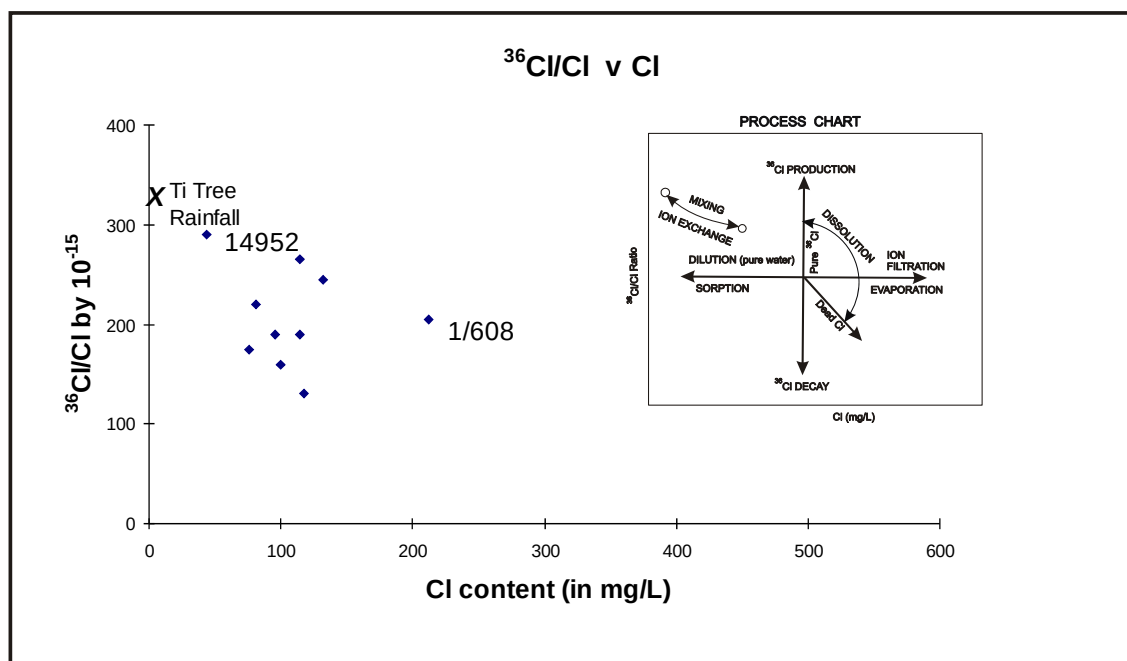


Figure 7-5 Plot of $^{36}\text{Cl}/\text{Cl}$ versus chloride for Hermannsburg Sandstone process trends are shown by arrows. If the concentration of chloride in rainfall by evaporation is assumed to account for groundwater chloride concentration of around 100 mg/L, then the range of data points is most (from the process chart) readily explained as radioactive decay of Chlorine – 36. The outliers to this trend 14952 and 1/608 can be explained by differing amounts of evaporation affect. The Data for the Ti Tree rainfall is after Keywood, (1995).

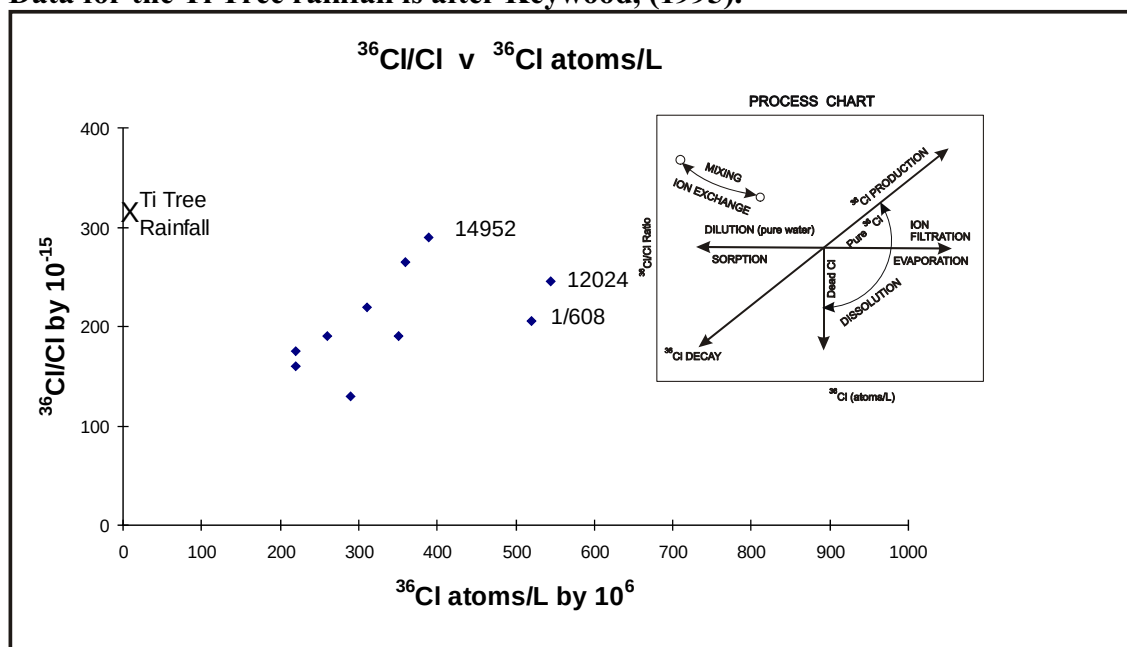


Figure 7-6 Plot of $^{36}\text{Cl}/\text{Cl}$ versus ^{36}Cl atoms for Hermannsburg Sandstone sites sampled for this study, process trends are shown by arrows. This diagram also shows a ^{36}Cl decay trend like Fig. 7.3. Data points not on the decay trend shown by the main cluster of data points can again be explained by different amounts of evaporation affect. These data support the conclusion that radioactive decay is the main reason for $^{36}\text{Cl}/\text{Cl}$ variations within the Hermannsburg Sandstone and that consequently groundwater age varies by hundreds of thousands of years between some sample points.

It should be noted that while the magnitude of likely error for these $^{36}\text{Cl}/\text{Cl}$ ratios has been computed by the ANU and included in Table 7.1, these errors are too small to be included as error bars on these plots.

It should also be noted that no aquifer ever has exactly consistent chloride content when sampled along flow paths. NT Government records show that even samples taken from the same bore at different intervals will have slightly differing chloride contents. As discussed above (Section 7.1) this variation can arise from slight differences in the amount of evaporation during recharge or even addition of subsurface chlorides. It is because of this that ^{36}Cl results are initially evaluated by way of process charts, as shown in Figure 7.2, so that the likely cause of variation of chloride concentration between samples can be seen. Given this expected variation, statistical appraisal of ^{36}Cl results by way of r^2 values of lines of best fit etc. on say $^{36}\text{Cl}/\text{Cl}$ v Cl plots is never applied. Indeed there is no instance of statistical analyses of trend lines for $^{36}\text{Cl}/\text{Cl}$ or ^{36}Cl atoms versus chloride plots reported in any of the literature cited in this thesis. Thus, while the result plots shown in Figure 7.5 and 7.6 are useful to look for relevant trends, like any graphical technique, some caution should be exercised when interpreting results. For instance manipulation of axis scales can change the apparent significance of any process trend observed. For example, if larger scale axes had been used in Figure 7.5 the decay trend observed might have been more pronounced. Conversely, if smaller scale axes had been used no significant trend may have been discernable as data points would plot as a scatter filling the graph. To illustrate that the decay trend seen here is real and not an artefact of manipulation of plot axes, the ^{36}Cl decay results are compared graphically to many other ^{36}Cl groundwater results from other studies in Chapter 8 below.

This clear decay trend, an unusual luxury in ^{36}Cl groundwater studies (see Chapter 8), allows these data to be interpreted without contemplating un-measurable complex sources and sinks of chloride within the aquifer. For example the limited range of chloride in the samples here (44 - 212 mg/L, Table 7.1) is reasonably explained as variation in evaporation during recharge and discharge or in the dissolving of some residual sub surface chloride left over from evapotranspiration processes en route to the aquifer, rather than an intra aquifer source or sink of chloride effect.

The variation between the highest and lowest $^{36}\text{Cl}/\text{Cl}$ ratio is about one half life for all samples from the Hermannsburg Sandstone. At Palm Valley a significant variation between sampled $^{36}\text{Cl}/\text{Cl}$ ratios is also apparent when bore RN 4508 is compared to either RN 12024 or West Spring (Table 7.1). Thus, if a shallow groundwater with some radiocarbon activity (e.g. West Spring) was taken as a likely input ratio, (a strategy adopted for some Australian ^{36}Cl studies e.g. Kellett et al., 1990; Torgersen et al., 1991; Mazor, 1992), groundwater age would vary by about one ^{36}Cl half life (300 ka) between West Spring and RN 4508.

7.2.3. Factors affecting the use of ^{36}Cl as a chronometer.

7.2.3.1. Introduction

In Section 7.1 a review of factors that may affect the use of ^{36}Cl decay to date groundwater were presented. These factors are considered below in relation to the results from Palm Valley.

7.2.3.2. Input ratio

In Section 7.1.31 a review of studies examining fallout of ^{36}Cl to the Earth's surface was presented. The validity of the observed ^{36}Cl data at Palm Valley is complemented by recent work elsewhere in central Australia. Keywood (1995) measured atmospheric $^{36}\text{Cl}/\text{Cl}$ ratio in precipitation at Ti Tree (250 km north east of Palm Valley) at 325×10^{-15} . This value compares to the least decayed data point shown on Figure 7.6 (290×10^{-15} at bore RN14952 Injarrtnarma). Furthermore, this value is approximately the same as that calculated using the formula of Phillips (2000) discussed in Section 7.1.3.1.

The variation between the highest and lowest $^{36}\text{Cl}/\text{Cl}$ ratio is about one half life for all samples from the Hermannsburg Sandstone. At Palm Valley a significant variation between sampled $^{36}\text{Cl}/\text{Cl}$ ratios is also apparent when bore RN 4508 is compared to either RN 12024 or West Spring (Table 7.1). Thus if a shallow groundwater with some radiocarbon activity (e.g. West Spring) was taken as a likely input ratio, (a strategy

adopted for some Australian ^{36}Cl studies e.g. Kellett et al., 1990; Torgersen et al., 1991; Mazor, 1992), groundwater age would vary by about one ^{36}Cl half life (300 ka) between West Spring and RN 4508.

Therefore assigning a $^{36}\text{Cl}/\text{Cl}$ input ratio of around 300 by 10^{-15} for groundwater studies in this region has some credence. If the assumptions pertaining to equation (2.2) are assumed valid, and an input ratio of 325 by 10^{-15} is used, groundwater age is calculated to vary by over 300 000 years in the Hermannsburg Sandstone (Table 7.1).

Given that $^{36}\text{Cl}/\text{Cl}$ ratios are noted to vary with season (Keywood, 1995) and rainfall amount (Kniess et al., 1994) an exact input ratio may be impossible to estimate. Thus while an indication of relative ages remains feasible, predicting actual age of groundwater using ^{36}Cl decay maybe somewhat problematical. An error function of say at least around +/- 20 % may be the best way to view estimates of absolute groundwater age at Palm Valley. This implies correlation of recharge to past Quaternary pluvial events may also only be an approximation here.

7.2.3.3. Past changes of ^{36}Cl fallout rate

The potential for ^{36}Cl fallout to have been different in the past has been discussed in Section 7.1.3.2. While potential complications are recognised from this phenomenon it is highly unlikely that ^{36}Cl fallout has ever been less than at present. Thus, the relative difference in $^{36}\text{Cl}/\text{Cl}$ ratios, if taken to be a result of radioactive decay, indicate around 300 ka distinction between some groundwater sampled at Palm Valley.

7.2.3.4. Epigene Production

Epigene ^{36}Cl production in the upper few metres of the Earths crust is reviewed in Section 7.1.3.3. This review concluded that due to the relatively fast movement of groundwater compared to the rate of epigene ^{36}Cl production that in most instances epigene ^{36}Cl production can be ignored (e.g. Phillips, 2000). There is no evidence that suggests this general conclusion should not also be valid at Palm Valley.

7.2.3.5. Hypogene production.

Hypogene production of ^{36}Cl is reviewed in Section 7.1.3.4. In general, hypogene ^{36}Cl production rates are low. For instance, the maximum $^{36}\text{Cl}/\text{Cl}$ secular equilibrium for sedimentary rocks is around 10×10^{-15} . Furthermore, it is only when groundwater $^{36}\text{Cl}/\text{Cl}$ ratios approach hypogene production rates that its affect on ^{36}Cl decay age determination is significant.

As the lowest $^{36}\text{Cl}/\text{Cl}$ ratio at Palm Valley is $130 \text{ by } 10^{-15}$ it is unlikely that, if typical hypogene production rates apply (i.e. sandstone $R_{\text{se}} \text{ max } 10 \times 10^{-15}$), hypogene production is a significant factor here. The only way hypogene production is likely to affect results here is if the Hermannsburg Sandstone has an unusually high uranium content.

To investigate this possibility samples from bores at Palm Valley were examined for trace element content by Inductively Coupled Plasma Atomic Emission Spectra (ICPAES) techniques. The results of these analyses are presented in Table 7.2 where it can be seen that as U content does not exceed $9 \mu\text{g/L}$, which is within the normal range expected for groundwater (Hem, 1985).

No whole rock chemistry analyses of the Hermannsburg Sandstone were conducted for this study. Simpson et al. (1991) however, reports XRF analyses from 20 sites in the Hermannsburg Sandstone from near the top of the Palm Valley anticline only 3 km north of the main stand of Palms. While Simpson et al. (1991) do not report a uranium measurement, thorium levels are reported. The Th concentrations reported are never more than 14 parts per million (ppm) and usually well less than 10 ppm.

Table 7.2 Trace element groundwater chemistry from 3 Palm Valley sites

		BORE ID		
ELEMENT		4508	12024	14616
All results in µg/L				
Ag		0.01	<0.006	0.01
Al		273.39	4.71	45.41
As		2.70	2.85	0.35
Ba		87.30	77.15	45.47
Be		0.10	0.01	0.01
Bi		<0.02	<0.02	<0.02
Cd		8.48	2.69	2.73
Ce		0.48	0.01	0.23
Co		0.27	0.11	0.16
Cr		6.36	0.73	4.62
Cs		0.39	0.09	0.09
Cu		3.77	2.06	32.43
Dy		0.08	0.01	0.03
Er		0.04	0.01	0.01
Eu		0.04	0.02	0.03
Ga		1.99	1.61	1.02
Gd		0.11	0.00	0.04
Ge		0.17	0.04	0.05
Ho		0.02	0.00	0.01
La		0.17	0.02	0.16
Li		33.81	14.43	12.19
Lu		0.01	0.00	0.00
Mn		25.44	<0.07	46.98
Mo		0.43	0.85	0.18
Nb		<0.03	<0.03	<0.03
Nd		0.34	0.02	0.21
Ni		23.64	2.47	2.70
Pb		26.03	0.64	10.90
Pr		0.07	0.00	0.05
Pt		<0.009	<0.009	<0.009
Rb		20.30	9.64	5.21
Sb		0.05	0.03	<0.02
Sc		<0.11	0.67	<0.11
Se		3.32	6.36	3.08
Sm		0.08	<0.009	0.04
Sn		<0.07	<0.07	<0.07
Sr		285.22	372.35	204.96
Ta		0.03	0.03	0.02
Tb		0.01	0.00	0.01
Th		0.13	0.01	0.01
U		1.12	8.79	2.37
V		0.92	19.43	0.30
W		0.22	0.12	0.08
Y		0.45	0.06	0.11
Yb		0.04	0.00	0.01
Zn		318.20	55.60	151.33
Zr		0.13	0.11	0.08

The less than (<) values are detection limits for the method

As Th (a daughter product of U decay) is nearly always more abundant than uranium in rocks (Hem, 1985) these data are taken to indicate that U levels are not anomalously high in the Hermannsburg Sandstone. Examination of Gamma Ray geophysical logs of bores drilled in the Hermannsburg Sandstone held in the NTG database show a typical sandstone low count response, this is indicative of lower U and Th levels than those typically found in clays or shales.

Consequently, it is concluded that hypogene ^{36}Cl production is not a significant consideration when assessing ^{36}Cl results from Palm Valley.

7.2.3.6. Anthropogenic Sources

Anthropogenic ^{36}Cl production (mainly from surface testing of nuclear weapons) is reviewed in section 7.1.3.1. Elevated $^{36}\text{Cl}/\text{Cl}$ ratios have been attributed to weapons testing elsewhere (e.g. Davis et. al., 2000). As $^{36}\text{Cl}/\text{Cl}$ ratios are consistently at or below known nearby atmospheric ratios (Keywood, 1995) and carbon-14 values are less than 100 %MC, there is no prima facie evidence to suggest ^{36}Cl results at Palm Valley are complicated by bomb pulse affects.

7.2.3.7. Addition of “dead” chloride.

In Chapter 8 it is noted that many previous attempts to use ^{36}Cl decay to date groundwater have suffered because subsurface addition of chloride is indicated and consequently ^{36}Cl decay results were liable to ambiguous interpretation. At Palm Valley the plots of ^{36}Cl and Cl data (Figs. 7.5 & 7.6 discussed above) do not indicate that subsurface addition of Cl has occurred.

