AGSO

Australian Groundwater Quality Assessment Project
Report No. 4

A Groundwater Quality Assessment of Shallow Aquifers in the Darwin Rural Area, Northern Territory

Volume 1: Text

by

Bruce Radke, Karina L. Watkins & John Bauld

AGSO Record 1998/20

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AUSTRALIAN
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A Groundwater Quality Assessment of Shallow Aquifers in the Darwin Rural Area, Northern Territory

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EXECUTIVE SUMMARY

The expansion of intensive rural-based industries and rural residential development within the Darwin Rural Area constitutes a potential risk to the underlying groundwater resources. Both urban and rural sectors of the Darwin region utilise groundwaters from the relatively shallow, regional aquifers in the Litchfield Shire. During the late dry season of 1995, the Australian Geological Survey Organisation (AGSO) carried out a groundwater quality assessment of the shallow aquifers of the Darwin Rural Area. Groundwater samples were recovered from 36 private supply bores and two springs in the Howard River Catchment, portions of the adjoining Adelaide River, and the further-removed Berry Creek-Darwin River Catchments. Samples were analysed for physical parameters, environmental isotopes and a comprehensive range of inorganic, organic and microbial constituents including heavy metals and trace elements, nutrients, pesticides and faecal indicator bacteria.

The shallow aquifer system is composite, comprising unconfined siliciclastic sandstones (low permeability but high specific yield) of the Cretaceous Darwin Member that overlie a weathered zone (silicified, brecciated, karstified) of the Proterozoic Coomalie Dolomite (high fracture permeability but low specific yield). Groundwater is modern with apparent ages of 12 to 50 years and has very low TDS. However, aquifer lithology still significantly influences the groundwater chemistry. Generally groundwater in the upper Cretaceous aquifer is relatively acid (pH <5) and of very low TDS (<50 mg/L) compared to that in the Coomalie Dolomite where it has equilibrated with the carbonates and increased both in pH (up to 7-8) and TDS (up to 225 mg/L). The latter aquifer is the most common and preferred abstraction source because of higher flow rates and superior water quality.

Groundwaters from the weathered Dolomite, and from Cretaceous sediments that lie within discharge zones of the Dolomite aquifer, were of excellent inorganic chemical quality. These were characterised by near neutral pH, low TDS, low nutrient concentrations, and very low trace element and heavy metal concentrations. For example, the maximum, mean and median concentrations of nitrate-N were, respectively, 2.08, 0.25 and 0.12 mg/L. All analyte concentrations were below NHMRC health guideline values for drinking water, except for one bore with high iodide. Groundwaters from some areas in the Howard River Catchment approached or exceeded the aesthetic guideline value for iron (0.3 mg/L). Organic pesticides were not detected in the Darwin Rural Area groundwaters despite historically high use of insecticides and termiticides in the region. The combined effects of high ambient temperatures, low pH of initial recharge waters, and the general propensity of insecticides and termiticides to bind strongly to soils, would facilitate their degradation and/or immobilisation.

Faecal indicator bacteria (FIB) were detected in 31% of groundwater samples. Where the source of contamination can be inferred with some confidence, domestic septic tanks proximal to bores are considered the most likely cause. While contamination pathways are presumed to follow those for natural recharge, our data do not enable us to preclude the possibility that FIB may gain access to the water table due to deficiencies of bore construction and/or casing integrity. We recommend that these possibilities be investigated prior to any subsequent survey of FIB occurrence. Indigenous microbial populations were generally low. *Burkholderia pseudomallei*, the causative agent of melioidosis, was in 14% of groundwater samples. Consistent with it's apparent widespread occurrence in tropical waters, muds and soils, the presence of *B. pseudomallei* was not obviously associated with FIB or other groundwater constituents.

Groundwater within the aquifers constitutes a mixing system with recharged rainfall and intruded seawater as end members. Ionic ratios that are comparable to seawater, and mixing curves interpreted from $^{36}Cl/Cl$ ratios, indicate a seawater component of up to 0.2% within the aquifers in the lower Howard and Adelaide River (Harrison Dam area) Catchments. The variable fracturing and inferred preferential flowpaths of high transmissivity in the Coomalie Dolomite, as well as its presence down to 20m below sea level, confers vulnerability to increased salinisation by seawater intrusion when groundwater abstraction exceeds annual recharge. Seawater intrusion provides another pathway by which any contaminants from nearby coastal or estuarine areas could be introduced into the aquifer. In such dilute groundwaters, small increases in salinity are readily discernible and provide a sensitive measure of the intrusion process.

The 1995 groundwater quality assessment revealed only slight anthropogenic contamination, evident through the presence of faecal indicator bacteria. The recovery of short-lived FIB from about one-third of samples indicates that both particulate and soluble contaminants can move rapidly to the aquifer. Consequently, the aquifer system appears vulnerable to further contamination commensurate with increased land use intensity in the groundwater recharge areas. This survey was undertaken during the late dry season, a time when the groundwater table was lowest and natural recharge was minimal. During the wet season, recharge distance is reduced by an order of magnitude as the water table rises to within two metres of the surface and the risk of rapid transfer of contaminants from ground surface to groundwater is increased. Given the seasonal disparity in hydrological behaviour, high priority should be accorded to acquiring a comparable wet season groundwater quality benchmark for subsequent monitoring and development of appropriate protection strategies.

ACKNOWLEDGEMENTS

This report is the summation of a large team effort from the collaboration of several organisations and from many contributors: technicians, scientists, and administrators from the Australian Geological Survey Organisation, Northern Territory Power and Water Authority, Northern Territory University, Menzies Laboratory, NT, Australian National University, and commercial analytical laboratories. Most of the bores sampled were privately-owned and we thank the landholders for their approval for access and their cooperation to facilitate sampling of the installations.

Contributors to the initiation of the study, planning, sample collection, sample analysis and interpretation were:

Australian Geological Survey Organisation, Canberra, ACT

John Bauld -project conception and microbiological interpretation
Terry Brown -cartographic services
Eleanor Laing - ion chromatograph analyses; natural isotopes
Alexandra Plazinska - microbiological preparations and determinations
Sue Powell - microbiology sample collection and preparation
Peter Ryan - field logistics
John Spring - field survey and sampling, major ion analyses
Nerida Steel -ICPMS analyses; data verification, QA/QC; data presentation
Karina Watkins - pesticide analysis and interpretation

Menzies School of Health Research, Darwin

Prof. David Kemp - provision of facilities for *Burkholderia* determinations
Heidi Smith-Vaughan, Yvonne Wood, and Sue Hutton - *Burkholderia* determinations

Northern Territory University, Mylly Point Campus- microbiological laboratory facilities

Jenny Brazier - providing logistical support

Water Resources Division, Power and Water Authority, N.T

Peter Jolly - collaboration in initiation of the program
Don Pidsley - liaison for initial planning, hydrogeological information
Bill Bean -field survey advice and assistance

Karina Watkins assessed and documented the pesticide investigation, John Bauld the microbiology, and Bruce Radke the synthesis of inorganic chemistry, nutrients, isotopes, hydrogeological context, and final collation of the report.
In the preparation of this report, we acknowledge Patty Please for setting the format of the water quality report series. Jim Ferguson is thanked for his creative insights and constructive criticism during interpretation of the hydrochemistry, and Richard Creswell for discussion and interpretation of chlorine-36 data.

KEY TO ABBREVIATIONS IN TEXT

*** Analytes that are ionic species are generally documented in standard symbol form without valence state, except where the valence has direct relevance to the discussion.**

ARC	Adelaide River Catchment
CFU	colony forming units
Cp	*Clostridium perfringens* spores
D	deuterium
DO	dissolved oxygen
DRA	Darwin Rural Area
EC	electrical conductivity
EHRC	eastern Howard River Catchment
FC	faecal coliform bacteria (thermotolerant)
FE	faecal enterococci bacteria
FEP	iron-precipitating bacteria
FIB	faecal indicator bacteria
FS	faecal streptococci
GIT	gastrointestinal tract
HDNB	heterotrophic denitrifying bacteria
HIPB	heterotrophic iron-precipitating bacteria
HPC	heterotrophic bacteria plate count (R2A)
HRC	Howard River Catchment
MPN	most probable number
n	sample number of dataset
$\mathbf{n^1}$	sample number of dataset for correlation matrix
NHMRC	National Health and Medical Research Council
P <0.01	probability of correlation >99%; highest level of significance
P <0.05	probability of correlation >95%; high level of significance
$\mathbf{P_{10}}$	10th percentile of a frequency distribution
$\mathbf{P_{50}}$	50th percentile of a frequency distribution (median)
$\mathbf{P_{90}}$	90th percentile of a frequency distribution
R2A	medium for heterotrophic bacteria plate count
σ	standard deviation of a frequency distribution
$\mathbf{t_{1/2}}$	half life
TDS	total dissolved solids
TU	tritium activity
WHO	World Health Organisation
WHRC	western Howard River Catchment

Contents : **VOLUME 1**

TABLES

DIGITAL DATA FILES

RAWDATA.XLS - Raw data from 1995 AGSO Groundwater Quality Assessment Project in the Darwin Rural Area

QCDATA.XLS - Data (QA/QC checked) grouped by surface drainage catchments

Contents : **VOLUME 2**

Text figures and Appendices are presented sequentially in Volume 2.
All Bar Graphs of Analytes are located in Appendix A.

FIGURES

A. APPENDICES

Figures and Tables of Appendices

1. INTRODUCTION

Groundwater is an important resource in rural and urban Australia where increasingly it is extracted for drinking, industrial and agricultural purposes. About 20% of the nation's total water requirements are presently met by groundwater (AWRC, 1987), though this proportion may be as high as 50-100% in large areas of inland, arid-zone Australia or transiently higher in areas subject to extended drought conditions.

The quality of the nation's groundwater resources is of growing concern to water managers in all States. Groundwater quality (ie., its acceptability as judged by domestic, industrial, agricultural or environmental criteria) is determined by both natural processes and human activities. Even contaminant-free groundwater may be unusable as a consequence of toxic levels of naturally occurring components such as cadmium, fluoride or arsenic. Historically, in Australia, resource definition has dominated groundwater investigations and groundwater quality has been synonymous with salinity and its relationship to irrigation-induced land salinisation. However, during the past decade groundwater quality has increasingly come to be assessed by additional factors such as nutrient, toxic chemical and microbiological loads, concomitant with increasing awareness of the vulnerability of groundwater resources to contamination.

Knowledge of the present status of groundwater quality and its improvement or degradation with time, together with a clear understanding of the determinative biogeochemical processes and hydrogeological framework, are essential prerequisites to managing one of our nation's essential natural resources. There is, however, a disquieting lack of information about the quality of Australia's groundwater resources. For example, the application of agrochemicals (eg insecticides, herbicides, fungicides and fertilisers) continues to be extensive and widespread in areas of irrigated agricultural production throughout the nation. Groundwater resources underlying these areas are commonly exploited for domestic and town water supplies, as well as for irrigation, and/or pumped to adjacent surface waters for disposal. The impact of these human activities on Australia's groundwater resources is essentially unknown yet potentially of far-reaching health, environmental and economic significance to resource management.

It was in response to this situation that AGSO (then the BMR) commenced investigations in 1990 which evolved into the Australian Groundwater Quality Assessment Project. Reconnaissance studies were carried out in four States (New South Wales, Queensland, South Australia, and Victoria) in cooperation with the relevant State water management agencies during the period 1990-1992 (Bauld 1994b).

Following these reconnaissance studies AGSO received support through the Prime Minister's 1992 Statement on the Environment. Funds were provided during 1993-1996 for AGSO to assess groundwater quality "in key areas of national priority". Such areas were identified in consultation with State water resource management agencies and their groundwater quality assessed through cooperation or collaboration between AGSO and the State agencies.