7.2.3.8. Cl/Br ratios

Many workers (e.g. Andrews and Fontes, 1993; Mazor, 1992; Davis et al., 1998a, 2000; see Section 7.1.4) recommend comparing groundwater Cl/Br ratios, with reference to those of seawater, as a check for addition of extra aquifer derived chloride. The results of four Cl/Br analyses from water samples collected in 2002 are shown in Table 7.1. As these ratios are less than the Cl/Br (mass) ratio of seawater (i.e. 290,

Hem, 1985), which is also expected in inland Australian rainwater due to loss of chloride from sea salt aerosol by volatilisation with H_2SO_4 and HNO_3 (Keywood et al., 1997), an atmospheric source of chloride can be assumed here. It should be noted that inland rainfall with Cl/Br ratios less than seawater have also been described in Nigeria by Goni et al., 2001.

Given the significance of subsurface chloride addition to ^{36}Cl decay dating studies it is worth looking at Cl/Br ratios in more detail. As part of her investigation into rainfall across a north to south transect of continental Australia, and a west to east transect across Western Australia, Keywood (1995) also recorded Br levels in precipitation. Bromide and chloride concentrations from precipitation were determined by Ion chromatography. Given the low concentrations recorded, accuracy of Br analyses are reported by Keywood (1995) to be less (9.6%) than those of Cl (0.31%). Even with these accuracy constraints compilation of these data allow a check on atmospheric Cl/Br ratios in the central Australian region.

Table 7.3 shows a compilation of Cl/Br ratio values calculated from Keywood's (1995) data obtained from her central Australian sample stations (i.e. stations that are a similar distance from the coast as Palm Valley.). Figure 7.7 shows the location of these stations and a graphical display of the data presented in Table 7.3. These data confirm that Cl/Br levels are indeed below the seawater ratio of 290 in inland Australian precipitation. Seasonal and perhaps amount related variation in precipitation composition along with the limited accuracy of the Br measuring technique probably preclude quantitative use of the recorded atmospheric Cl/Br ratios to determine actual amounts, if any, of subsurface Cl addition. Nevertheless, these values indicate groundwater Cl/Br ratios in central Australian aquifers should be below the seawater ratio when there is no contamination by subsurface derived chloride.

Thus, comparison of groundwater Cl/Br data to the seawater ratio is seen to be an appropriate technique to investigate the sources of chloride in central Australian aquifers. Furthermore, contamination of groundwater by windblown halite (i.e. a possible source of dead chloride that could lower $^{36}\text{Cl}/\text{Cl}$ ratios in groundwater) derived from distant central Australian playas (i.e. halite Cl/Br = 1000+, Davis et al., 1988b) is not indicated here.

Table 7.3 Keyword's (1995) central Australian atmospheric Cl/Br (mass) ratios

STATION	SEASON	RAIN (mm)	Cl ug/L	Br ug/L	Cl/Br (mass)
Carnegie	A91	16	170.15	0.80	213
Carnegie	W91	153	181.50	3.19	57
Carnegie	SP91	1	187.88	0.80	235
Carnegie	S91	55	372.21	2.40	155
Carnegie	A92	194	195.32	7.19	27
Carnegie	W92	31	167.67	1.60	105
Carnegie	SP92	20	203.12	3.19	64
Carnegie	S92	33	38.99	1.60	24
Gunbarrel	A91	36	256.65	1.60	161
Gunbarrel	W91	118	120.52	2.40	50
Gunbarrel	SP91	14	197.45	1.60	124
Gunbarrel	S91				
Gunbarrel	A92	265	141.08	4.79	29
Gunbarrel	W92	31	221.55	1.60	139
Gunbarrel	SP92		0.00	0.00	
Gunbarrel	S92	79	75.86	2.40	32
Everard Jn	A91	11	147.11	0.00	
Everard Jn	W91	118	97.13	3.19	30
Everard Jn	SP91	50	278.27	1.60	174
Everard Jn	S91		0.00	0.00	
Everard Jn	A92	191	163.06	6.39	26
Everard Jn	W92	22	153.85	1.60	96
Everard Jn	SP92				
Everard Jn	S92				
Wintinna	W92	27	296.35	3.19	93
Wintinna	SP92	134	233.96	7.19	33
Wintinna	S92	31	322.58	1.60	202
Wintinna	A93	31	152.43	3.99	38
Wintinna	W93	49	375.75	5.59	67
Wintinna	SP93	66	272.95	4.79	57
Wintinna	S93	74	223.33	3.99	56
Wintinna	A94	43	198.51	3.99	50
Alice Sp	W92	10	81.53	0.80	102
Alice Sp	SP92	69	163.06	3.99	41
Alice Sp	S92				
Alice Sp	A93	149	77.99	18.37	4
Alice Sp	W93	14	189.29	1.60	118
Alice Sp	SP93	62	400.57	6.39	63
Alice Sp	S93	85	114.50	3.19	36
Alice Sp	A94	2	54.95	0.00	
Tennant Ck	W92	0	5.67	0.00	
Tennant Ck	SP92	57	236.44	3.99	59
Tennant Ck	S92				
Tennant Ck	A93				
Tennant Ck	W93	5	25.17		
Tennant Ck	SP93	59	404.11	7.19	56
Tennant Ck	S93	56	804.68	11.18	72
Tennant Ck	A94	0	14.18	0.00	
MEAN Cl/Br AT STATIONS					MEAN Cl/Br
Carnegie					79
Gunbarrel					70
Everad Jn					70
Wintinna					65
Alice Springs					32
Tennant Ck.					62

NB. A = Autumn, W = Winter, SP = Spring, S = Summer.

Note also different period measured for WA sites. Data derived from Keyword, 1995.

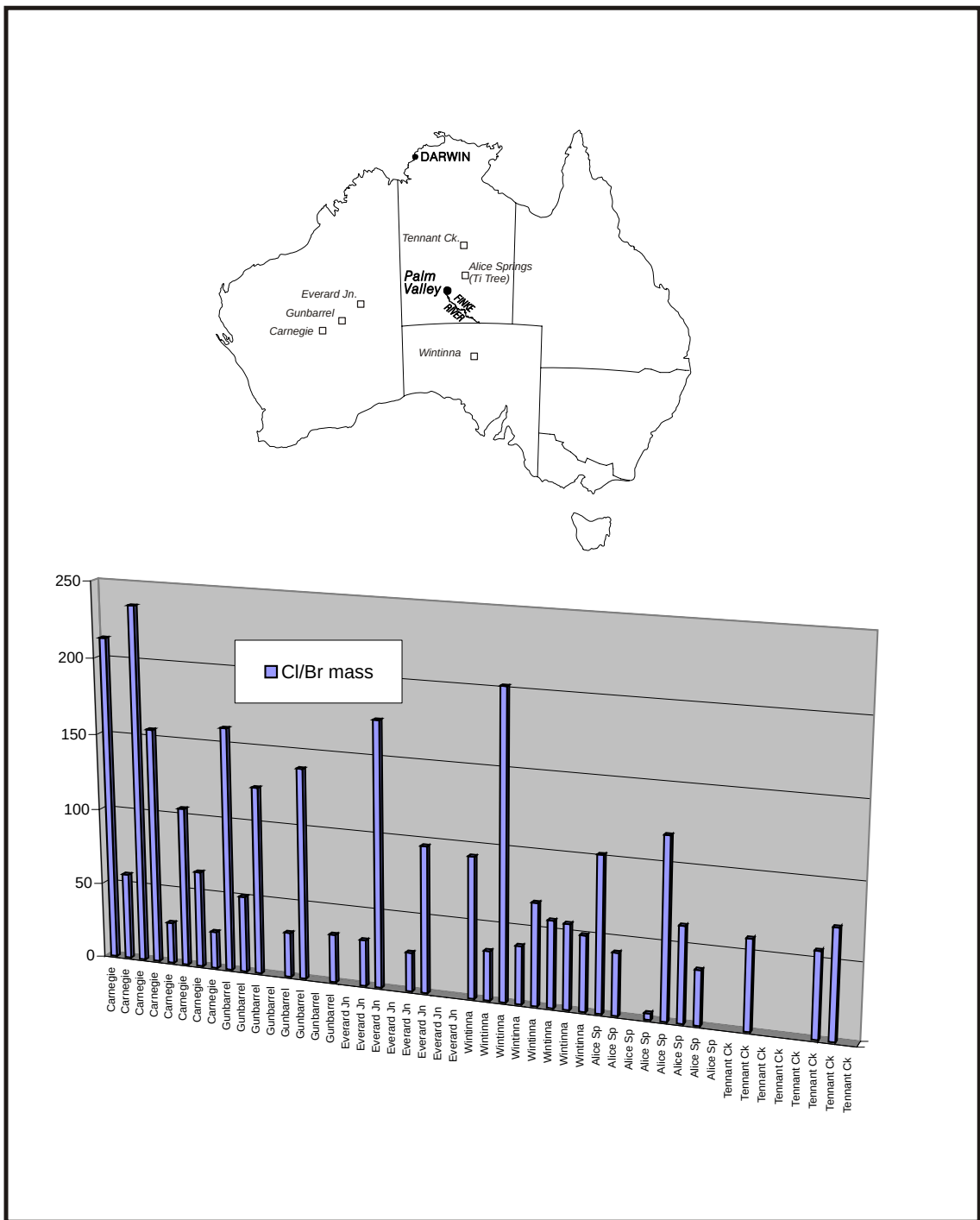


Figure 7-7 Inland Australian atmospheric Cl/Br ratios as recorded at several stations over several seasons by Keywood, 1995. The location of these stations in relation to Palm Valley is shown. The graphical display of the Cl/Br data for each season sampled at each station is based on data presented in Table 7.3. Actual seasons sampled vary slightly between WA and the SA and NT stations (see Table 7.3). These data confirm that atmospheric Cl/Br levels are below the seawater ratio of 290 in inland Australian precipitation.

7.2.3.9. Complementary data

Edmunds (1995), Edmunds and Smedley, (2000), Edmunds et al. (2003) and Guendouz et al. (2003) note that other chemical factors, given the right conditions, can sometimes be used as a proxy to indicate groundwater age. For instance in confined aquifer systems decrease in nitrate concentration can be taken as an indication of an increasingly reducing environment and hence increase in groundwater age. Similarly, some trace elements such as Lithium behave conservatively and are not typically subject to solubility constraints. Therefore, such elements can be used as a proxy indicator of relative groundwater age as concentration is expected to increase along a flow path as dissolution associated with groundwater evolution continues. The Hermannsburg Sandstone is unconfined and apart from the data shown Table 7.2 no other trace element data are available. Thus, no other complementary chemical indicators of groundwater age are available for this study.

7.3. Conclusion

The plots of $^{36}\text{Cl}/\text{Cl}$ ratio against ^{36}Cl atoms (Fig. 7.6) and chloride (Fig. 7.5) show no apparent loss or gain of chloride within the aquifer. These data and other considerations outlined above all support radioactive decay as being the cause of variation of $^{36}\text{Cl}/\text{Cl}$ ratios within the Hermannsburg Sandstone at Palm Valley. Hence groundwater age varies from recent to around 300 ka at Palm Valley.

8. Relevance of this study

8.1. Background

The use of ^{36}Cl decay dating to provide a window beyond the radiocarbon dating range for groundwater resource assessment was championed with the advent of suitable AMS techniques in the late 1970s. The review of ^{36}Cl decay dating studies outlined below, however, shows that the early promise has since been rendered a controversial technique. It seems that depending on opinion, results to date have been difficult or impossible to interpret. Many of the data suites from previous studies display these ambiguous trends with no clear decay component when plotted on a $^{36}\text{Cl}/\text{Cl}$ versus Cl chart (see Section 8.2.4).

The controversial status of ^{36}Cl decay dating of groundwater is mirrored in textbooks on isotope hydrology. Clark and Fritz (1997) express doubt on the validity of the technique when subsurface chloride addition is indicated. However Phillips (2000) thinks ^{36}Cl decay dating is still feasible when well over 50% of aquifer chloride is derived from subsurface sources.

8.2. Review of groundwater ^{36}Cl decay studies

8.2.1. Introduction

Studies of groundwater using ^{36}Cl as a tracer have been undertaken in many aquifers around the world. While there have been many applications of ^{36}Cl in groundwater studies it is commonly acknowledged (eg. Davis 1998a; Andrews and Fontes, 1992; Phillips, 2000) that interpretation of results has often been difficult. This is usually because of doubt about sources and sinks of ^{36}Cl in the subsurface and/or the magnitude of atmospheric $^{36}\text{Cl}/\text{Cl}$ ratio at time of recharge.

This is particularly so for groundwater dating where, as previously discussed in Section 7.1, the $^{36}\text{Cl}/\text{Cl}$ ratio may be used to estimate ages of groundwaters only if certain assumptions are made (Andrews and Fontes, 1992). Davis et al. (2000) note in most instances that the main problem with ^{36}Cl dating is an inverse relationship between chloride concentration and $^{36}\text{Cl}/\text{Cl}$ ratio being observed in the aquifer system. Indeed Andrews and Fontes (1993) make the general observation that dating of groundwater using ^{36}Cl cannot be undertaken when chloride is added along flowpaths. However, in many ^{36}Cl groundwater studies (discussed below) addition of chloride in the subsurface has been accounted for and age estimates made. Phillips (2000) states ^{36}Cl decay dating should be feasible even when up to 90% of groundwater Cl is aquifer derived in most instances. The necessity of estimating/assuming the amount and rate of chloride addition over long time periods must, however, diminish the reliability and accuracy of the ^{36}Cl method in these circumstances.

8.2.2. Renowned ^{36}Cl decay groundwater studies

8.2.2.1. Great Artesian Basin

An example which deals with the issue of chloride addition along flow paths is the pioneering ^{36}Cl decay dating Australian studies in the Great Artesian Basin (GAB). The ^{36}Cl decay dating of the GAB groundwater by Bentley et al. (1986a) and Torgersen et al. (1991) have been reinterpreted by Mazor (1992), Mazor and Nativ (1994) and Andrews and Fontes (1992, 1993). These reinterpretations question the groundwater age determinations presented as it is considered that sources and sinks of chloride along basin flow paths were inadequately accounted for.

The original authors argue that they have recognised and allowed for the addition of Cl^- along flow lines (down dip) in these basins. Data plots show general trends of $^{36}\text{Cl}/\text{Cl}$ and ^{36}Cl to decrease along perceived slow flow paths, ^{36}Cl decay commensurate with expected range of hydrogeological parameters and likely atmospheric $^{36}\text{Cl}/\text{Cl}$ inputs is indicated, thus some addition of Cl^- at a slow rate is invoked to explain increase of chlorinity along flow path. Andrew and Fontes (1992, 1993) argue that mixing of two

$^{36}\text{Cl}/\text{Cl}$ end members in the aquifer, one at atmospheric level, the other at aquifer secular equilibrium, can equally well explain these ^{36}Cl and Cl^- data. This point is then illustrated with theoretical mixing curves plotted on $^{36}\text{Cl}/\text{Cl}$ against Cl^- concentration diagrams. Andrews and Fontes (1993) show that variation of the mixing rate (from 100+ millions of years to instantaneous) of subsurface derived Cl^- with input atmospheric derived Cl^- to attain observed aquifer Cl^- levels has no discernible affect on mixing trend lines. Given this potential ambiguity, Andrews and Fontes (1993) state ^{36}Cl decay dating of old groundwater should be limited to cases where chlorinity is constant. In reply, Torgersen and Phillips (1993) note among other points that the extreme example of instantaneous mixing is not evident as ^{36}Cl concentration decreases down flow path and therefore there is a discernible component of ^{36}Cl decay in the GAB waters and therefore ^{36}Cl decay dating of groundwater in the GAB is sound.

Mazor (1992) Mazor and Nativ (1994) and Mazor (1995) introduce a concept of stagnant groundwater that may affect some parts of the GAB, and postulate measured $^{36}\text{Cl}/\text{Cl}$ ratios only reflect aquifer secular equilibrium values and not ^{36}Cl decay and thus no dating is possible. This concept, which is in contrast to standard theories of groundwater flow (eg Toth 1995), has been refuted by various other workers (Kellett et al. 1993; Phillips, 1993). Fontes and Andrews (1993b) also question much of the interpretation made by Mazor (1992) of previous ^{36}Cl groundwater studies. Mazor (1993a,b,c) reiterates his arguments in a series of replies to this criticism but there is no apparent resolution of these differences of opinion.

The debate on the applicability of ^{36}Cl decay dating in the GAB and elsewhere is not yet resolved. Clark and Fritz (1997) in their text on isotope hydrogeology discuss the ^{36}Cl data for the GAB and reiterate the arguments raised by Andrews and Fontes (1992). They plot GAB groundwater samples on a $^{36}\text{Cl}/\text{Cl}$ versus Cl^- diagram and illustrate how a mixing process between a subsurface high Cl^- low ^{36}Cl brine and a low Cl^- higher ^{36}Cl recharge water also explains the GAB results. Clark and Fritz (1997) do, however, concede that the difference in ^{36}Cl activities between recharge and distal groundwaters in the GAB indicate water is at least 300 ka (one ^{36}Cl half life) old. This discussion which incorporates aspects of several opinions on ^{36}Cl decay dating in the GAB illustrates that the use ^{36}Cl as a dating tool is still somewhat controversial.

Subsequent ^{36}Cl studies have been undertaken in the GAB. Radke et al. (2000) in their compilation of all GAB hydrochemical data note that ^{36}Cl data only provide limited information on groundwater flow rates as in much of the GAB $^{36}\text{Cl}/\text{Cl}$ ratios are commensurate with expected in situ ^{36}Cl production rates. In other areas, interpretation of ^{36}Cl data requires an estimate of the magnitude and rate of Cl addition to the aquifer to be made. Radke et al. (2000) note an inverse relationship between $^{36}\text{Cl}/\text{Cl}$ ratio and alkalinity and speculate that further work on this association may allow ^{36}Cl decay age determinations to be extrapolated further into low $^{36}\text{Cl}/\text{Cl}$ regions of the GAB.