Between July 1993 and June 1996 groundwater samples were acquired from 553 bores in nine catchments during 15 field operations around the country. Three of the nine catchments and 39% of the groundwater samples acquired were from within the Murray-Darling Basin. Most of the catchments investigated were both shallow and associated with irrigated agricultural production (Bauld, 1996). All States and Territories except the ACT were represented.

Darwin Rural Area

From discussions with staff of Water Resources Division, Power and Water Authority, the Darwin Rural Area was identified as significantly lacking in groundwater quality information. The component catchments were also facing substantial development pressure from both the west and south with more intensive rural-based industries and rural residential development.

The objectives of Project activities in the Darwin Rural Area were as follows.

- To benchmark groundwater quality for 1995. The region is undergoing rapid expansion and it is important to have a comprehensive data set of groundwater quality data with which to compare in future studies. This involves clear display of the analytical results for quick assessment and characterisation of the groundwater quality.

- To understand the hydrogeological processes of the region through hydrochemical evaluation. These processes include evolution of the groundwater, recharge to the aquifer and surface-groundwater interaction.

- To define any zones that may be affected by anthropogenic activities. These can be areas that have already been affected or recharge zones that have the potential to be affected.

- To provide information to assist in the sustainable management of natural resources.

For five weeks in September-October 1995, an AGSO Groundwater Quality Assessment Team collected groundwater samples from monitoring and supply bores from the defined survey area; principally within the Howard River Catchment, but extending into the adjoining Adelaide River Catchment, and the Berry Creek region.

2. DARWIN RURAL AREA

2.1 INTRODUCTION

The Darwin Rural Area (Darwin Rural Water Management District) contains a variety of land uses which include relatively intensive rural residential development, a range of agricultural activities, and conservation areas. Groundwater in the underlying aquifers provides irrigation and domestic supply including a significant contribution to Darwin's water needs. There is relatively limited information available about the impact of human activities on the quality of the underlying groundwater.

The Howard River Catchment was selected as the area of highest priority for AGSO's work in the Northern Territory after consultation with, and on the recommendation of, the Power and Water Authority (PAWA). Field activities were carried out in collaboration with PAWA. The Northern Territory University (NTU) provided access to Science Laboratories at the Mylly Point Campus to carry out components of the microbiological laboratory work. The Menzies School of Health Research provided staff and facilities for *Burkholderia* sp. determinations.

Research activity of PAWA is centred in the undeveloped parts of the Howard River catchment (known as Howard East). A Landcare project looks at landuse impacts throughout the entire Darwin Rural Area of which the Howard River Catchment comprises approximately 30-40%. The Litchfield Landuse Plan (Northern Territory Department of Lands and Housing,1990) indicates the spread of bores and landuse type within the Howard River Catchment.

2.2 LOCATION

The Darwin Rural Region lies entirely within the Litchfield Shire which envelops Darwin City on its eastern, southeastern and southern boundaries. Three areas have been investigated within this region; the Howard River Catchment, the Fogg Dam - Harrison Dam area of the Adelaide River Catchment, and the Berry Springs area of the Berry Creek-Darwin River Catchment (Figure 2.2.1).

2.3 GEOLOGY

Proterozoic

Outcrop of Early Proterozoic units in the study area is limited, due to an extensive cover of Mesozoic sedimentary rocks and Cainozoic sediments (Figure 2.3.1).

Within the Darwin Rural Area, the basement rocks consist of Early Proterozoic metasediments with some interlayered tuffaceous and volcanic units (Figure 2.3.1). In the northeast, dolomitic marble and dolomitic siltstone predominate. Elsewhere shale, siltstone, sandstone and quartzite are the main rock types of the basement. These metasediments have been tightly folded and now generally dip in excess of 60 degrees. Low grade regional metamorphism has imparted a moderate foliation and in places the fine-grained rocks are slate or phyllite, and sandstones have been silicified in part.

Major stratigraphic units of the Lower Proterozoic sediments are the Wildman Siltstone, Whites Formation, and Coomalie Dolomite (Figure 2.3.2). This latter unit comprises magnesite, dolomitic marble, and minor calcareous para-amphibolite and metalutite (Pietsch *et al.*, 1987).

In the hiatus of 1700 million years between the Lower Proterozoic and Cretaceous periods, terrestrial weathering and erosion produced a highly irregular but relatively level karst surface on the Coomalie Dolomite, a surface now identifiable by the presence of quartz breccia, solution cavities, and silicified dolomite.

Within the area sampled in the Howard River and Adelaide River Catchment, the Early Proterozoic sedimentary rocks are equivalent to those from which uranium and base metals were mined in the Rum Jungle area. As such, these are deemed to have potential to host base metal and uranium mineralisation (NT Dept. of Lands and Housing, 1990).

Mesozoic

During the Cretaceous, the Darwin and Wangarlu Mudstone members of the Bathurst Island Formation (Figures 2.3.1, 2.3.2)were deposited under marine conditions.

The Mesozoic sedimentary rocks consist predominantly of claystone, mudstone, and sandstone. In the subsequent 60 million years since their accumulation, erosion and deposition under marine and terrestrial conditions has produced the present land surface. In the Darwin area, the sequence is flat-lying and generally less than 40 metres in thickness. Outcrops are commonly claystone which has been partly silicified and as such, is more resistant to weathering processes.

Cainozoic

The Cainozoic sequence form a veneer over most of the area (Figure , and comprises Tertiary to Quaternary laterite and soils (Figure 2.3.2, 2.3.3). Unconsolidated sand, ferruginous and clayey, sandy and gravelly soils form remnants of the Koolpinyah surface (Story, 1969). The soil is derived mainly from Cretaceous sediments.

2.4 PHYSIOGRAPHY, CLIMATE AND SOILS

Physiography

In the study area, most of land is flat, rarely rising more than 45 metres above sea level. Developed land lies predominantly between 7.5 and 30 metres AHD. Physiography ranges from rocky escarpments where the plateau gives way to gentle slopes, then to mangrove forests or inland lagoons, occasional rock outcrops, intermittent streams, and several springs, in particular Howard and Berry Springs which are sources of perennial streams. Prominent lagoons, particularly Lambells, Girraween, McMinns all form part of a complex surface drainage system. It is not certain whether these billabongs are remnants of former drainage systems, or the result of solution and subsidence of the underlying rock (Story, 1969). Although most indirectly connect to the Howard River, they usually cannot drain to the coast during normal rainfall. Instead, these lagoons function as stormwater retention basins, gradually recharging groundwater.

The physiography of the catchment is largely determined by the geology of the region and the pattern of erosion since the Tertiary.

Land Systems

Land systems, tracts of land that have recurring patterns of landform, soil and vegetation, are grouped into landform divisions. The Darwin Rural Area comprises predominantly a plateau, the Koolpinyah surface of Williams (1969), and lesser dissected foothills and alluvial plains.

The plateau surface, comprises level terrain and undulating footslopes with some more rugged and dissected terrain. Soils are generally well drained and site drainage is good. Dissected foothills comprise hills, ridges, and alluvial flats that are generally suitable for development, having well-drained soils and good site drainage.

Outwash flood plains of the plateau surface form the alluvial plains which comprise sandy, silty, or clay soils, generally in areas of poor drainage.

Within the study area, that covered in the Howard and Adelaide River Catchments is predominantly on the Koolpinyah Surface, with alluvial plains present in the upper and lower Howard River Catchment. In the Berry Springs area, comparable terrain is present but the alluvial plains are a larger component than seen in the other areas.

Climate

The climate of Litchfield Shire is monsoonal with two distinct seasons, wet and dry. The wet season may last as long as 7 months from October to April, with most monsoonal rain falling between December and March. The mean annual rainfall is 1659 millimetres, but annual rainfall is variable between 1100 and 2400mm. 97% of annual precipitation occurs during the wet season and tends to occur in high intensity, short duration storms (NT Dept. of Lands and Housing, 1990)..

Temperature varies little during the year. The maximum temperature is between 29 and 35°C for 330 days. The minimum temperature varies between 18 and 27°C for 327 days. October and November are the hottest months when the mean maximum is 33° and the mean minimum is 25.5°C. The coolest month is July with a mean maximum temperature of 30°C, and a mean minimum of 19°C.
The early morning mean monthly relative humidity during the wet season often exceeds 80% while afternoon humidity is generally 10 to 15% below this. During the dry season, early morning humidity is commonly 65 to 69%, while afternoon mean monthly relative humidities drop to around 40%.

Open "A" class pan evaporation for the region is approximately 3000 mm yr^{-1} (Cook *et al.*, 1997).
Average daily evaporation is greatest in September and October, with around 8.55 millimetres. The lowest average daily evaporation of 6 millimetres is in February.

Prevailing winds follow a seasonal pattern. From October to March, westerlies and north-westerlies influence the region. Winds are from the east and southeast from April to July. During August and September wind direction is variable as the seasons change. The Darwin region is tropical coastal and may be exposed to tropical cyclones at any time during the period of November to April. Periodicity is about once in every two or three years, but the region may be sufficiently far enough inland to escape the most severe cyclonic winds (NT Dept. of Land and Housing, 1990).

Soils

The surface drainage catchments lie predominantly on the Koolpinyah surface, level terrain that is freely drained and with acid or neutral soils (Story, 1969).

In the western area of the Howard River Catchment there are predominantly gradational and uniform gravelly red soils and minor deep red loamy soils that occur on the flat or dissected Koolpinyah surface and on the alluvial flats of the larger rivers. Within the Howard River and tributaries, the soils may be deep uniform grey or yellow sands and minor gradational red-yellow soils. All are non-calcareous and most are sandy or earthy, and on the lateritic plains often stony as well.
In the eastern Howard River Catchment, similar soil types are predominant, but with additional gradational gravelly yellow soils and remnant red soils.

In the Fogg Dam area of the Adelaide River Catchment, this latter soil type covers west of Lambells Lagoon, while on the western side of Harrison Dam, these gradational gravelly yellow soils occur with remnant gravelly and deep loamy red soils, and uniform sandy soils on lower slopes.
A catenary pattern of soil types is widespread, generally with coarse gravelly soils on the upper slopes, sandy leached soils on the middle slopes, and texture-contrast soils on the lower slopes and alluvial flats, those on the alluvial flats often having a columnar structure in the B horizon. These differences correspond fairly closely with differences in the vegetation (Hooper, 1969).

Vegetation

Vegetation in the eastern Howard River Catchment is dominated by a eucalypt savanna, an open eucalypt forest with small inclusions of paperbark swamps and monsoon rainforest patches in the wetter areas. Vegetation composition and structure of the tropical woodland are relatively homogeneous in this catchment. The overstory canopy averages 13m in height, with a complex vertical structure comprising, *Eucalyptus miniata, E. tetradonta, E. porecta, Erythrophleum chlorostachys, and Terminalia ferdinandiana* (Hatton *et al.*,1997) . The understory is speargrass which senesces shortly after the end of the wet season.
In the northeastern region of the eastern side of the catchment, the open forest gives way to mixed woodland and tall open forest. Eastwards towards the Humpty Doo area of the Adelaide River Catchment, woodland and mixed forest-woodland changes to open forest and sedgeland with herbaceous swamp vegetation (Story, 1969).

2.5 LAND USE

The land use pattern of the study area is influenced by the proximity of the area to urban Darwin which provides employment to many rural residents. While much of region is woodland and undeveloped, a majority of the developed land is either 2 hectare or 8 hectare lots. Many of these, and especially the smaller lots are used almost exclusively for residential purposes. This study covers predominantly the developed rural residential areas in the Howard River Catchment, Fogg Dam area in the Adelaide River Catchment, and around Berry Springs in the Berry Creek - Darwin

River Catchment (Figure 2.5.1). Here land tenure is predominantly freehold, with small reserves and vacant crown land. Native bushland is more prevalent on leasehold land which is only present in the eastern Howard River and Adelaide River Catchments.