Love et al. (2000) sampled bores in the western GAB in South Australia and note that unmeasurable rates of diffusion of Cl from aquitards and potential past secular variation in atmospheric ^{36}Cl fallout preclude determination of absolute groundwater age in the western GAB. They prefer to use $^{36}\text{Cl}/\text{Cl}$ data to compute relative age differences (hence groundwater flow velocity) between sample points. Love et al. (2000) show Cl concentration decreases along flow path in some areas and propose upward leakage with increasing head may remove solutes from the aquifer. The possibility that decrease in chloride concentration downdip may also occur as the result of less evaporation due a different climatic regime at the time of recharge is also noted. This situation, which is contrary to that found in the eastern GAB (Bentley et al., 1986b), allays some of the concerns raised by Andrews and Fontes (1992) for ^{36}Cl studies in the GAB discussed above.

In a follow up study, Lehmann et al. (2003) calibrate the western GAB ^{36}Cl data presented by Love et al. (2000) with Krypton-81 measurements and calculate some bores to have around 80% subsurface derived Cl, which they consider unsuitable for ^{36}Cl decay dating. The technique of age dating groundwater with ^{81}Kr is only suitable for confined aquifers and has the logistical inconvenience of requiring large volumes of sample for analyses and is a major technical undertaking (Collon et al., 2000) which explains in part why this isotope has not used in conjunction with ^{36}Cl more often. Sturchio et al. (2004) have now developed a ^{81}Kr measurement technique that requires less sample volume (2 tonne), if such improvements in sampling logistics continue this technique may be more readily applied in future groundwater studies.

The hydrological characteristics of the GAB have also been used as a template for a hypothetical reactive transport modelling exercise of ^{36}Cl decay and aquitard diffusion of ^{36}Cl by Bethke et al. (2000). This study concludes groundwater age in the GAB is probably older than that indicated from Darcy flow calculations, however many of the assumptions needed for previous studies in the GAB still need to be invoked for this work. Park et al. (2002) developed this modelling exercise further noting the potential limitations of ^{36}Cl decay dating given conditions similar to those found/perceived in the GAB. Among these potential limitations, it is noted ^{36}Cl decay age cannot be interpreted when groundwater is only moderately saline ($\text{Cl} = 75 - 150 \text{ mg/l}$). Park et al. (2002) assume an input Cl concentration to their model of 23 mg/l , as used in previous GAB studies, thus the threshold percentage of subsurface derived Cl that precludes ^{36}Cl decay dating based on this work is around $65 - 85 \%$.

8.2.2.2. Milk River

The International Atomic Energy Agency (IAEA) sponsored study of the Milk River Aquifer, southern Alberta, Canada by Phillips et al. (1986b) encountered similar problems to the GAB, in that chloride concentration increases down flow path in this aquifer also. The results were difficult to interpret here as this aquifer is considered much more hydrochemically and hydraulically complex than the GAB. Phillips et al. (1986b) reconcile ^{36}Cl decay age and hydraulic data by proposing the additional chloride is derived from an ion filtration process and discount the possibility that additional Cl^- is sourced from the flushing of connate brines. In a subsequent appraisal of this aquifer Hendry and Schwartz, 1988 prefer a diffusion model to account for additional Cl^- , and deduce a younger groundwater age in the aquifer than Phillips et al. (1986b). Nolte et al. (1991) obtained further ^{36}Cl data and further developed a Cl^- diffusion flux model for the aquifer and estimated the maximum groundwater age to lie between the respective age estimates of 2 Ma and 0.5 Ma by Phillips et al. (1986b) and Hendry and Schwartz (1988). Fabryka-Martin et al. (1991) resolved the conflict on theories of the source of additional Cl^- to this aquifer by proposing an intra aquifer origin as the dominant source. Other processes such as ion filtration and diffusion from aquitards are still considered potentially valid origins of extra Cl^- , but in a minor capacity only. Fabryka-Martin et al. (1991) propose local diffusion of saline water primarily from low permeability units within the Milk River Formation as the simplest

explanation of source of additional Cl^- within the Milk River Aquifer. A common subsurface input source for all halides in the aquifer is indicated as halide ratios approach constant values along flow paths. Even though up to 90 % of the chloride at the distal ends of this aquifer may be derived from subsurface origins Fabryka-Martin et al. (1991) still calculate groundwater age from ^{36}Cl decay data at around 1 Ma.

Mazor (1992), in a similar vein to his criticisms of the GAB ^{36}Cl studies mentioned above, questions whether the Milk River Aquifer is hydraulically continuous. Phillips (1993) again refutes Mazor's interpretation and cites many studies that confirm the hydraulics of the Milk River Aquifer.

Andrews and Fontes (1992) also discuss the Milk River Aquifer ^{36}Cl results and note high ^{36}Cl inputs compared to predicted local atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios may reflect a component of ^{36}Cl produced in the epigene zone or barring this it may mean that bomb ^{36}Cl is leaking through confining beds which may confuse interpretation. As mentioned above (section 7.1.3.3) epigene production is now considered an unlikely complication in groundwater studies. A recent empirical study of shallow groundwater $^{36}\text{Cl}/\text{Cl}$ ratios in the USA (Davis et al., 2003) now show higher ratios than previously predicted for this region of North America. Thus this indication of leakage of bomb ^{36}Cl , noted by Andrews and Fontes (1992) may now not be significant.

Frohlich et al. (1991) give an overview of Milk River Aquifer studies and support the work of Fabryka-Martin (1991) to explain the various Cl^- addition mechanisms proposed. Frohlich et al. (1991) also notes that ^{36}Cl decay age estimates, with in situ production accounted for, were only around 30% older than those calculated using zero in situ production. However, it is also noted that when groundwater chloride reaches approximately 500 mg/l in the Milk River Aquifer, in situ production dominates the ^{36}Cl signature. Hence no reliable ^{36}Cl decay ages are considered likely when chloride content is high. The high atmospheric $^{36}\text{Cl}/\text{Cl}$ (input) ratios compared to predicted subsurface in situ ^{36}Cl production rates help the application of ^{36}Cl decay dating at Milk River.

Clark and Fritz (1997) however, in keeping with points raised by Andrews and Fontes (1992) make the comment that at distal ends of this aquifer the ^{36}Cl brought in with the additional subsurface Cl^- reflects the residence time of the brine and that no ^{36}Cl decay

dating is possible. This interpretation, which is in contrast to conclusions drawn by Phillips (2000) in another isotope hydrology text book again illustrate the differing opinions on the applicability of ^{36}Cl decay dating when addition of subsurface Cl^- is apparent. Phillips (2000) presents plots that show $^{36}\text{Cl}/\text{Cl}$ ratio and ^{36}Cl concentration to decrease with distance along flow path to back his argument. Process charts, like those shown in Figure 7.2, which are used by Andrews and Fontes (1992) to illustrate the ambiguity of ^{36}Cl decay dating when subsurface additions of Cl^- occur in the GAB are not illustrated. Instead Phillips (2000) presents a diagram that, given certain assumptions (i.e. atmospheric $^{36}\text{Cl}/\text{Cl}$ 30 times greater than in situ secular equilibrium) shows subsurface production of ^{36}Cl from additional subsurface Cl would not be expected to dominate atmospheric ^{36}Cl in low salinity groundwater until 500 ka of residence and when over 90% of Cl^- was derived from subsurface sources. Given this debate, it is readily appreciated that at the Milk River Aquifer the validity of ^{36}Cl decay dating is controversial. This is largely due to the uncertainty regarding the source and rate of subsurface additions of chloride that occur within the aquifer post recharge.

8.2.2.3. Magadi-Natron Basin

Another ^{36}Cl study that has sparked debate in the literature is the examination of Magadi-Natron Basin in the East African Rift, near the Kenyan-Tanzanian border, by Kaufman et al. (1990). They date brine in the basin at around 760 ka by comparing $^{36}\text{Cl}/\text{Cl}$ ratios in dilute modern waters with those found in the brine. To do this the assumption is made that the basin is a closed system with Cl derived from accumulated precipitation since the basin was formed. Concentration by evaporation and continual mixing of a component of dilute recharge with recirculating brine is also assumed.

Fontes and Andrews (1993a) comment on this work in the Magadi-Natron Basin and dismiss the attempt to use ^{36}Cl decay to date brines as they consider that there are too many uncertainties in the estimated input (atmospheric) $^{36}\text{Cl}/\text{Cl}$ ratio used and epigene and hypogene ^{36}Cl production are not accounted for adequately. Furthermore, they note the influence of bomb peak ^{36}Cl fallout in the closed system has not been calculated and that mass balance considerations of retaining all Cl fallout within the basin in the period proposed could not be accommodated unless considerable halite was deposited.

Kaufman et al. (1993) respond by noting that the inherent uncertainties in estimating atmospheric fallout of ^{36}Cl , bomb peak fallout, epigene and hypogene production and past atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios can equally be invoked to refute the arguments of Fontes and Andrews (1993a).

In his text book chapter on ^{36}Cl Phillips (2000) cites the Kaufman et al. (1990) work in a discussion on ^{36}Cl as a tracer for salinity studies without mention of the subsequent debate outlined above. It is not known if this is a tacit rebuttal of Fontes and Andrews (1993a) concerns. This point notwithstanding, it is apparent from the Magadi-Natron study that when uncertainty of sources and sinks of Cl in the subsurface exist, doubts about the viability of ^{36}Cl decay dating method will also exist.

8.2.2.4. Mazowsze Basin

Dowgiallo et al. (1990) sampled the Oligocene aquifers of the Mazowsze Basin in Poland for ^{36}Cl analyses. The results are taken to indicate ^{36}Cl decay has occurred and that some groundwater is over 200 ka old, however, the likelihood of addition of subsurface derived chlorides is noted.

Zuber et al. (2000) criticise this interpretation as it does not match their understanding of the flow dynamics where maximum residence time is expected to be only 35 ka and that no trend of $^{36}\text{Cl}/\text{Cl}$ or ^{36}Cl decreasing along flow path in the aquifer is discernible. Furthermore, it is noted that noble gas data indicates these groundwaters are connected to the atmosphere. It is argued that the differences in $^{36}\text{Cl}/\text{Cl}$ ratios observed in this basin (488 to < 20 by 10^{-15}), taken to indicate ^{36}Cl decay by Dowgiallo et al. (1990), may be explained by variation in the amount of epigene ^{36}Cl production at different recharge sites. This potential for complications of $^{36}\text{Cl}/\text{Cl}$ interpretation due to recharge waters picking up epigene produced ^{36}Cl and thereby causing differences in $^{36}\text{Cl}/\text{Cl}$ inputs throughout the aquifer was originally noted by Andrews and Fontes (1992) when discussing the Milk River Aquifer. As mentioned above, it is now generally thought unlikely that epigene production is a significant factor to be considered in ^{36}Cl groundwater studies, particularly at altitudes less than 2000 m. Thus it may be that unknown complications of the flow system and subsurface chloride need to be resolved before assessing $^{36}\text{Cl}/\text{Cl}$ data for this basin.

Further potential for complication is noted by Zuber et al. (2000) in that hydrochemistry of the Oligocene aquifer is described as a mosaic throughout the basin and factors such as the influence of salt diapirs and discharge from underlying Mesozoic units are called upon to explain variations in chloride concentrations. This observation suggests that not all sources and sinks of chloride to the aquifer are known and therefore reliability of the ^{36}Cl decay dating by Dowgiallo et al. (1990) is problematic. These uncertainties may equally render some of Zuber et al. (2000) conclusions on groundwater age uncertain.

It is apparent that, as noted by both Dowgiallo et al. (1990) and Zuber et al. (2000), more information is needed to properly assess groundwater age in the Mazowsze Basin. The process chart of $^{36}\text{Cl}/\text{Cl}$ versus Cl presented by Dowgiallo et al. (1990) illustrates the complexities in the chloride cycle of this basin, as no clear trends are discernible.

8.2.2.5. Murray Basin

The studies of ^{36}Cl in the Murray Basin in south-eastern Australia by Kellett et al. (1990) and Davie et al. (1989) have also resulted in some debate. In this basin, decreasing $^{36}\text{Cl}/\text{Cl}$ with increase in chloride concentration is taken to show addition of dead Cl to the confined aquifer and not ^{36}Cl decay. The ^{36}Cl data are considered roughly consistent with expected atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios in the vicinity and are used to elucidate recharge processes. Mazor (1992) by way of a graphical technique to determine $^{36}\text{Cl}/\text{Cl}$ input ratio considers evidence of ^{36}Cl decay exists and that some of the groundwater in the Murray Basin maybe very (100s ka) old. Kellett et al. (1993) and Fontes and Andrews (1993b) dismiss most of the points raised and propose that Mazor (1992) invokes assumptions that do not match the known hydrological environment to support his controversial arguments. Some of this debate also considered likely atmospheric $^{36}\text{Cl}/\text{Cl}$ inputs in the Murray Basin region. Simpson and Herczeg (1994) as outlined previously, also discuss aspects of the atmospheric $^{36}\text{Cl}/\text{Cl}$ ratio in this region.

8.2.3. Other Studies that attempt ^{36}Cl decay dating

8.2.3.1. Introduction

Studies that attempt ^{36}Cl decay dating of groundwater are still reported in the literature. These studies have seemingly not attracted the same level of debate on ^{36}Cl decay dating as that outlined above for the GAB and Milk River Aquifer systems. As most of these studies also show an inverse Cl to $^{36}\text{Cl}/\text{Cl}$ relationship, the literature debate outlined above is probably equally applicable to some of these studies. The reason for a lack of debate may reflect a general acceptance of the limitations of ^{36}Cl decay dating and/or the untimely deaths of both John Andrews and Jean-Charles Fontes who led much of the discussion on the application of ^{36}Cl decay dating in aquifers without constant chloride content. Some geothermal systems, as discussed above in section 7.1.3.4, have also been dated using the ingrowth of ^{36}Cl compared to estimates of host rock ^{36}Cl secular equilibrium rates.

8.2.3.2. International studies

Penny et al. (2003) present some $^{36}\text{Cl}/\text{Cl}$ ratio data from two transects in a coastal plain aquifer in Alabama, USA as a small part of an integrated groundwater study. If natural ^{36}Cl decay along flow paths is assumed groundwater ages >100 ka are calculated. Such ages are commensurate with the known hydraulic characteristics of this aquifer. Caution is recommended when viewing these data as progressive mixing from low ^{36}Cl high Cl residual evaporate brines is known to occur in this region. This uncertainty is reflected by the fact that the $^{36}\text{Cl}/\text{Cl}$ versus chloride concentration chart presented shows no clear decay trend. The low chloride and decreasing $^{36}\text{Cl}/\text{Cl}$ ratio along flow path data presented for the eastern transect look, on face value, promising for the application of ^{36}Cl decay dating. Perhaps further investigation in this area will better define ^{36}Cl decay ages along this transect.

Sturchio et al. (2004) correlate six $^{36}\text{Cl}/\text{Cl}$ ratio results from the Nubian aquifer in Egypt against ^{81}Kr decay age results and fit a decay curve to estimate ^{36}Cl decay ages. Discordance of ^{81}Kr - ^{36}Cl ages of some samples are attributed to subsurface addition of Cl or hypogene ^{36}Cl . Different atmospheric $^{36}\text{Cl}/\text{Cl}$ input ratios between some samples

are also noted to be a possible explanation of this discordance. Sturchio et al. (2004) conclude these results demonstrate the vulnerability of ^{36}Cl decay dating integrity to subsurface Cl additions, whereas the new ^{81}Kr decay dating method they present is considered much less vulnerable to interpretation problems associated with subsurface sources or sinks of Kr. When these $^{36}\text{Cl}/\text{Cl}$ ratios are compared to Cl concentration, an inverse relationship between Cl and $^{36}\text{Cl}/\text{Cl}$ ratio is apparent rather than a decay trend. Thus uncertainty about the amount and rate of subsurface Cl addition render the ^{36}Cl decay aspects of this study liable to ambiguous interpretation like the GAB discussed above.

Cresswell et al. (2000) present ^{36}Cl data from three deep wells and a spring from the Kathmandu Basin in Nepal and make some preliminary estimates of groundwater age. of between 200 and 400 ka. The ages are considered feasible within the hydrogeological context. A slight increase in Cl^- concentration with decrease in $^{36}\text{Cl}/\text{Cl}$ is, however, evident from this limited data set. Given this flag for potential difficulties of interpretation of ^{36}Cl results (e.g. Andrews and Fontes, 1992) and the lack of chemical or other isotope data to corroborate this story, the estimate of groundwater age is rightly considered provisional.

Zhou et al. 2001 report on ^{36}Cl results measured in the Hebei Plain in eastern China. Differences in $^{36}\text{Cl}/\text{Cl}$ ratio measured at surface (62×10^{-15}) and deep borehole (23×10^{-15}) were used to calculate that some groundwater in Quaternary sediments is over 250 ka old. This interpretation relies upon the assumption that ion filtration is a valid process (see Fig 7.2) that can reconcile differences in chloride concentration between some samples. This assumption and the fact that only four analyses are available make this calculation of groundwater age potentially dubious as other processes such as addition of subsurface chloride may equally well explain these limited results. It may be that ongoing work on these heavily stressed aquifers in the North China Plain (e.g. Foster et al., 2004) will refine the use ^{36}Cl decay dating in this region.

8.2.3.3. Australian Studies

8.2.3.3.1. Attempted ^{36}Cl decay dating

Several other Australian studies apart from the GAB and Murray Basin discussed above have attempted to date groundwater using ^{36}Cl decay as a chronometer.