The early history of horticulture (fruit and vegetable crops and nurseries) and agriculture (field crops and animal husbandry) in the area was not noted for successes. In more recent years there has been an unprecedented upsurge of interest in horticulture on both commercial and semi-commercial or hobby farm basis. The range of vegetables and fruits produced includes cucurbits, paw-paws bananas, citrus, pineapples, tomatoes, capsicum, custard apples, rambutans, carambolas, jackfruit, mangoes in large numbers, egg plant, pumpkins, other mixed vegetables, cut flowers and nursery plants. Approximately 64% of produce is marketed in southern states, 4% overseas, and the balance locally. Current agricultural production includes poultry farming, piggeries, crocodile breeding, dairying, grazing of cattle, goats, horses, buffalo and fodder production (Northern Territory Department of Lands and Housing,1990).

Mining is almost entirely restricted to extraction of materials for the construction industry. This has not been monitored.

Projected growth is firmest for intensively-farmed horticultural crops, possibly a six-fold increase in the total regional horticultural area up to the year 2040. Within the next 20 years, the three to five fold increase in irrigated horticultural area represents an additional 6 000 to 10 000 hectares (Northern Territory Department of Lands and Housing,1990).

2.6 WATER USE

Local aquifers are currently exploited by both the Power and Water Authority for urban usage, and private landholders for domestic, horticultural, and agricultural activities. The predominant aquifer with greatest yields is the weathered zone of the Coomalie Dolomite. Substantial future development of the rural region is predicted. If a three to five fold increase to 2010 (Northern Territory Department of Lands and Housing,1990) eventuates, it will bring not only greater demand on the groundwater resources, but will significantly increase anthropogenic impact on the recharge area.

3. PROJECT FRAMEWORK

3.1 PREVIOUS WORK AND DATA SOURCES

An historical perspective on the Darwin water supply is presented by Binch (1979) who notes that earlier usage of the McMinns aquifer, before 1972, provided 25 ML/day to supplement water from Manton Dam. Following completion of the Darwin River Dam in 1972, groundwater abstraction ceased initially but with rapid expansion of the city and region, there was renewed interest in the McMinns area in the late 1970's. Coffey and Partners Pty Ltd (1980, 1981) carried out a feasibility study for the development of a major borefield in the McMinns- Benhams Lagoon. This borefield was required to be capable of contributing groundwater at 60 ML/day and suitable for incorporation into the Darwin water supply system. Jolly (1983) delineated the borefield for this objective, and determined the effects of this potential extraction on existing and proposed developments in the region.

Held *et al.* (1995) and Hatton *et al.*(1997) studied transpiration and evaporation of a eucalypt savanna region within the eastern Howard River catchment and subsequently a water balance of this tropical woodland ecosystem has been completed (Cook *et al.*, in press) which provides dating of the groundwaters.

Initial work on groundwater contamination in the region was by Port (1982) and W.D. Scott and Co. Pty Ltd, *et al.* (1983). Jolly (1983) also assessed the impact of a fully-developed rural area on the Coomalie Dolomite aquifer. He differentiated potential contamination and migration rates in the lateritised profile of Cretaceous sediments, the Cretaceous Darwin Member and the weathered Proterozoic Coomalie Dolomite. Wilson (1992), in water quality surveys of both surface and groundwater of the region, established trace metal, nutrient, and pesticide levels. The herbicides Atrazine and Prometryn were detected in bore RN 21649, Berry Springs farming area, in March-April, 1992. Retesting of this groundwater a few weeks later did not detect these compounds. The insecticide heptachlor epoxide was detected in well RN 9619 at Humpty Doo in October-November, 1992 (data sheet of Wilson, 1992).

Bore hydrographs and temporal series of physical and chemical characteristics of groundwater were provided by PAWA.

3.2 HYDROGEOLOGY

Groundwater Provinces

From a regional perspective, the studied catchments cover two overlapping groundwater provinces: the Melville groundwater province defined by the Cretaceous sedimentary Darwin Member sequence; and the underlying Proterozoic Pine Creek province, with predominantly fractured-rock aquifers.

Aquifer Sequence Characteristics

The aquifer system can be conceptualised as a combination of shallow unconfined aquifers comprising unconsolidated sediment, overlying a more permeable semi-confined aquifer in highly weathered fractured carbonates (Figure 3.2.1). Jolly (1983) identified three aquifers: the lateritised profile of the Cretaceous sediments; the brown sandstone at the top of the bottom unit of the Cretaceous Darwin Member; and the weathered Lower Proterozoic Coomalie Dolomite.

Recharge through the lateritised profile of the Cretaceous sediments is primarily through solution tubes which enable recharge waters to reach the aquifer with little or no purification (Jolly, 1983).

The hydraulic behaviour of the shallow Cretaceous component ultimately controls the supply potential of the combined system as the shallow layer is first recharged by rainfall, and this layer supports evaporation and transpiration losses.
Existing potentiometric data indicates that water movement through the sandy claystone (Middle member of the Bathurst Island Group) is faster than expected from a uniform sequence of this lithology.

Leakage from the Cretaceous Bathurst Island Formation (Figure 2.3.1, 3.2.1) to the weathered Coomalie Dolomite aquifer is not well defined but in the McMinns borefield, a leakage coefficient of 1×10^{-4} day $^{-1}$ was calculated by Jolly (1983).

The Lower Proterozoic Wildman Siltstone and the Whites Formation subcrop on the western and southern edges of the Coomalie Dolomite-Bathurst Island Formation aquifer system. The top of the weathered zone of each of these formations has been lateritised . Aquifer development in these formations is poor with bore yields usually less than 1 L/s.
The main aquifer exploited is the weathered top of the Coomalie Dolomite because of its high hydraulic conductivity, even though it has low specific yield. Storage is primarily provided in the overlying Cretaceous sediments which have low permeabilities but comparably higher specific yield (Figure 3.2.1). The composition, and consequently the local aquifer characteristics of the weathered Coomalie Dolomite are dependant on the original unweathered lithology. Where the Coomalie

Dolomite has significant proportions of schistose sediments, the weathered zone usually consists of clayey sediments with low water yields, generally less than 5 L/s. Where dolomite predominates in the formation, groundwater yields from the weathered zone are often in excess of 20 L/s and capable of supplying in excess of 60 L/s (Jolly, 1983). In earlier borefield exploration, Jolly (1983) used seismic refraction to differentiate more productive zones from within the weathering zone of the Dolomite. Schists give more varied groundwater yields.
The aquifers tapped for sampling in this study are identified in Table 3.2.1. and the spatial variation of aquifer type, and the western extent of the Coomalie Dolomite is outlined in Figure 3.2.2.

There are seasonal extremes in rainfall and streamflow in the Darwin Rural Area. Wet season hydrology is dominated by heavy rains, with monthly runoff as high as 80% of rainfall. Runoff ranges between 33% of rainfall in average years to 48% in wet years. During this period, unconfined aquifers can be recharged to the level of the land surface. Streamflow declines rapidly following cessation of the rains, and groundwater levels recede by as much as 10 metres over the long dry season. The character of the dry season discharge is difficult to estimate due to the combination of low topographic relief, complex hydrogeology, and potentially strong interactions with the atmosphere (Hatton *et al.*, 1997).

The minimum sustainable yield is considered equivalent to aquifer throughflow. The volume of water associated with the dry season watertable recession has been used as an upper limit of throughflow and thus potential supply. An alternate water balance by modelling Vardavas (1988) proposes that all dry season discharge is through local evapotranspiration because there was effectively no dry season baseflow associated with groundwater discharge. There can be some dry season streamflow, but the hydraulic connection with groundwater is uncertain; leakage from perched surface waters may be significant in sustaining dry season flow.

Groundwater flowpaths may not always be toward local stream networks nor defined by catchment topographic boundaries (Held *et al.*, 1995). Consequently gauging of dry season streamflow is not necessarily sufficient to assess dry season groundwater throughflow (Hatton *et al.*,1997). Assessment of sustainability requires quantification of dry season groundwater discharge via evapotranspiration versus lateral movement in the aquifer system, as well as understanding how extraction might interact with recharge capacity and rainfall of the system.

Groundwater level

The water table occurs in the overlying Cretaceous Bathurst Island Formation which comprises interbedded mudstone, siltstone and sandstone (Jolly, 1983). In most areas, the water table rises to within 2m of the land surface by the end of the wet season and recedes to 8 to 10 metres below land surface (25-27m AHD) throughout the study area by the late dry season. Some piezometric evidence suggests that the seasonal lagoons and portions of the Howard River may not be hydraulically connected to groundwater during the dry season (D. Pidsley, *pers. comm.*, 1997)

In the eastern Howard River catchment, the annual water level variation beneath the eucalypt savanna averages approximately 7m (Figure 3.2.3). A downward head gradient exists in the upper sequence at all times of the year, averaging between 0.01 and 0.03m m^{-1}. There are some anomalies to this gradient in the lower range of groundwater levels. The gradient is typically greatest towards the end of the wet season when the water table is highest, and declines during the dry season, consistent with groundwater recharge occurring during the wet season (Cook *et al.*, in press).

The difference between gravimetric water contents measured between saturation and field capacity, and magnitude of the seasonal water level variation (7m) would suggest a dominance of swelling clays in the soil zone. With such a water level fluctuation, a water deficit of 400-500mm is implied at the end of the dry season. Most of this water is involved in wetting the soil to the equilibrium content (250-400 mm), and only a further 100-150mm is required to raise the water table (Cook *et al.*, in press). They estimate a recharge rate of approximately 200mm yr^{-1} for a water table 4m below groundsurface, based on groundwater age gradients and assuming both a constant porosity of approximately 25%, and one-dimensional flow.

Age of the groundwater

Tritium activities in groundwater of the Howard River Catchment have the greatest range, from 0.2 to 2.3 TU, indicating apparent groundwater ages from <25 to 60 years old (Figure 3.2.4).
Adelaide River catchment has a narrow TU distribution of 1 to 1.5 indicating apparent ages of between 25 and 40 years. In the Berry Creek- Darwin River Catchment, groundwater has a comparable TU range to the Adelaide River Catchment but with a weighting to the upper value.
These age estimates are consistent with an apparent CFC-12 groundwater age of between 30 and 40 years for the East Howard River Catchment (Cook *et al.*, in press). Less reliable ^{14}C activities suggest a groundwater age of between 35 to 500 years, but ^{13}C concentrations indicate that exchange with aquifer carbonates has occurred and has lowered the ^{14}C concentration (Cook *et al.*, in press)

In the Howard River Catchment, there is a general increase of TDS and pH with age (Figures 3.2.4; 4.2.3; 4.2.5). This contrasts a narrower but intermediate apparent age range for both the Adelaide and Berry Creek Catchment groundwaters (Figure 3.2.4).

Groundwater movement and recharge

In the McMinns-Benhams Lagoon area, potentiometric levels studied by Jolly (1983) in the wet season of February 1983 showed that the perennial lagoons on the eastern side of the Howard River are not in direct connection with the aquifer in the weathered Dolomite. Groundwater movement in the weathered Dolomite is from the topographically higher to topographically lower areas and the discharge areas are primarily the Howard River and tributaries, Black Jungle Swamp, creeks flowing into the black soil plain on the eastern side of the study area, creeks and swamps to the east and northeast of the mouth of the Howard River, and throughflow to the north, out of the study region. Daily discharge was calculated at approximately 70ML, and 40×10^6 m^3 annually. Groundwater discharge from the Cretaceous sediments to ground surface are estimated to be of the same order annually as for the weathered Dolomite (Jolly, 1983).

Jolly (1983) calculated annual recharge to be of the order 70×10^6 m^3. He proposed main recharge to be in the topographically high areas and with groundwater movement from topographically high to low areas, as indicated by both potentiometric (Figure 3.2.7) and total hardness contours.