In the Northern Territory of Australia ^{36}Cl results from Amadeus Basin aquifers have been reported by Jacobson et al. (1994) and Cresswell et al. (1999b). Age dating of groundwater is basically attempted by comparing the $^{36}\text{Cl}/\text{Cl}$ ratios from shallow bores with $^{36}\text{Cl}/\text{Cl}$ results obtained from deep petroleum exploration wells that intercept the same aquifer at depth. While ages of several hundreds of thousands of years are determined, which is in keeping with the known flow dynamics of this basin, there is a readily observable inverse relationship between $^{36}\text{Cl}/\text{Cl}$ ratio and Cl concentration which needs to be accounted for. Cresswell et al. (1999b) deal with this potential interpretation problem by estimating a rate of addition of subsurface chloride so ^{36}Cl decay dating can be attempted. A mixing rate of 0.2 mg/L of Cl^- per 1000 years is assumed and plotted as a best fit to link data plot points from shallow and deep samples on a $^{36}\text{Cl}/\text{Cl}$ versus Cl content diagram. No heed is given to any of the concerns raised by some workers (as discussed above for the GAB) about the validity of ^{36}Cl decay dating when subsurface additions of chloride are present. While the air drilled petroleum exploration holes in the Amadeus Basin gave a rare opportunity to sample deep aquifers, the significant but difficult to quantify addition of surface make – up water and compressed air during drilling has the potential to complicate the interpretation of ^{36}Cl results. This is evidenced by the results of some the samples taken while drilling the Palm Valley 8 exploratory gas well. At 990 m depth a concentration of ^{14}C equal to 29 pmc (i.e. less than 30 ka old) was recorded (NT Government bore file RN 16018), however, the 897 m sample above is recorded to have a $^{36}\text{Cl}/\text{Cl}$ of 99×10^{-15} which is taken to indicate an age of several 100 ka using regional shallow bore $^{36}\text{Cl}/\text{Cl}$ ratios of around 176×10^{-15} as an input ratio, as did Cresswell et al. (1999b). The 990 m sample was the lowest conductivity water produced from the hole and was thought at the time of sampling to be the least contaminated by drilling fluids when drilling was monitored in 1994 (NTG, Water Resource Branch file No. 60.16). The

sample at 928m recorded a ^{14}C concentration of $< 2\%$ pmc (i.e. beyond detection range of ^{14}C). The difficulty in deciphering these results, where apparent age is not correlated to depth, highlight the difficulties in obtaining uncontaminated groundwater samples during potentially favourable air drilling of petroleum wells. While air drilling of petroleum wells in the consolidated sediments of the Amadeus Basin gives a rare opportunity to access deep aquifers, the attempts to sample groundwater as a piggy back operation to petroleum drilling has resulted in some doubts of groundwater sample integrity. Incorporation of groundwater sampling into the well prognosis (e.g. packer test of aquifer) from the outset is probably the only, but expensive, way to ensure groundwater sample integrity from deep aquifers intersected by hydrocarbon drilling operations.

Cresswell et al. (1999a) report on $^{36}\text{Cl}/\text{Cl}$ results from bores spread over a wide area of arid country west of Alice Springs. Samples for ^{36}Cl analyses were opportunistically obtained during a survey of drinking water quality from bores in the region. Consequently no specific hydrogeological system was investigated by such methods as sampling sequential bores down dip in the same aquifer. Nevertheless, some preliminary conclusions on groundwater age based on apparent ^{36}Cl decay were attempted. $^{36}\text{Cl}/\text{Cl}$ ratios from 18 bores are observed to roughly fall into two distinct populations with $^{36}\text{Cl}/\text{Cl}$ ratios of 170 and 205×10^{-15} . The higher value was taken as an indication of input $^{36}\text{Cl}/\text{Cl}$ ratio in the area and the lower group to represent groundwater 80 ka old, which may match an interglacial pluvial event. While no inverse trend of $^{36}\text{Cl}/\text{Cl}$ ratio and Cl^- is apparent from these results, chlorinity varies markedly and different degrees of evaporation for each sample needs to be assumed (rather than subsurface Cl^- addition etc) to assess groundwater age from these results. These assumptions, discordance with ^{14}C data (all samples have measurable ^{14}C) and measured atmospheric $^{36}\text{Cl}/\text{Cl}$ ratio in the region (325×10^{-15} , Keywood, 1995), mean reliability of this interpretation is uncertain. Other interpretations such as all water is less than 40 ka old as indicated by ^{14}C results and $^{36}\text{Cl}/\text{Cl}$ variation is due to differing amounts of contamination by subsurface Cl or ^{36}Cl addition remain valid alternatives. Interpretation of this data set may benefit from consideration of additional chemical data and better integrating physical hydrogeological factors.

Jacobson et al. (2000) present some ^{36}Cl and other isotope data from Cainozoic and underlying Palaeozoic aquifers near Ayers Rock (Uluru), Northern Territory. Considerable discordance of ^{14}C and ^{36}Cl indicated ages from most samples were taken to indicate subsurface mixing of different ‘vintages’ and possibly some diffusion of modern ^{14}C below the water table. A few samples with ^{14}C concentration below detection limits gave the slightly lowest $^{36}\text{Cl}/\text{Cl}$ ratios and these data allowed an age of over 200 ka to be calculated for some samples. The plots of ^{36}Cl data from this region on ^{36}Cl atoms against Cl (mg/L) and $^{36}\text{Cl}/\text{Cl}$ against Cl (mg/L) charts did not, however, show any clear ^{36}Cl decay trend. On comparison with the processes charts shown in Figure 7.2, data points from this study are seen to plot along a dilution – evaporation process line. This lack of clear ^{36}Cl decay trend line and discordant isotope ages make interpretation of these results complicated. While it may be that these data are a consequence of complex hydrogeology in the region, a better understanding of chloride flux in the subsurface would aid interpretation here.

Bureau of Rural Sciences (2001), as part of an assessment of low permeability strata to house nuclear waste in the centre of South Australia, measured ^{36}Cl in nine bore holes. Due to a large variation in chlorinity between samples a ^{36}Cl atoms against Cl (mg/L) plot showed these samples to be distributed along a dilution – evaporation line. Although such a trend usually precludes ^{36}Cl decay dating, the authors note that if two distinct evaporation trends are assumed, then a difference of 100 ka is indicated between trend lines. As no consideration of possible subsurface addition of chlorides or how these samples maybe hydraulically related is undertaken, the reliability of such an interpretation is uncertain. Further work is needed to confirm these estimates of groundwater ages.

8.2.3.3.2. *Unsuitable for ^{36}Cl decay dating*

Several previous Australian studies have considered uncertainties on sources and sinks of subsurface chloride and/or lack of great hydraulic age to preclude the use ^{36}Cl as a groundwater dating tool.

Commander et al. (1994) and Turner et al. (1995) present some ^{36}Cl results from Palaeochannel aquifers in the Goldfields region of Western Australia but found probable mixing of remobilised playa salts in these hyper-saline aquifers hindered any quantitative interpretation of ^{36}Cl results.

Hostetler (2000, 2002) presents some ^{36}Cl data from shallow bores in the Alice Springs region of the Amadeus Basin. Because there is no observed relationship between ^{14}C and $^{36}\text{Cl}/\text{Cl}$ he considers groundwater too young to be dated by the ^{36}Cl decay method. No decay trend is evident from $^{36}\text{Cl}/\text{Cl}$ v Cl plots of these analyses, though as different unconnected aquifers have been sampled in part, this does not necessarily preclude ^{36}Cl decay.

Turner et al. 1992 found $^{36}\text{Cl}/\text{Cl}$ ratios in shallow groundwater with variable chlorinity in some inland catchments in NSW, Australia to all be of a similar magnitude and hence not be suitable for ^{36}Cl decay dating. The magnitude of $^{36}\text{Cl}/\text{Cl}$ ratios was noted to be higher than the expected atmospheric ratios for this latitude; however, subsequent upwards revision of expected atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios in Australia (Keywood, 1995, 1998) may now mean most of these data are closer to expected atmospheric ratios. Nevertheless ^{36}Cl decay dating of groundwater in these small catchments is unlikely to be feasible as groundwater is thought move very rapidly (Shekarforoush, 2000).

Thorpe and Davidson (1990) measured $^{36}\text{Cl}/\text{Cl}$ ratios from confined aquifers in the Perth Basin, Western Australia and found that the $^{36}\text{Cl}/\text{Cl}$ ratios were very low (< 10 by 10^{-15}). As these values could approximate both the input $^{36}\text{Cl}/\text{Cl}$ atmospheric ratio at this coastal setting and expected in situ ^{36}Cl production from sandstones, no ^{36}Cl decay dating of groundwater was possible.

Jacobson et al. (1991) ran a few samples for ^{36}Cl determination from various depths in a couple of exploratory bores drilled at Lake George near Canberra, Australia. They concluded no ^{36}Cl decay ages were determinable as mixing and dilution rather than ^{36}Cl decay were the dominant processes evident from $^{36}\text{Cl}/\text{Cl}$ against Cl^- and ^{36}Cl against Cl plots. Interpretation was further complicated as the sample with the lowest $^{36}\text{Cl}/\text{Cl}$ ratio, at 100m in bore 353, had a significant tritium value compared to other samples.

While some of these studies may benefit from additional data and further examination of local hydrology, they illustrate that the ^{36}Cl method is certainly not suitable in all locations.

8.2.4. Discussion

Table 8.1 shows a summary of the groundwater ^{36}Cl studies discussed in the preceding sections. There are, comparatively, a large proportion of Australian studies listed in this table. This is probably both a reflection of ready access to some unpublished data sets from within Australia and the keen interest in potentially old groundwater resources in this arid continent. Apart from the Australian studies the other studies cited in this table are readily obtained from publications. Some of these international studies are classified as being occurrences where the application of ^{36}Cl decay dating was considered unsuitable for a variety of reasons. These studies have not been discussed in the text due to brevity considerations but are shown in Table 8.1 to complete the review of ^{36}Cl groundwater literature.

Figure 8.1 shows a plot of $^{36}\text{Cl}/\text{Cl}$ versus chloride content for the studies that have been identified as attempting ^{36}Cl decay dating of groundwater. On comparison of this Figure with the process chart shown in Figure 7.2 it can be seen that apart from the data of Penny et al. (2003) no data set shows a clear ^{36}Cl decay trend. When these data are viewed with Cl concentration plotted on a log axis, as shown in Figure 8.2, it can be seen that the low chloride aquifer from Alabama (Penny et al., 2003) also does not show a ^{36}Cl decay trend.

For the purpose of comparison and to give a regional perspective for this study Figure 8.3 shows the results of all the Australian ^{36}Cl groundwater studies cited above. On comparing this figure with the process chart shown in Figure 7.2 it can be seen that no Australian study cited shows a clear ^{36}Cl decay trend. Many factors such as the addition of chloride, dissolution of vadose chlorides and variations in Cl concentration due to different evapotranspiration effects have been invoked to estimate a ^{36}Cl decay age in some of these instances.

Table 8.1 ³⁶Cl groundwater studies discussed in the text

Reference	Location	Study	Lithology	Clear ³⁶ Cl decay trend ?	comments
³⁶Cl decay age estimated					
Cresswell et al., 1999a	Australia	Westen Water	sed's/ volcanic	no	regional study, samples not necessarily hydraulically connected.
Cresswell et al., 1999b	Australia	Deep Amadeus	sed's	no	deep aquifers sampled via gas well drilling, sample integrity not ideal?
Mazor, 1992	Australia	Murray Basin	sed's	no	Re-Interpretation of Davie et al., 1989 data
Love et al., 2000	Australia	GAB western	sed's	no	Part of Nth transect shows decay trend, see also ⁸¹ Kr by Lehmann et al., 2003.
Bentley et al., 1986.	Australia	GAB	Sed's	no	hydraulic indication of old groundwater, ³⁶ Cl/Cl approaches secular equilibrium as above
Torgersen et al., 1991	Australia	GAB	sed's	no	Compilation of all chemical and isopic data from GAB
Radke et al., 2002	Australia	GAB	sed's	no	mixed lithology, clays sands
BRS, 2002	Australia	Radwaste, S.A.	sed's	no	
Sturchio et al., 2004	Egypt	Nubian Aquifer	sed's	no	Deep confined aquifer, old water ⁸¹ Kr used to help calibrate age
Cresswell et al., 2001	Nepal	Kathmandu Basin	sed's	no	Sand and clay interbeds with some lignite, very low Cl in part
Dowgiallo et al., 1990.	Poland	Mazowsze Basin	sed's	no	multi layered lithology, Cl origins potentially complex
Phillips et al., 1986b	Canada	Milk River	sed's	no	Large basin, hydraulic data indicate old water
Nolte et al., 1991	Canada	Milk River	sed's	no	as above
Zhou et al., 2001	China	Hebei Plain	sed's	no	Limited sample size, preliminary results?
Penny et al., 2003	USA	Alabama	sed's	no	Mixed lithology Basin, subsurface halite known in region, low Cl content
Kaufman et al., 1990	Africa	Magadi- Natron	sed's/volcanic	no	Infilled basaltic graben, large variation in Cl content
no ³⁶Cl decay age considered feasible					
Davie et al., 1989	Australia	Murray Basin	sed's	no	subsurface Cl input identified, ³⁶ Cl data elucidates recharge, contrast Mazor, 1992
Kellett et al., 1990	Australia	Murray Basin	sed's	no	as above
Commander et al., 1994	Australia	Goldfields WA	sed's	no	Mixed sed lithology of paleo channels, salt lakes hydraulically connectec
Turner et al., 1992	Australia	NSW Murray Basin	sed's	no	Little variation in ³⁶ Cl ratio
Turner et al., 1995	Australia	Goldfields WA	sed's	no	as above
Hostettler, 2002	Australia	Amadues	sed's	no	regional study, samples not necessarily hydraulically connected.
Jacobson et al., 1991a	Australia	Lake George	sed's	no	Mixed lithology, Cl decrease with depth, playa brine mixing
Andrews et al., 1994	England	Midlands Triassic	sed's	no	Subsurface mixing of Cl identified
Purdy et al., 1996	USA	Aquila	sed's	no	³⁶ Cl increases along flow line (Bomb ³⁶ Cl ?)
Moran and Rose, 2003	USA	Nevada	sed's	no	Subsurface input of Cl identified
Le Gal la Salle et al., 1995	Niger	Illumenden Basin	sed's	no	Data plots indicate near secular equilibrium, subsurface Cl input also identified

Table 8.1 ³⁶Cl groundwater studies discussed in the text

Reference	Location	Study	Lithology	Clear ³⁶ Cl decay trend ?	comments
Fontes et al., 1984	Algeria	Sahara	sed	no	likely hypogene production and subsurface Cl input identified
Yecieli et al., 1996	Israel	Dead Sea	sed	no	Mixing of rain water and ancient playa brines indicated as source of Cl in Dead Sea
Balderer et al., 1997	Hungary	great hungarian plain	sed	no	Input of subsurface Cl identified
Examples of epigene production effect					
Andrews et al., 1986	Sweden	Stripa	hard		Determined neutron flux of granite, ³⁶ Cl data used to trace Cl origins
Aquilina et al., 2002	France	Thau lagoon	hard/ carbonate	no	Ingrowth of hypogene ³⁶ Cl used to estimate age
Balderer and Synal, 1996	Turkey	Antolia	sed & hard	no	hypogene ³⁶ Cl used as tracer to study origin and mixing of groundwater
Gascoyne et al., 1994	Canada	Manitoba	hard	no	Hypogene production precludes decay dating, ³⁶ Cl useful as tracer
Thorpe and Davidson, 1990	Australia	Perth Basin	sed	no	³⁶ Cl/Cl ratios close to both atmospheric and secular equilibrium
Mahara et al., 2001	Sweden	Aspo	hard	no	no ³⁶ Cl decay age possible due to hypogene affect
Lehmann et al., 1990	Switzerland	Nagra	hard	no	no ³⁶ Cl decay age possible due to hypogene affect
Rao et al., 1996	USA	Vallero? Caldera	hard/ carbonate	no	Indication of age from hypogene production, ³⁶ Cl useful tracer to study Cl origins
Fehn et al., 1994	USA & Germany	Rochester program	sed & hard	no	Ingrowth of hypogene ³⁶ Cl used to estimate age
Lippmann et al., 2003	South Africa	Witwatersand	sed	no	Ingrowth of hypogene ³⁶ Cl used to estimate age
Examples of Bomb ³⁶Cl as tracer					
Herczeg et al., 1997	Australia	Murray Basin/ Gambier L/s	carbonate	n/a	Recharge study, high ³⁶ Cl/Cl taken to indicate bomb ³⁶ Cl affect
Cook et al., 1994	Australia	Murray Basin/	sed	n/a	recharge study
Murad and Krishnamurthy, 2004	UAE	North Oman Moutains	hard & sed	n/a	Bomb ³⁶ Cl used as tracer, mixing of groundwater identified
Cambell et al., 2003	USA	Yucca Mountain	volcanics	n/a	Tracer study, deep penetration (>200m) of modern rain indicated in vadose zone
Liu et al., 1995	USA	Arizona	soil	n/a	recharge study
Scarlton et al., 1990	USA	Texas	sed	n/a	recharge study
Norris et al., 1987	USA	Yucca mountains	soil	n/a	recharge study
Larsen et al., 2003	Zimbabwe	Zambesi	sed	n/a	recharge study, inconclusive

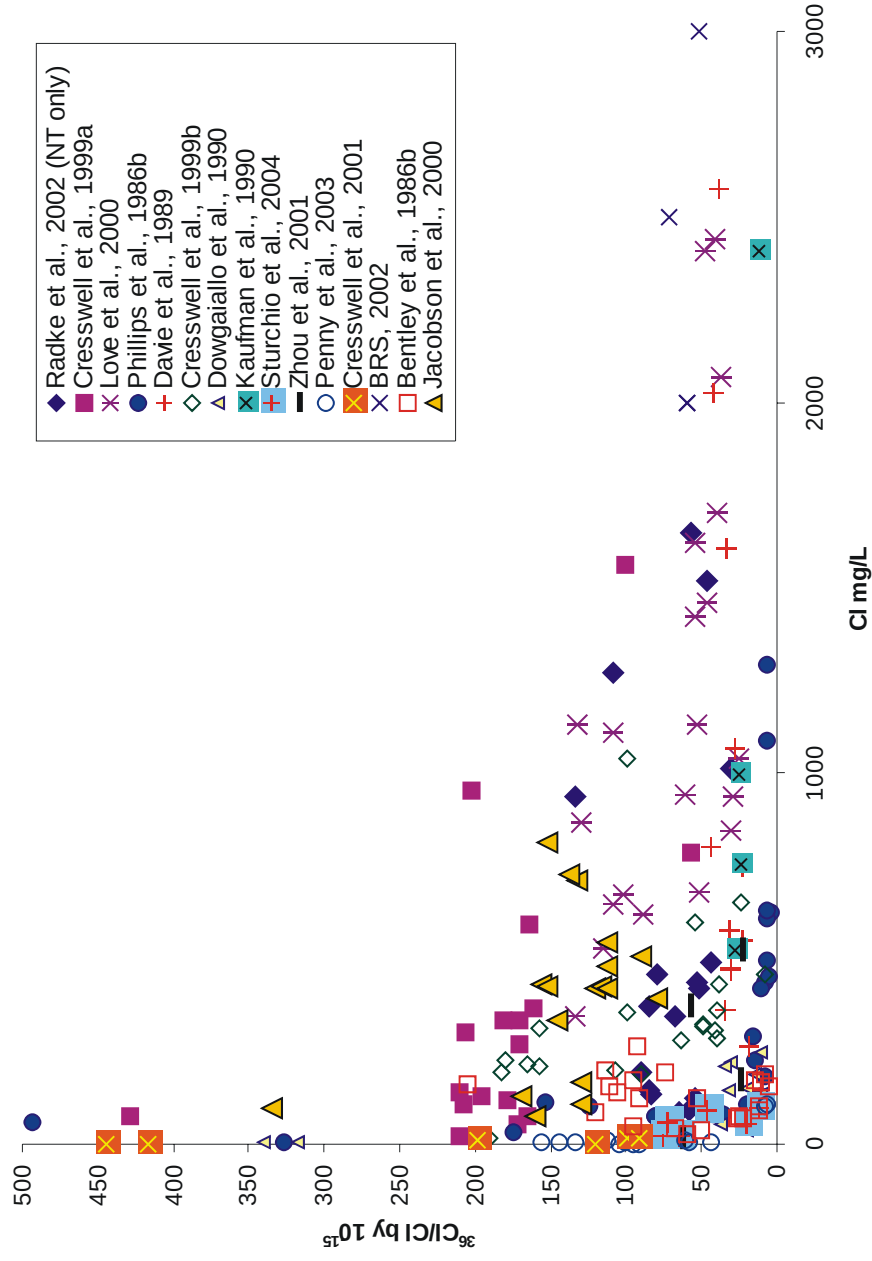


Figure 8-1 . $^{36}\text{Cl}/\text{Cl}$ versus chloride content for the studies that have been identified as attempting ^{36}Cl decay dating of groundwater.

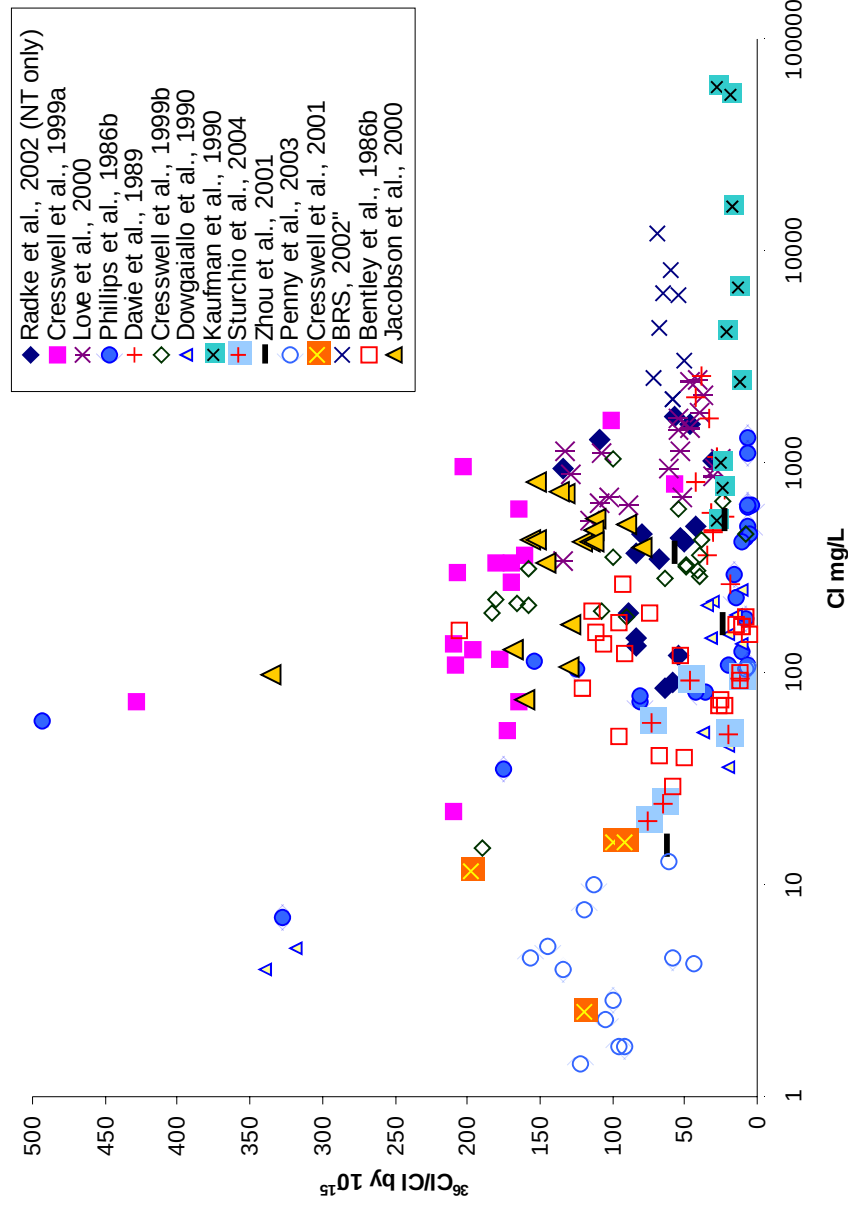


Figure 8-2 The same data set as Fig. 8.1 with $^{36}\text{Cl}/\text{Cl}$ versus the log of Cl^- concentration. On comparison with Figure 7.2a it can be seen that no clear decay trends are apparent. Note a) for the sake of clarity only the NT portion of the GAB (Radke et al., 2000) data set has been plotted, and b) the Bureau of Rural Science (2002) data has been estimated from graphical plots only and may therefore be slightly inaccurate c) The process trends will be slightly different because of the logarithmic Cl^- concentration scale.

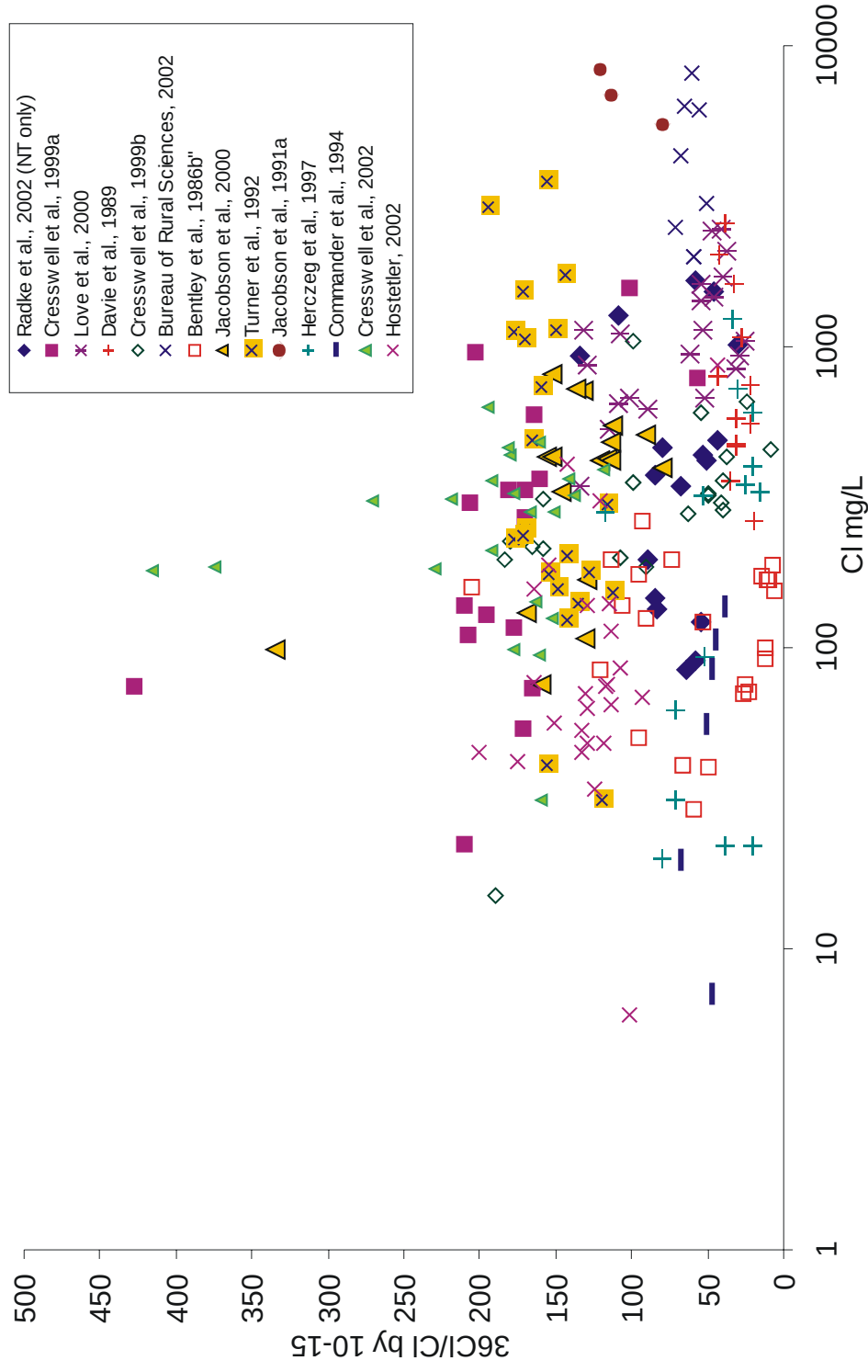


Figure 8-3 $^{36}\text{Cl}/\text{Cl}$ versus the log of Cl^- concentration for all of the Australian ^{36}Cl groundwater studies cited in the text. Again on comparison with Figure 7.2a it can be seen that no clear decay trends are apparent.

However, from the data shown in Figure 8.3 and discussion presented above regarding interpretation of ^{36}Cl decay data (e.g. considerations of Andrew and Fontes, 1992) the lack of a clear decay trend in these studies renders any such age estimate ambiguous.

8.2.5. Conclusion

Previous attempts at ^{36}Cl decay dating of groundwater have been controversial. Uncertainties on the provenance of subsurface chlorides often manifested as an observed inverse relationship between $^{36}\text{Cl}/\text{Cl}$ ratio and chloride concentration along flow path has been the chief concern. There seems to be two schools of thought – those that think ^{36}Cl decay dating is still possible even when well over 50% of Cl is derived from subsurface sources post recharge and those that think indications of subsurface chloride additions preclude the use of the ^{36}Cl decay dating method.

In nearly every instance where ^{36}Cl decay dating of groundwater has been attempted chloride to $^{36}\text{Cl}/\text{Cl}$ relationships are such that no clear decay trend is evident. In some instances supporting hydrologic evidence such as decrease in ^{36}Cl content along flow paths perceived to have very slow flow rates exists, however, there is a school of thought that doubt that a ^{36}Cl decay age has been proved. In short, where ^{36}Cl decay dating has been attempted to date, results are ambiguous.

8.3. Comparison to other studies

The work at Palm Valley, central Australia, outlined above and summarised by Wischusen et al. (2004), presents a suite of ^{36}Cl data showing a distinct decay trend (Figs 7.5 & 7.6). No subsurface additions of ^{36}Cl or Cl are apparent and results are consistent with a viable flow model (Fig 9.2). When these results are compared to other ^{36}Cl decay studies, as shown on Figure 8.4, it can be seen that the Palm Valley results stand alone in displaying a clear decay trend. This pattern is also observed when results are compared to data from all other previous Australian studies Figure 8.5.

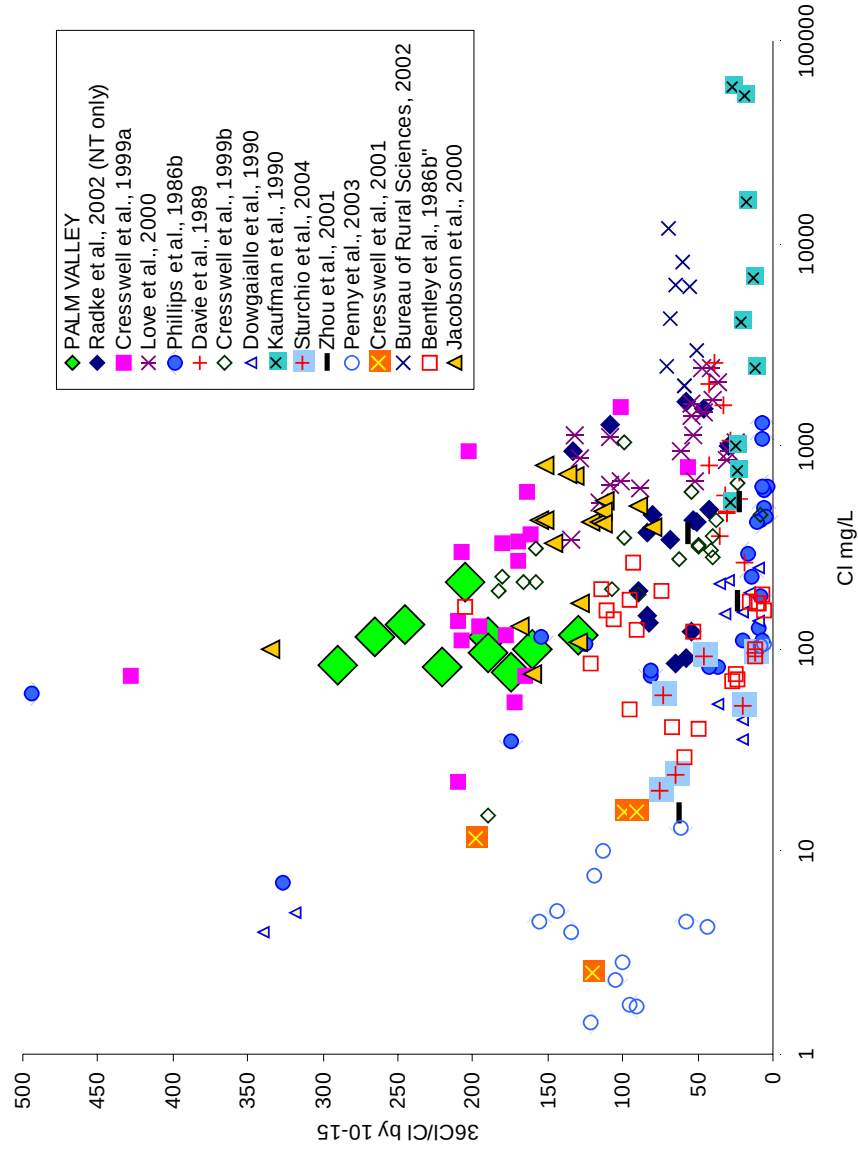


Figure 8-4 $^{36}\text{Cl}/\text{Cl}$ versus the log of Cl^- concentration for the studies that have been identified as attempting ^{36}Cl decay dating of groundwater (i.e. Fig 8.2) compared to the results of this study at Palm Valley On comparison with Fig. 7.2a it is evident that the results from Palm Valley are alone in displaying a clear (vertical) decay trend. Note a) for the sake of clarity only the NT portion of the GAB (Radke et al., 2000) data set has been plotted, and b) the Bureau of Rural Science (2002) data has been estimated from graphical plots only and may therefore be slightly inaccurate.