Potentiometric Surface

The potentiometric surface of the groundwater, in the middle of the wet season, generally follows topography and drainage (Figure 3.2.7). During a typical dry season, the potentiometric surface (Jolly,1983, Figure 2.1b) plateaus close to the level of Howard River at about 20 to 25m AHD within its immediate catchment. Significantly, the gradient towards the Black Jungle Swamp to the east is steeper and the surface descends to about 5 m AHD at the swamp, indicating greater throughflow and discharge eastwards. This steep easterly-sloping groundwater surface compared to the subdued higher surface in the Howard River Catchment, indicates an expected migration of the groundwater divide westwards in the progression from wet to dry seasons.

Hydrograph Data

Annual fluctuation of the piezometric surface in the Howard River Catchment can be summarised by reference to two sites, an undisturbed woodland (Figure 3.2.3), and an extractive borefield (Figure 3.2.6). In the undisturbed tropical woodland that is typically found on the eastern side of the Howard River, the groundwater surface shows high amplitude annual oscillations from maxima of between 0.5 and 2m below ground surface at the peak of the wet season in February, to minima of 9 to 12m at the end of the dry season in October to November. This indicates annual fluctuations in the groundwater of between 8 and 11 metres (D. Pidsley, *pers.comm.*).

Within an extractive borefield on the western side of the Howard River Catchment similarly large annual amplitude variations occur (Figure 3.2.6). However since 1980, the minima have steadily dropped by 7.5m between the dry seasons of 1980 and 1994. In this same period, wet season maxima for the groundwater surface have become more fluctuant from year to year, with a 4m difference in maximum levels between1992 and 1993, of 11 and 7 m below surface. This appears to indicate that the borefield is steadily increasing drawdown during the dry season, but with more erratic

Registered Bore Number	Location	Yield L/sec	Top of screen	Bottom of screen	Aquifer lithology	Interpreted Aquifer Formation
western Howard River Catchment						
RN 7071	Girraween Lagoon	25.0	41	52	mdst., sltst., dol	Kld,Ppc
RN 9225	Howard S. Caravan Park	6.3	?	47	qtz, sandstone	Kld,siPpc
RN 6310	Girraween Lagoon	70.0	63	67	cavitous dolomite	Ppc
RN 20255	Gunns Point Road	?	?	25	?	?
RN 27525	Lot 4183, Bronzewing Av.	8.0	30	34	sand, gravel, qtz	Kld, siPpc?
RN 25917	Lot 90, Hillier Rd.	0.8	?	87	black siltstone	Ppw
RN 25619	Lot 36, Callistemon Rd.,	6.0	27	38	dolomite	Ppc
RN 21995	30 Lacy St., Howard Springs	1.8	27	36	sandstone	Kld
RN 8825	Lot 4, Melaleuca Rd.	6.3	42	55	clay, sd., qtz., dol	Kld, siPpc
RN 27871	70 Barker Road	3.0	44	71	fractured siltstone	Ppw
RN 28032	65 Dichondra Rd.	2.0	53	56	qtz breccia, sst.	Kld?,siPpc
RN 24728	63 Whitewood Rd.	5.0	28	30	sst brecc, qtz, dol.	wPpc, Ppc
RN 27374	Lot 3811, Geodoran Rd.	3.0	41	52	frac.sst, sand	Kld
RN 27050	107 Power Rd.	10.0	64	66	cavity in dolomite	Ppc
RN 8450	Lot 40, McMinns Drive	1.3	21	25	gravel; qtzite	siPpc
RN 20780	Lot 235, Whitewood Rd.	10.0	45	61	sltstone & blk shale	Kld, Ppw?
RN 27687	Lot 2661, 34 Zill Rd.	4.0	40	43	dolomite & cavities	Ppc
RN 9421	Howard Springs Reserve	1.0	16	21	sand	Kld?
RN 22387	Lot 34, Strangways Rd.	?	?	?	?	?
eastern Howard River Catchment						
RN 22069	McMinns, off Gunn Pt. Rd.	0.3	12	18	clay & laterite	Czl
RN 22068	McMinns off Gunn Pt. Rd.	0.3	34	36		Kld?
RN 26455	Humpty Doo, 65 Ridley Rd.	6.0	38	41	gravel & dolomite	Kld?,siPpc, Ppc
RN 21374	Humpty Doo, Lot 5 Pioneer Drive	8.0	32	40	cl. gravel, sil. dolomite	Kld, siPpc
RN 25034	Lot 2293, Dodson Rd.	5.5	62	72	dolomite	Ppc
RN 21398	off Gunn Pt., Rd.	40.0	56	63	qtz., frac. dol., cavity	siPpc?, Ppc
Adelaide River Catchment						
RN 25371	Sect. 1553, Middle Pt. Rd.	23.5	33	35	dolomite, cavity	Ppc
RN 29733	"Top Bananas", Alphtonia Rd.	5.0	48	60	sst, qtz, frac. dol.	Kld, Ppc
RN 24997	Lot 3 Miniata d., Lambells Lagoon	10.0	45	45	qtz., frac. dolomite	siPpc, Ppc
RN 21343	Sect. 1548, Middle Pt. Rd.	25.0	29	39	porcell., fr.dol., cavity	Kld, Ppc
RN 4223	Sect. 1560, W, Middle Pt. Rd.	37.9	36	45	dolomite	Ppc
RN 27743	Sect. 1544, Middle Pt. Rd.	18.8	51	53	qtz., dolomite	siPpc
Berry Ck - Darwin River Catchment						
RN 21427	Berry Springs	6.9	20	26	qtz gravel, sand, gravel	Kld?, siPpc?
RN 26686	Sect. 2352, Berry Springs	40.0	42		dolomite, cavity, sst	Ppc
RN 26779	Berry Spr., Hopewell/Kentish Rds	6.0	68	70	dolomite	Ppc
RN 25232	behind Berry Springs School	10.0	61	65	qtz gravel;fr. dolomite	siPpc, Ppc
RN 20319	20 Southport Rd., Berry Springs	2.5	22	23	?	?