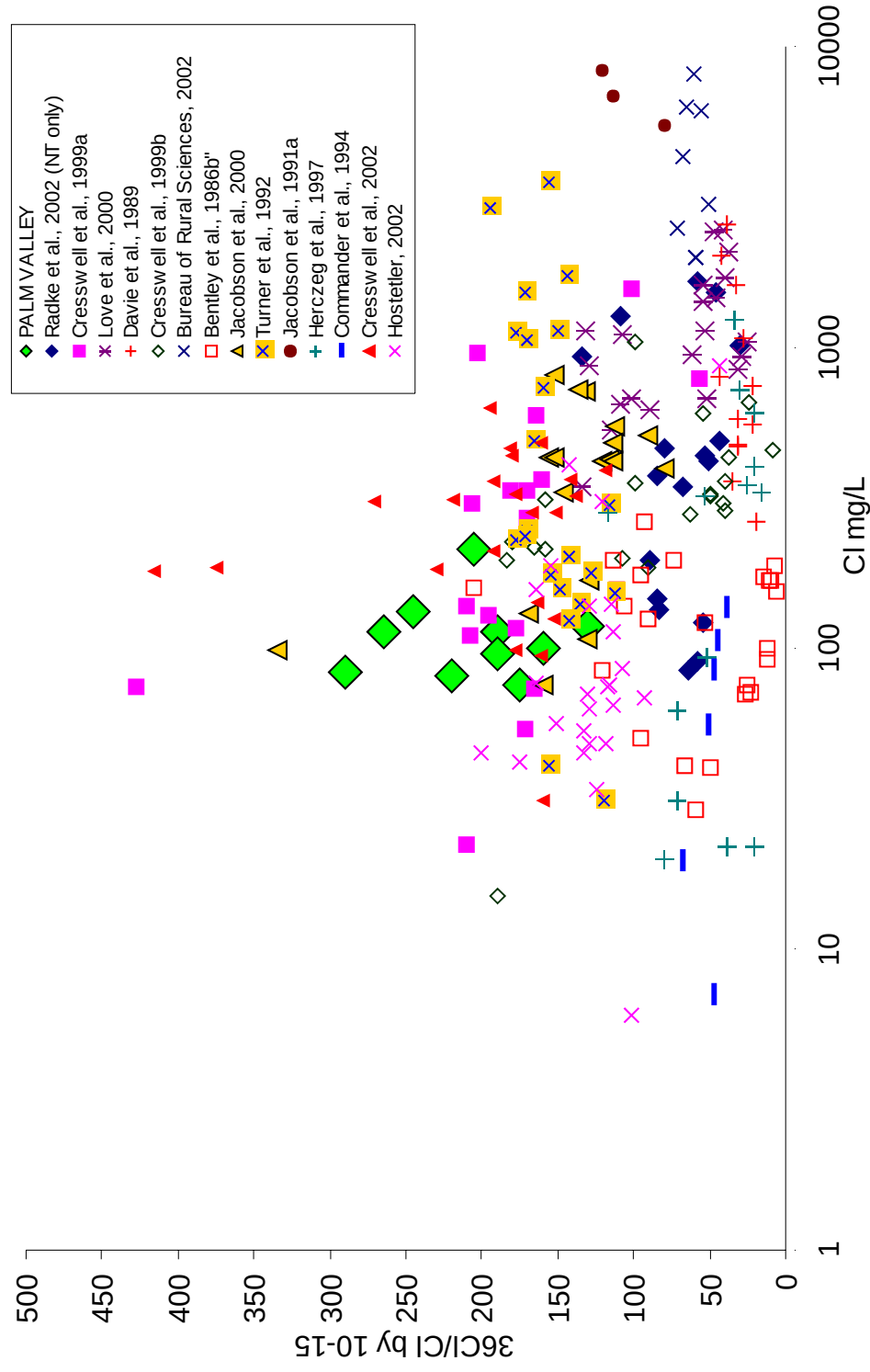


Figure 8-5 $^{36}\text{Cl}/\text{Cl}$ versus the log of Cl^- concentration for all of the Australian ^{36}Cl groundwater studies cited in the text (i.e. Fig 8.3) compared with the results from Palm Valley. Again on comparison with Figure 7.2a it is evident that the results from Palm Valley are alone in displaying a clear (vertical) decay trend.

While it may be that further work or alternative hypotheses are developed to refute this interpretation, it is worth considering why this study, seemingly rare among ^{36}Cl decay studies, allows an unambiguous interpretation of ^{36}Cl decay.

8.3.1. Discussion

Most ^{36}Cl decay studies (Table 8.1) have, naturally enough, been orientated to aquifers with potential for old groundwater. This has meant that large confined sedimentary aquifers have usually been sampled (e.g. GAB, Milk River). Given bores in such environments are deep and expensive to drill, existing water supply bores comprise most of the sample points. These bores are therefore constructed to maximise yield rather than provide a sample window to discrete aquifer horizons.

Thus in many instances sample integrity of ^{36}Cl samples cannot be assured as doubts exist as to which formation(s) have provided chloride to the sample. For example, bore screens may be set so that several lithologies are intersected and/or in the case of gradational aquifer – aquitard contacts found in many basins, inadvertently set adjacent intra aquitard sand lenses rather than the main aquifer. If only some samples within a suite of analyses contain a mix of water and/or chloride derived from two sources with different $^{36}\text{Cl}/\text{Cl}$ ratios due to age of chloride or hypogene production rates, the interpretation of results can be difficult or at least ambiguous. This is because a plot of data points on any $^{36}\text{Cl}/\text{Cl}$ against Cl or ^{36}Cl diagram would then be expected to show a scatter rather than any clear trend such as decay or solely addition of dead chloride.

Furthermore, the intercalation of aquitards and aquifer horizons in many sedimentary settings means natural leakage of chlorides from aquitards into aquifers can be ongoing along flow paths, which adds further potential complication to interpreting ^{36}Cl results. Fabryka-Martin et al. (1991) note that even intra aquifer low permeability horizons are probably the source of the increasing halide concentrations observed along flow paths in the Milk River Aquifer that complicate the interpretation of ^{36}Cl results.

Another potential complication is the fact that many basins previously sampled are stressed due to groundwater extraction. This may then result in the equilibrium that

existed for many years under natural conditions being upset. Such a change of conditions may alter rates of leakage of chlorides from aquitards at various parts of an aquifer system, which could also complicate interpretation of results.

Another scenario, which may also cause problems, is when chloride concentrations vary markedly due to differing concentration by evapotranspiration effects at the time of recharge. For instance, an older more evaporated parcel (low $^{36}\text{Cl}/\text{Cl}$, high Cl) of water further along the aquifer flow path when plotted with modern less evaporated water parcel nearer the start of the flow path (higher $^{36}\text{Cl}/\text{Cl}$, lower Cl) may give the impression of addition of dead chloride when plotted on a $^{36}\text{Cl}/\text{Cl}$ versus Cl process chart. Such considerations are why tracers indicative of chloride provenance such as Cl/Br ratios are recommended (e.g. Davis et al., 1998a) accompaniments to ^{36}Cl decay studies.

Recharge mechanisms may also be a relevant factor. In some instances, such as large arid inland sedimentary basins where direct recharge rates are low, it may be that very old chloride held in a thick vadose zone slowly (and erratically?) mixes along groundwater flow paths mainly derived from indirect recharge along basin margins or streams. The potential for such an effect to complicate the determination of subsurface chloride and stable isotope origin is developed in detail by Wischusen (1998) when discussing groundwater chemistry of the Cainozoic Basins a few hundred kilometres north of Palm Valley. The hazard of vadose zone salts contaminating groundwater systems is demonstrated by a study in the semi arid Murray Basin of south eastern Australia by Leaney et al. (2003). They note that increased mobilization of vadose salts due to enhanced recharge rates following land clearing may result in the salinization of important underlying fresh groundwater resources. Direct recharge rates are thought to be very low in some inland Australian Basins. For example Kruseman (1997), in a discussion on the Cainozoic Western Murray Basin in South Australia, notes the water flux of very saline water (chloride 10000 to 20000 mg/L), below 2m depth under eucalypt vegetation and above the 30m deep watertable, to be between 0.04 and 0.06 mm/yr (about 1m in 20000 years). So in some regions it is feasible that very old (100+ ka) chlorides slowly leak into much younger, saturated groundwater flow paths. Thus old stored vadose zone chlorides derived from a slow direct recharge mechanism may also have the potential to complicate the interpretation of ^{36}Cl decay results in some

instances. While this consideration may also be a factor in considering ^{36}Cl results for the Hermannsburg Sandstone, the stable isotope data (Section 6.1.2) that plot along the LMWL indicate little evidence of an evaporation effect. Hence, assuming some evaporation effect would be discernible from stable isotope data plots if a direct recharge mechanism contributed significantly to groundwater composition, there is no evidence that a direct (vadose zone) recharge mechanism contributes chlorides to the Hermannsburg Sandstone. However, it is noted that apportioning the contribution of various recharge mechanisms to an aquifer is a very difficult task (e.g. Lerner et al., 1990). Hence measuring the effect of differing recharge mechanisms on $^{36}\text{Cl}/\text{Cl}$ ratios in an aquifer is also likely to be a difficult task.

All samples at Palm Valley are taken from the Hermannsburg Sandstone, an extensive, thick (> 900m) outcrop of Devonian litharenite. This unit is described as a monotonous sequence of fine to very coarse grained sandstones with only very rare sandy siltstone interbeds (Jones, 1972). The high energy deposition environment (in response to nearby orogenic event) of this sandstone means apart from occasional mud clasts that virtually no aquitard material is associated with this unit. As all samples at Palm Valley are taken from areas of outcrop, the nearest significant aquitard occurs in the underlying Parke Siltstone formation, many hundreds (>500) of metres below sampling points. Thus, in effect, samples from this study are sourced completely from only one lithological unit, mixing of waters or chlorides derived from different lithologies are unlikely. Consequently, integrity of ^{36}Cl samples is assured in this instance.

The demonstration of a distinct suite of ^{36}Cl decay data from such a setting suggests that to be given a chance to assess ^{36}Cl decay, future studies should strive to sample water derived from only one common lithological unit. In many previous study sites however, ensuring such integrity of samples may prove very expensive and logistically challenging (e.g. electric logging, setting packers etc).

8.3.2. Conclusion

Determination of $^{36}\text{Cl}/\text{Cl}$ ratios has been likened to identifying one particular sugar grain from a room full of sugar. Consequently, it stands to reason that ^{36}Cl decay dating of groundwater is likely to be unusually sensitive to contamination by outside aquifer sources of chloride. Consequently, all efforts to minimise potential ambiguity on the

provenance of chlorides including maintaining sample integrity whenever possible seem justified. While such measures cannot necessarily counter unfavourable conditions such as distribution of lithologies, disruption of hydraulic equilibrium due to extraction or additional ^{36}Cl production factors, the successful application of the ^{36}Cl decay method at Palm Valley shows that ^{36}Cl decay dating can be a viable tool for studying groundwater systems.

9. Discussion

9.1. Flow

9.1.1. Flow threshold?

The isotope and hydraulic indicators of old groundwater in aquifers raises the question of whether groundwater actually flows or whether groundwater age is a result of zero flow conditions. For instance there is some speculation that there may be a threshold gradient in some media below which groundwater does not flow (e.g. Neuzil, 1986; Bernadiner and Protopapas, 1994). Similarly, it is also noted that groundwater gradients in some instances may be the result of coupled flow (an osmosis and ultrafiltration effect) or even geologic factors such as subsidence. Under such conditions non-Darcian behaviour (i.e. no direct proportionality between flow and groundwater gradient) might be expected (Neuzil, 1986).

While feasible mechanisms to cause such effects can be speculated upon, there is little or no experimental evidence to prove them. This is because the theoretical conditions for such phenomena (coupled flow etc) cannot be readily reproduced or measured in a laboratory due to the very low hydraulic conductivities and gradients involved. Neuzil (1986) reports experiments that have recorded Darcian flow behaviour at hydraulic conductivities lower than 10^{-10} m/day, though this requires high artificially created gradients (around 10^2). In the 1930's a series of experiments conducted by the United States Geological Survey proved Darcian flow valid in porous media at gradients as low as 10^{-5} (Meinzer and Fishel, 1934; Fishel, 1935).

The simultaneous testing of flow at very low gradients and very low hydraulic conductivities remains problematical due to the prohibitive lengths of time involved. However, as the hydraulic conductivity and gradient measured at Palm Valley (i.e. $k > 10^{-5}$ m/day, gradient $> 10^{-4}$, Section 4.3 and Table 4.1) are well within the normal range expected for Darcy flow behaviour, it is reasonable to assume groundwater is indeed moving through the Hermannsburg Sandstone.

9.1.2. Diffusion from flow in fractured aquifers

Burton et al. (2002) note that using environmental tracers to date groundwater in fractured rock aquifers may be affected by dispersion and diffusion effects which can result in apparent tracer ages older than actual hydraulic age. In a detailed study using modern multi tracers (e.g. chlorinated fluorocarbons) and nested piezometers they note such effects are difficult to quantify and, in their study of the effects of aquifer anisotropy on groundwater ages in a fractured sedimentary aquifer in Pennsylvania, note while diffusion may effect computed ages by an unknown amount, the pattern of relative ages should not be altered.

Even though the Hermannsburg Sandstone is in part a fractured rock aquifer, effects of diffusion on apparent isotope age are not considered for this study. This is because, as detailed in Chapter 4, this aquifer is considered a granular porous medium of significant porosity and permeability that is only occasionally fractured. While some discrepancy between matrix and fracture groundwater residence times may exist in some instances, the use of the continuum approach for studying regional groundwater flow caters for this by conceptualising fractures as repeating large pores within the system (Fetter, 1993). Thus, radiocarbon data are not considered to have been affected by this phenomenon. Furthermore, any diffusion of Cl^- from fractures to the matrix is only likely to affect Cl^- concentration but not alter groundwater $^{36}\text{Cl}/\text{Cl}$ ratios. Hence indicated ^{36}Cl decay ages are unlikely to be affected by diffusion from flow through fractured media.

9.1.3. Flow model

9.1.3.1. Introduction

The data presented above shows the groundwater isotope data at Palm Valley to be discordant. That is, if groundwater simply moves from west to east down gradient, as shown in Figures 4.7 and 4.9, then an increase in groundwater age to the east should be

matched by decreasing activity of both ^{14}C and ^{36}Cl down gradient. For instance, bore RN 12024, which is 5 km away and down gradient from bore RN 4805, is more radioactive than the up gradient bore. Similarly, Road Spring has more ^{14}C but a lower $^{36}\text{Cl}/\text{Cl}$ ratio than RN 12024 further down gradient. It should be noted, that the variation in cation chemistry (Chapter 5) and the fact that many of the sites sampled are discharge zones, discounts the likelihood that these discordant data can be explained by simple mixing of old groundwater with modern rainfall. Given these considerations, a hydraulic model that accounts for the distribution of isotopically discordant groundwater along a seemingly continuous west to east regional flow system (Brown et al. 1990; see also Fig. 4.7) needs to be developed.

In the past such discordant isotope data in the same basin has been taken as evidence for compartmentalisation of groundwater and support for a lack of hydraulic continuity in some basins (Mazor, 1992). Toth (1995), however, has long argued that hydraulic continuity should exist even if low permeability barriers are present. In developing his argument that hydraulic continuity is expected even in large sedimentary basins, Toth (1995) describes groundwater flow within a unit basin model.

9.1.3.2. Toth unit basin model

In a unit basin three distinctly different groundwater flow regimes are noted - recharge, midline and discharge regions characterised by descending, lateral and ascending flow respectively. However, when significant topographical variations exist composite flow patterns are superimposed on the unit basin flow pattern (Toth, 1995).

An example of the composite flow pattern arising from topographical affects on a simple homogenous aquifer as constructed by Toth (1995 - also discussed by Freeze and Cherry, 1979) is shown in Figure 9.1 where the superposition of different scale (order) flow systems can be clearly seen. Given the topographic expression of the outcropping Hermannsburg Sandstone aquifer seen at Palm Valley (see Figs. 3.9 & 9.3) and in fact along the whole region of outcrop between Areyonga and Injarrtnama (Fig. 4.7), it can be reasonably assumed that groundwater flow patterns as least as complicated as that shown in Figure 9.1 exist within the Hermannsburg Sandstone if Toth's model holds true.

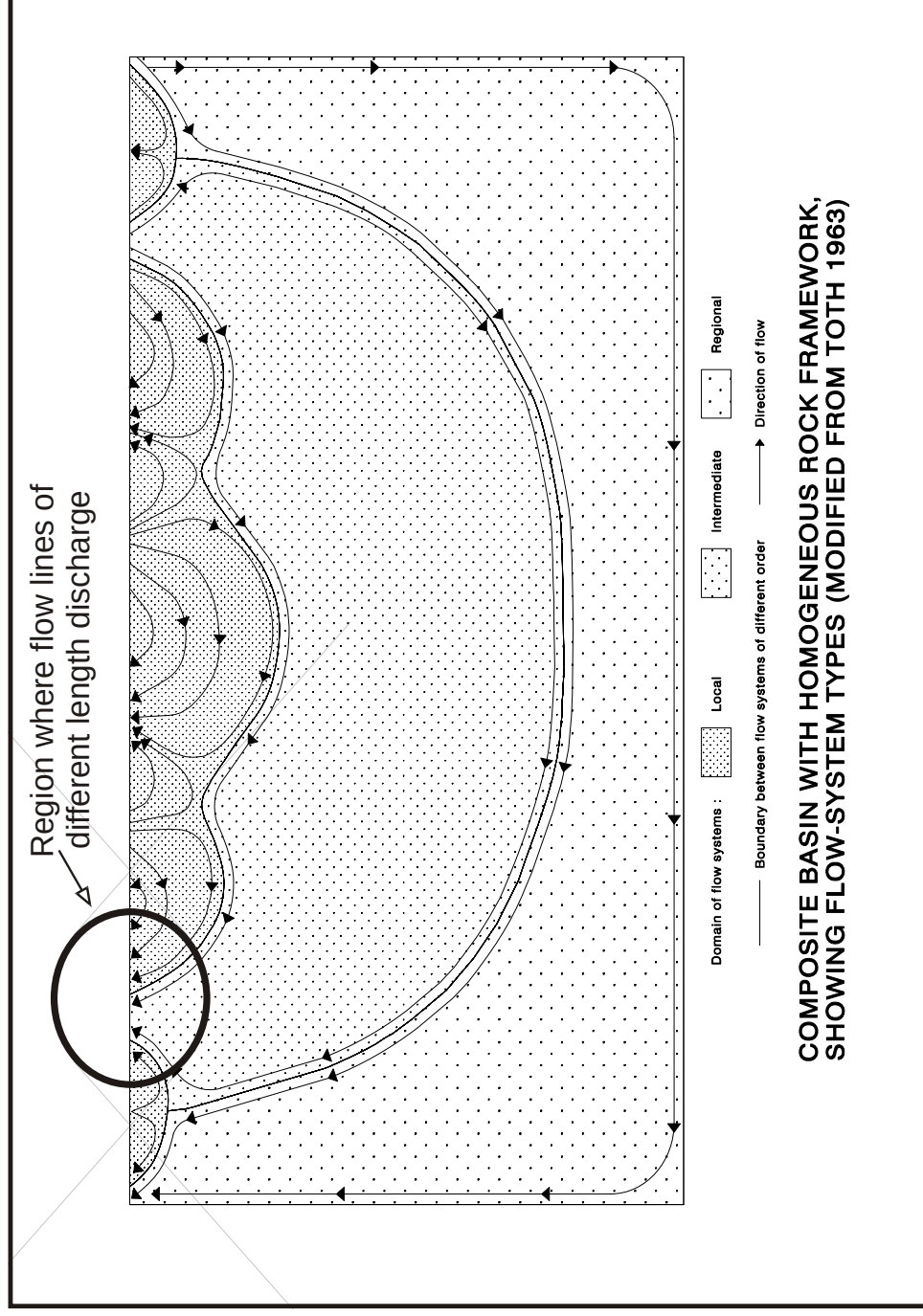


Figure 9-1 Composite Flow Patterns, Unit Basin Flow system in areas with significant topography. Schematic of composite flow patterns expected in a Unit Basin flow system in areas with significant local topography. The composite patterns are characterised by laterally alternating recharge-discharge regions where different domain flow systems may discharge in close proximity as shown in the area highlighted. After Toth, (1963, 1990, 1995).

As the Hermannsburg Sandstone is probably anisotropic (Brown et al. 1990) with hydraulic conductivity greater parallel to bedding, it is probable that flow patterns are more complex than shown in Figure 9.1. Indeed Toth (1995) and Ophori and Toth (1990) show variable flow length patterns calculated for heterogeneous aquifers with varying topography to be similar in style but more complex when compared to the homogeneous aquifer model. While this likelihood of more complex flow paths in the Hermannsburg Sandstone is noted, actual distribution of aquifer heterogeneity within the Hermannsburg Sandstone is unknown, thus the simpler homogeneous aquifer model is used for illustrating the potential complexity of flow patterns at Palm Valley.

Such an approach is considered valid by Domenico and Schwartz (1998, p83) when discussing regional flow in basins; “Although the ideal homogeneous case is contrary to field observations, it is merely a condition in the mathematical development, not an assumption necessary to the general validity of the theory. Further, the steady state solutions do not deny the existence of a fluctuating upper boundary of flow”.

While the validity of Toth's flow model is still debated (e.g. Mazor, 1996; Laing, 1996), the flow patterns outlined, even in a homogeneous aquifer, appear complicated enough to explain how seemingly discordant isotope ages could be found nearby in the same aquifer. For example the two bores RN 14616 and RN 4805, which have ^{14}C contents (Table 6.1) approaching levels unsuitable for dating (indicated age > 25 ka, Andrews and Fontes, 1993), have significantly different ^{36}Cl contents (Table 7.1). As these bores have much the same: depth of sample point, stable isotope composition, ^{14}C content and water type (bicarbonate waters with slightly different $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios, e.g. 1 and 1.3 respectively) it is readily conceivable that the different $^{36}\text{Cl}/\text{Cl}$ ratios observed at each bore are due to variations in groundwater flow path length.

Thus ^{36}Cl (groundwater age) variance may be explained as the sampling of either different flow cells or different flow paths at Palm Valley.

The regional topography shows the Palm Valley area (see Figs. 3.9 & 4.7 and Plate 3.3) to be part of the Palm Plain, a low-lying flat area surrounded by high hills. On a regional scale this suggests the whole Palm Plain has the potential to have areas where groundwater flow lines of various length may discharge in close proximity, as

illustrated in Toth's homogenous model, Figure 9.1. This scenario and relation of topography to the Palm Valley area is shown in Figure 9.3.

9.1.3.3. Conceptual model

Figure 9.2 shows a conceptual model based on Toth's work on groundwater flow in an isotropic aquifer with topographic effect at Palm Valley. It can be seen that even assuming a simple isotropic aquifer a flow pattern complicated enough to explain the seemingly discordant isotope data at Palm Valley may still result. Data from Palm Valley gas well number 3 shows water level within the Hermannsburg Sandstone at the apex of the Krichauff Range (see Fig. 9.3) at around 627m. This is in keeping with the conceptual model. If analogous flow systems are assumed to be equally likely at the other sites sampled along the large outcrop of Hermannsburg Sandstone (i.e. Hermannsburg, Areyonga, and Injarrtnama, Fig. 4.7), then the similar isotope and chemistry data observed at these sites (Tables 5.1 and 7.1) may be explained in the same manner.

In Section 4.3.5 an analytical model of flow in the Hermannsburg Sandstone is presented. A range of feasible average linear velocities, based on drilling data and pump tests, allow analytical modelling. For instance, if a low k value is adopted as being representative of the Hermannsburg Sandstone, as evidenced by some of the testing near Palm Valley (i.e. k = around 0.0025 m/day, see RN14161 and 4508 Table 4.1) a water age of 300 ka would (using Eq. 4.4 and the hydraulic properties presented in Section 4.3.5) represent travel through 9 km of the Hermannsburg Sandstone occurred before reaching Palm Valley. Alternatively, if an average linear velocity an order of magnitude larger (0.025 m/day i.e. around double the mean k value of 0.06 m/day calculated from all results shown in Table 4.1) is assumed, then a water age of 300 ka would represent travel through 90 km of the Hermannsburg Sandstone. It is entirely feasible given the extensive outcrop of Hermannsburg Sandstone (Fig. 4.7) that water could have recharged at a point 9 to 90 km away and is now discharging (or in a shallow bore) at Palm Valley. Any future numerical model that was developed for this area would also need to be based on these data. As there are no bore hydrographs at Palm Valley future numerical modelling would probably be a steady state, fairly broad

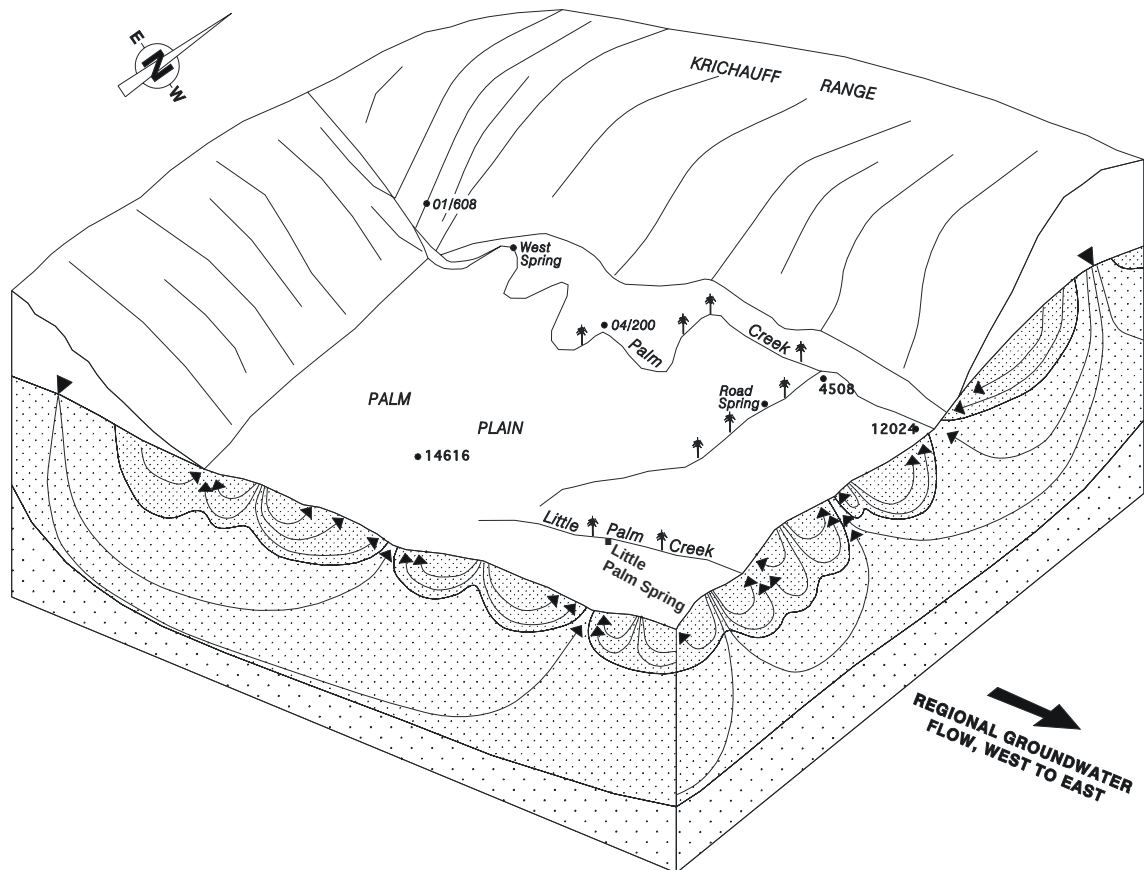
scale approximation and not necessarily much of an improvement on the existing modelling of Brown et al 1991.

The groundwater ages calculated from ^{36}Cl decay data are credible when compared to the hydraulic analytical model. The flow pattern conceptual model is based on the Toth model which was developed purely on mathematically derived hydraulic principles. Consequently it is considered that the hydrogeological conceptual model developed here is adequately tested against both mathematical and hydraulic principles.

9.2. Sustainability

9.2.1. Introduction

Assessment of groundwater resources often involves determinations on how best to manage an extraction program so that perpetuation of a useful resource is maintained with no undue consequences for the environment. Such assessments usually require that a sustainable or safe yield of an aquifer be calculated. The concept of sustainable or safe yield can be difficult to define in many instances and has long been the subject of debate (e.g. Thies, 1940; Schoeller, 1959; Todd, 1959; Bredehoeft, 1997; Alley et al., 1999). At Palm Valley the interest centres on the likelihood that natural groundwater flow in the Hermannsburg Sandstone can sustain the flora refuge.



**SCHEMATIC CONCEPTUAL FLOW MODEL
FOR THE PALM VALLEY AREA**

Figure 9-2 Schematic conceptual flow model for the Palm Valley area. Different domain (order) flow systems are shown to discharge at several locations and to have different orientations depending on topography. Localised flow cells are shown superimposed on the regional scale west to east flow direction shown in Figs 4.7 and 4.9. The potential for differing length flow paths and/or a mixture of different length flow paths discharging at some locations is illustrated.

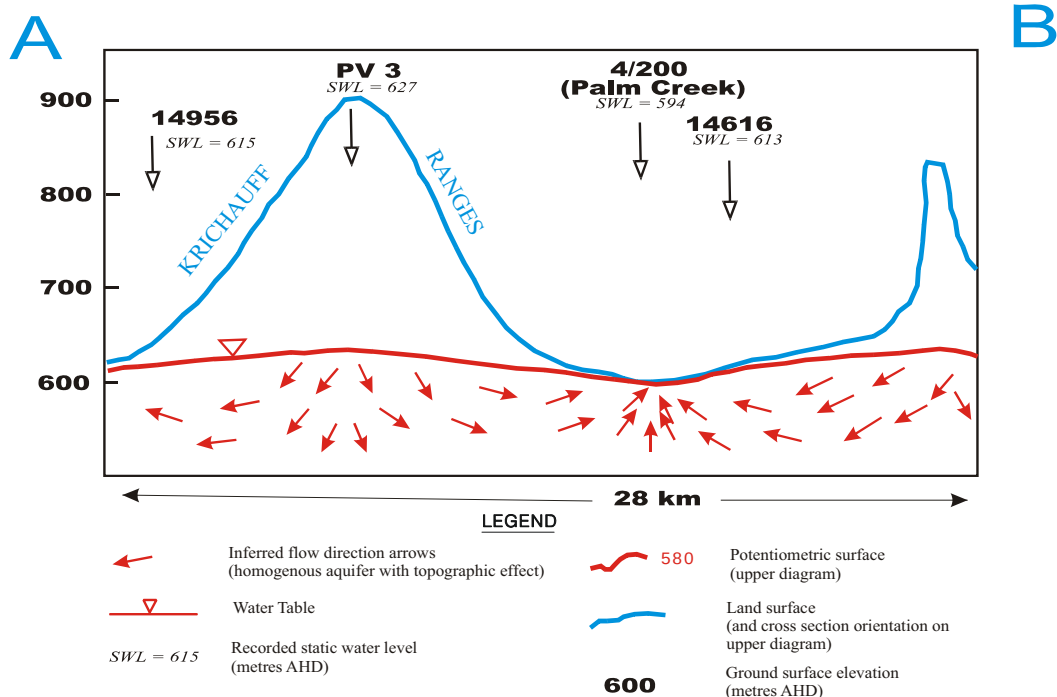
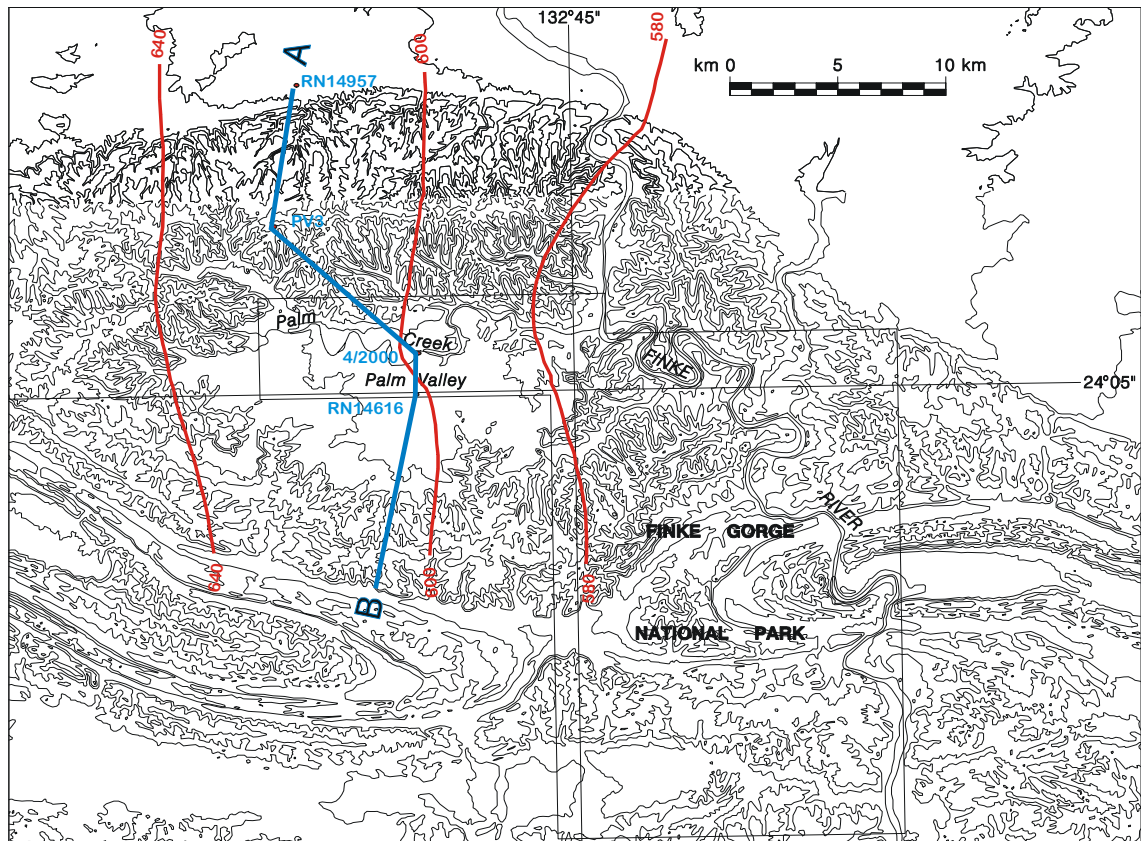


Figure 9-3 Regional topography of the Palm Valley area with variable flow path lengths. The regional topography of the Palm Valley area and a schematic of how discharging groundwater can be expected to have variable flow path lengths at the topographically lower Palm Valley area. This diagram is in keeping with the work of Toth shown in Fig. 9.1 and assumes the Hermannsburg Sandstone to be a homogenous aquifer for the purpose of this illustration.

In arid areas, groundwater recharge is often irregular, and the natural groundwater flow of an aquifer may then vary with time. This implies that the determination of the likelihood and magnitude of recharge are important factors in assessing arid groundwater systems. Lerner et al. (1990) and Foster (1988) note that the determination of recharge is extremely difficult in arid areas.

There is no evidence of significant recharge (nor depletion) in modern times in the Hermannsburg Sandstone. Hydrograph records are, however, of relatively short duration (≈ 30 years). Thus, it may be that some recharge occurs at some locations under the current climatic regime. For example rare super floods associated with extreme southerly transgressions of the northern monsoon, thought to have occurred in the Holocene (e.g. Pickup et al., 1988; Bourke, 1998), may cause some recharge. The short duration of observed occasional modern day incursions of the northern monsoon (usually days) limits the likely significance of recharge from these events.

9.2.2. Palaeo-climate considerations

Jacobson et al. (1994) discuss the likelihood of Holocene and late Pleistocene recharge in the Amadeus Basin. Kershaw and Nanson (1993), Croke et al. (1996), Magee et al. (1995) and Nanson et al. (1992) present evidence for periods of thousands of years (interglacial pluvial) within the Quaternary glacial cycles when climate in central Australia may have been significantly wetter, particularly around 100 ka. These workers note some evidence for renewed wet conditions around 50 -35 ka may exist, however, this event may not have been as significant in central Australia as in south eastern Australia.

Nanson et al. (1998) note there is also some evidence for a possible wet period just prior to the last glacial maximum (22-26 ka) which may correlate with the evidence of ephemeral fluvial deposition also noted at about this time by Croke et al., (1996). Johnson et al. (1999) however, present evidence that the influence of the Australian monsoon in central Australia (Lake Eyre region) has declined since around 45-65 ka, which may limit the likelihood of significant recharge since this time.

Hesse et al. (2004) note that the palaeo-climatic reconstruction of the Australian arid zone is limited by many unconstrained variables that control climate proxies such as runoff, vegetation and aeolian processes. Given this uncertainty in reconstructing and accurately dating past climate events and notwithstanding the pitfalls of dating groundwater mentioned above, it is apparent more data are needed before definite correlation of groundwater ^{36}Cl decay ages and palaeo climate events can be made.

9.2.3. Discussion

If significant recharge to the Hermannsburg Sandstone is mainly restricted to periods of wetter climate such as at 50 or 100 ka, then groundwater $^{36}\text{Cl}/\text{Cl}$ ratios may be expected to be lower than rainfall ratios due to radioactive decay. If recharge last occurred such a long time ago then slow decay of hydraulic head would now be occurring. Given that the hydraulic modelling of Brown et al. (1990) derived groundwater travel times of several million years through the Amadeus Basin within the Hermannsburg Sandstone, it is likely, if significant increase in head during such recharge events is assumed, that these heads could take several hundreds of thousands of years to dissipate. Thus, groundwater features such as springs and seeps can be expected to have the potential to last without recharge through the arid periods associated with the Quaternary glacial cycles.

For instance based on Equation 7.2, groundwater at bore RN 4508 with a $^{36}\text{Cl}/\text{Cl}$ ratio of 130 by 10^{-15} may have been recharged at around 400 ka if the rainfall ratio of 325 by 10^{-15} recorded by Keywood (1995) at Ti Tree is taken as a likely input ratio. Even if the $^{36}\text{Cl}/\text{Cl}$ ratio measured from shallow groundwater at West Spring or bore RN 14952 is taken as a more reliable estimate of input ratio (i.e. Mazor, 1992), groundwater at RN 4805 is still calculated to have been recharged around 300 ka. Determination of the exact timing of recharge to this aquifer, given the complex flow paths, lack of data points and inherent uncertainty in estimating input ratio at time of recharge, is, however, speculative.

In other arid areas, such as Egypt, past Quaternary higher water table (pluvial) events have been determined by the uranium-series disequilibrium method dating of travertine spring deposits (e.g. Crombie et al., 1997). It is possible that older higher calcrete deposits at Palm Valley will yield similar information on the timing of past wetter

climates if dated. There are, however, some pitfalls in dating calcrete with this method: assumption of initial activities can be crucial (Sturchio and Binz, 1988) and, most importantly, calcrete must be assumed to have remained a closed system to U and Th since formation for an accurate age determination (e.g. Williams et al., 1993; Sturchio and Binz, 1988). Given the ready potential of calcrete to remobilise during repeated episodes of dissolution and precipitation (Arakel, 1991), processes that can lead to the cement of old calcrete being made of components of different ages (e.g. Geyh and Eitel, 1998), the timing of past pluvial events by applying uranium-series disequilibrium method may be no more, or perhaps even less, certain than the inferences drawn from ^{36}Cl decay dating of groundwater.

This range of groundwater ages and the complex flow path geometry discussed above indicate that the shallow groundwater supply thought to maintain the unique flora at Palm Valley is in part likely to be hundreds of thousands of years old. If Palm Valley has been a floral refuge during the arid phases of the Pleistocene glacial cycles, as speculated earlier, then fossil groundwater moving through the Hermannsburg Sandstone may be the key to the continued survival of the unique stand of remnant flora at Palm Valley.

Such a scenario, at least within the Hermannsburg Sandstone, provides a framework that offers indirect evidence for conclusions drawn by other studies in central Australia. The survival of remnant aquatic fauna noted by Davis (1995, 1997) in this region and evidence of human occupation 22 ka in central Australia - which would require permanent waters to be viable (Smith, 1987, 1989) - benefit from the identification of a flow system that is maintained even during hyper arid periods such as glacial maxima.

9.2.4. Conclusion

The computed age and proposed flow path mechanism of groundwaters within the Hermannsburg Sandstone indicate that systems dependent on natural groundwater flows such as Palm Valley should be sustainable. As flow may be maintained by slow decay of hydraulic head after interglacial pluvial recharge for considerable periods, modest developments such as the Hermannsburg Community water supply should also be sustainable.

10. Conclusion

10.1. Main conclusions

This study has examined and characterised the hydrogeology of Palm Valley and applied the ^{36}Cl decay dating method. The background and theory of this method have been reviewed and the results obtained assessed in context against other previous studies. The culmination of this work has allowed the development of a conceptual model that goes a long way towards outlining the link between groundwater and the presence of a flora refuge at Palm Valley. Like many other groundwater studies the complexity and scale of the physical and biological environments encountered by water as it moves through the aquifer system has prevented an exact understanding of all facets of the hydrologic cycle being gained. The data obtained and interpretations made do, however, provide a sound basis for any further work to build on. To demonstrate how the objectives of this study have been achieved or attempted a summary of pertinent conclusions developed throughout the thesis is presented below for each of the four objectives presented in Chapter 1.

Objective 1) Evaluate the hydrogeology, hydrochemistry and isotope chemistry of the aquifer underlying Palm Valley:

The biology (genetics and physiology) are not yet fully understood for the *Livistona mariae* though they do appear very closely related, if not the same species, to some tropical dwelling *Livistona* sp. palms in northern Australia. Exact proof of groundwater dependence is not yet available for this or any other *Livistona* species. Groundwater dependence is, however, inferred by many people due to the climate and limited distribution of these and many other desert dwelling palms elsewhere in the world.

Groundwater movement is very slow within the Hermannsburg Sandstone and hydraulically it can be conceptualised as a low permeability double porosity aquifer where water moves through both fractures and sandstone matrix. Groundwater is low salinity and bicarbonate rich. Slight variations in cation chemistry seem to indicate slight differences in reactions experienced along different flow paths. The stable

isotopes of water data (^{18}O and ^2H) indicate recharge has been rapid and via an indirect mechanism. Radiocarbon results range from modern to beyond the limit of detection.

Plots of $^{36}\text{Cl}/\text{Cl}$ v. Cl and ^{36}Cl show a decay trend and no apparent gain (or loss) of chloride within the aquifer. The $^{36}\text{Cl}/\text{Cl}$ ratios vary from around known modern atmospheric values to ratios consistent with over 300 ka of radioactive decay.

Objective 2) review the background theory and previous applications of ^{36}Cl decay dating of groundwater systems:

There is much consideration needed before using ^{36}Cl results as a decay dating tool. There are some uncertainties in assigning input values of $^{36}\text{Cl}/\text{Cl}$ ratios, not least because natural fallout of ^{36}Cl to the earth is yet to be categorically defined. Shallow groundwater $^{36}\text{Cl}/\text{Cl}$ are sometimes used as a proxy for input ratio when atmospheric ^{36}Cl fallout data are absent. Evidence of anthropogenic radioactive contamination and deviation from expected atmospheric Cl/Br ratios are the most appropriate criteria to test shallow water sample integrity in sparsely populated arid regions. While changes in ^{36}Cl fallout have occurred in the past, the nature of the variation in the Earth's magnetic field mean that it is unlikely that fallout has ever been less than at present; hence it is unlikely that ^{36}Cl decay method would ever underestimate age because a lower than present atmospheric input ratio operated at the time of recharge.

The effects of epigene ^{36}Cl production can usually be ignored for groundwater studies as the rate of build up and release is slow compared to the flux of groundwater. Hypogene production is usually only small (<10 by 10-15) when compared to atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios. Only when exceptionally high rock U and Th contents are suspected or measured groundwater ratios approach hypogene production levels is it an important consideration. There is some evidence that bomb produced ^{36}Cl is still being released into the environment via methyl chloride production from plants. Based on known global methyl halide budgets the significance of this effect seems slight though it remains possible in areas of heavy vegetation such as temperate forests, accordingly it is not a consideration in central Australia.

Uncertainties on the provenance of subsurface chlorides, often manifested as an observed inverse relationship between $^{36}\text{Cl}/\text{Cl}$ ratio and chloride concentration along flow path, has complicated previous ^{36}Cl decay dating of groundwater studies. The main problem is that addition of subsurface chloride makes decay age determination ambiguous as un-testable assumptions on the rate and amount of chloride addition need to be made.

Objective 3) apply the ^{36}Cl decay dating method at Palm Valley and critically assess results in the context of objectives 1) and 2):

The clear ^{36}Cl decay trend and indication of great groundwater age obtained for this study is significant. The application of the ^{36}Cl decay dating technique has provided an unambiguous set of results, an unusual occurrence when compared to other studies. This suggests some lessons may be gained from this work. The review of previous ^{36}Cl decay studies show the crucial factor to unequivocally apply ^{36}Cl decay dating is to ensure that no addition of chloride occurs along groundwater flow paths after recharge. At Palm Valley, this condition is apparently met due the considerable thickness and monotonous lithology of the Hermannsburg Sandstone. In addition, the very low extraction to aquifer storage ratio which exist for this aquifer mean that near natural hydraulic equilibrium conditions exist. These results highlight the importance of ensuring that groundwater which has only flowed through the same lithological unit should be compared for explicit ^{36}Cl decay dating. The amount of aquifer stress may also be a factor to consider. Given these results it may be that other studies which have usually used existing water production bores drilled through sedimentary succession of differing lithology have suffered because of a mixed lithological setting. For instance, as noted by Love et al. (2000) in the GAB, possible poor bore construction and/or lack of certainty on lithology type and aquifer horizon sampled may lead to problems with sample integrity in confined aquifer settings. In addition, the juxtaposition of different lithology types such as clays and sandstones means that mixing of chlorides derived from aquifer, aquitards and intra aquifer clay/shale horizons can be expected. Given the likelihood of mixed provenance of chloride where age and hence also ^{36}Cl content is anticipated, it is little wonder that many studies have produced $^{36}\text{Cl}/\text{Cl}$ against Cl or ^{36}Cl plots that do not provide unambiguous decay trends.

Determination of $^{36}\text{Cl}/\text{Cl}$ ratios has been likened to identifying one particular sugar grain from a room full of sugar. Consequently, it stands to reason that ^{36}Cl decay dating of groundwater is likely to be unusually sensitive to contamination by outside aquifer sources of chloride. Consequently, all efforts to minimise potential ambiguity on the provenance of chlorides including maintaining sample integrity whenever possible seem justified. In many previous study sites however, ensuring such integrity of samples may prove very expensive and logistically challenging (e.g. electric logging, setting packers etc).

In an effort to limit these uncertainties some of the most recent applications of this method have tried to obtain complementary age data from other techniques such as ^{81}Kr and ^4He (e.g.; Lehmann et al., 2003; Sturchio et al., 2004). While these other techniques also have their own problems of application and interpretation, the continued employment and refinement of many different dating techniques in conjunction with ^{36}Cl sampling offers the chance to reduce the ambiguity of dating groundwater in future studies. It is worth noting that even this study relied upon ^{14}C , stable C, H, and O isotopes, major-ion geochemistry, and hydraulic characteristics in combination with hydrologic modelling to support the conclusion that ^{36}Cl decay dating is feasible at Palm Valley. This point illustrates the maxim that as much data that it is possible to gather should be used in interpreting groundwater flow systems.

Objective 4) Determine the feasibility that groundwater maintains the flora refuge at Palm Valley:

The clear ^{36}Cl decay trend and indication of great groundwater age obtained for this study has also helped meet the objective of determining the feasibility that groundwater maintains the flora refuge at Palm Valley. The distribution of several vintages of groundwater discharging contemporaneously in close proximity allows a conceptual hydrogeologic model to be developed. This model, based on the standard mathematically derived Toth groundwater flow theory, shows these data are consistent with modern and mid to late Pleistocene groundwater discharging at Palm Valley. This model could represent recharge from several previous Quaternary pluvial events now discharges at Palm Valley though direct linkage to these climate drivers is yet to be proved. Whatever the nature of recharge, episodic or continuous, this conceptual model

demonstrates a flow system able to sustain dependent flora during previous Quaternary hyper arid phases. It is therefore feasible that groundwater maintains the palms at Palm Valley and that it has operated as a flora refuge since at least the mid Pleistocene.

10.2. Recommendations

Hydrogeology is a complex science, not only do groundwater flow and chemistry within an aquifer need to be characterised but ideally the mechanism, chemistry, spatial and temporal nature of all flows into and out of an aquifer also need to be measured for a complete understanding of a groundwater system. This study, like many other groundwater studies, suffers from the fact that not all these parameters have been determined. The task of dating groundwater is also a complex science – water of several vintages maybe mixed within an aquifer and different isotopes may indicate differing groundwater ages from the same sample (e.g. Bethke and Johnson, 2002). As this study concentrated on the radio-chlorine decay dating method I have included some recommendations on its application along with some specific points that should improve the understanding of the local hydrogeology and ecology.

The hydraulic understanding of Palm Valley is based on sparse data points and little or no monitoring data. While there is no pressing justification to disturb the National Park for installation of monitoring bores, the opportunity to do so during other future work projects such as shelter or road building should be considered. In fact as the Hermannsburg Sandstone is an important aquifer elsewhere in the central Australian region, a well funded designated study of the hydrogeology of the entire aquifer, would be of benefit for the management and allocation of water resources in the Northern Territory.

The link to groundwater and Palm survival is only circumstantial, irrefutable proof by way of studies linking tree physiology and groundwater use are desirable. The relict nature of the palms is also only circumstantial and yet to be proved. The work on genetic comparisons with near relatives should continue so that a quantitative estimate on the period of isolation for this palm can be made. Such an estimate may provide some corroboration of the conclusions drawn from the hydrogeologic conceptual model

developed. These points indicate that a more comprehensive understanding of the Palm Valley flora refuge will only be achieved by a multi disciplinary study. It is therefore recommended that future studies of probable groundwater dependant ecosystems such as Palm Valley in central Australia enlist a range of scientific disciplines to work on a collaborative basis. A start point for further work at Palm Valley could be the comparison of deuterium levels in xylem water of *Livistona mariae*, sampled after a long period (months) without rain, with the deuterium values of groundwater in the underlying Hermannsburg Sandstone. This may allow, in a similar manner to that outlined in the study by Lamontagne et al. (2005) for other tree species in northern Australia, an appreciation of the degree of groundwater dependence (at least at the time of sampling) of the *Livistona mariae*.

The flows into and out of the Hermannsburg Sandstone and the climate events that drive the hydrologic cycle are largely unknown or proven. Further work is needed to create a better knowledge of the water balances of this aquifer. Such information may allow the development of a functioning numerical model to aid the understanding and management of this aquifer. It is worth noting, however, that even after much study and expenditure some major exploited groundwater resources in arid central Australia such as the Alice Springs town supply and the Great Artesian Basin are yet to have water fluxes characterised to the extent that fully calibrated dynamic numerical models can be constructed. This suggests that the hydrogeology of large aquifers such as the Hermannsburg Sandstone in the arid zone is complex and therefore requires much further effort to be fully understood.

The atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios for this area have only been measured over a two-year period in early 1990s (Keywood, 1995). Knowledge of this crucial factor in the dating of groundwater would benefit from a long-term collection programme so that the relationship of $^{36}\text{Cl}/\text{Cl}$ ratio to the full suite of possible climatic conditions could be examined. For example the $^{36}\text{Cl}/\text{Cl}$ ratio of precipitation during the anomalous 'big wet' years of 1974 and 2000 in central Australia would be of interest as recharge may be significant for some aquifers only during these events.

Rainfall and dry fallout chemistry data are also meagre in central Australia; most future groundwater studies would benefit from a systematic collection of these data.

The chemical and isotopic data that forms the basis of this study is largely obtained from only one round of sampling. A better understanding of the system may be gained if repeat sampling of groundwater along with some data from rain and dry fallout were obtained.

It is worth analysing the Hermannsburg Sandstone to obtain some solid phase chemical data as an aid to any future geochemical studies such as reactive transport modelling using the PHREEQC (Parkhurst and Appelo, 1999) computer code.

The past hydrologic regimes that have existed at Palm Valley should be further examined – consideration of dating aquifer precipitate deposits such as the calcrete lenses noted in the area above the water table should form a part of any further groundwater studies at Palm Valley.

While the ideal of adequately accounting for all sources and sinks of chloride has long been recognised for successful ^{36}Cl decay dating, it has rarely been achieved. This may in part be due to the expense and logistical difficulties associated with maintaining sample integrity in large deep sedimentary basins. This study highlights that unambiguous ^{36}Cl decay results do occur in some natural systems; hence future studies should plan and budget for much effort in ensuring that only one lithological unit is sampled. In many instances, however, this may not be feasible. Better control on mixing end members by way of sampling solid phases and aquitard pore waters for halide signatures and $^{36}\text{Cl}/\text{Cl}$ ratios along with aquifer waters is recommended to add credence to interpretations of groundwater ages necessarily based on allowing for mixing of dead chlorides along flow paths etc. Where possible the use of complementary techniques such as ^{81}Kr and ^4He should also be considered.

11. References

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