Czl Laterite

Kld Cretaceous Darwin Member
siPpc weathered surface on Ppc
Ppc Proterozoic Coomalie Dolomite
Ppw Proterozoic Wildman Siltstone

Table 3.2.1 Bore locations with aquifer type, thickness and depth

recharge during wet seasons. The smoothed annual maxima appear to be to have a slight decline over this 15 year period.

3.3 SITE SELECTION FOR THIS STUDY

The determination of bore sites for groundwater quality sampling was based on the concerns of PAWA about sites of high risk of contamination and diverse land use. Additionally, other requisites were the existence of bores and associated data, availability, accessibility, bore diameter, flow rates and general quality, and desired spatial coverage.

A reconnaissance field visit was conducted by an John Bauld (AGSO)and Don Pidsley (PAWA) and a final selection of bores was made for the groundwater quality sampling trip that ran from September to November 1995.
Bore casing material was noted but not considered in the groundwater quality data interpretation. Because there were only a limited number of bores to be sampled, priority was not given to one casing material over another.

3.4 SAMPLE PROCEDURE: QUALITY ASSURANCE/QUALITY CONTROL

From September to October 1995, AGSO technical staff conducted a detailed sampling program of selected bore sites in the Darwin Rural Area. Sample line decontamination, filtering and solid phase extraction (for pesticide analysis) was conducted on site. The decontamination procedure, outlined in *Procedures and Notes for Pumping and Sampling of Low Yield/Small Diameter Bores for Water Quality Assessment* (AGSO Technical Support Section), was carried out on the pumping equipment to prevent cross-contamination between samples.

Microbiological samples were transported on the day of collection to an AGSO technical officer, based at NTU University, for analytical preparation. The details of the sampling procedures undertaken for this field program are outlined in AGSO (1996 a,b,c). A 5cm-diameter *Grundfos* submersible pump was used for all stages of the sampling process.

Quality Assurance/Quality Control (QA/QC) is a significant component of the AGSO Groundwater Quality Assessment Project, involving assessment of precision, accuracy and contamination through the use of duplicate, blank and spiked samples to monitor the sampling and analytical processes. The quality of resultant analyses are reviewed with the objective that the degree of QA/QC implemented should be proportional to the level of confidence required in the analytical results (Nielsen, 1991).

A high level of confidence is required because parameters are being measured that are related to human health risks; but additionally,

- the complexity of the sampling process can increase the possibility of error in the results;
- many of the parameters being measured are at very low concentrations and near the limit of detection imposed by current technology; and
- most importantly, parameters are being measured that are related to human health risks..

The QA/QC program for this study comprised a broad range of components including sampling protocols, sample custody, analytical methods, holding times, container and preservation requirements and packaging. In terms of the actual samples taken, there were three categories; blanks, duplicates and spikes.

Blanks:

Blanks were used to monitor contamination during any stage of the sampling and analytical process. Field equipment blanks were taken at the beginning, mid-way and at the end of the trip. A 'BEFORE' and an 'AFTER' blank was taken each time - one of distilled water, and one of distilled water after it was passed through the decontaminated pump system. Separate blank samples were taken for each of the sampling procedures for inorganic chemical, microbiological and pesticide analyses. 'Before' and 'after' blanks were taken at more frequent intervals for microbiological samples.

Duplicates:

Duplicate samples, as a test of precision in sampling and analysis, were taken every tenth sample and processed as for other samples. For interpretation of data, the average value of the two duplicates was utilised (if one value was below the limit of detection, then 0.5 x limit of detection was used as that value to calculate the mean).

Spikes:

A spike is a sample in which a known concentration of the analyte being analysed is added (or spiked) into the sample to test the accuracy of the analytical system. Samples were spiked in the field to enable an assessment of degradation from post-collection to point-of-analysis. A spiked sample was prepared every time a duplicate was taken. Spiked samples were prepared for minor ions, metals and nutrient, and pesticide analyses.

The analytical results including duplicate, spike and blank values are contained in Appendix A2 and in digital Datafiles at the back of this report - filename RAWDATA.xls. The analytical results with spike and blank values removed and duplicate values averaged are tabulated in Appendix A3 and contained on disc at the back of this report - filename QCDATA.xls (this data is ordered by surface catchment for ease of spatial interpretation).

QA/QC procedures for pesticides are provided in Appendix 6.6.

Assessment of Results

An assessment of the results from the blanks, duplicates and spikes provides an overall guide to the effect that field equipment contamination has on the analytical results and the precision and accuracy of the field and analytical processes.

Blanks

Generally the blanks indicated a minimum of contamination. Most analyses of blanks were below the limit of detection. Exceptions were boron, chromium, chloride, sulphate and dissolved organic carbon. The final blanks for **boron** were up to double the detection limits and analyses associated with these blanks were also approximately a factor of two higher. This suggests instrument calibration or zero error and consequently the analyses have been discarded. All other boron analyses were below detection limit.

Chromium analyses of the last pair of blanks were 6-8µg/L whereas previous blanks and all samples were below detection limit. Chromium analyses have been discarded.

With **chloride**, blanks returned a relatively consistent low value which indicated an instrument zero error. It was accordingly subtracted from all analyses. With **sulphate**, the first three blanks also returned consistent low values but the final blank was below detection limit. This also suggests instrument zero error which was probably corrected at or just prior to the last blank. This error was subtracted from all analyses.

Dissolved organic carbon had significant contamination in blanks. One 'BEFORE' blank and two 'AFTER' blanks had levels one to two orders of magnitude higher than recorded in any of the samples. These anomalies are ascribed to procedural error - where a methanol slug was passed in the line before an 'AFTER' blank was taken. Only 10% of all groundwater samples were above detection limit but had to be discarded.

Duplicates

Duplicate results are typically compared as Relative Percent Difference (RPD), (Nielsen, 1991) where:

$$RPD = \left| \frac{\text{sample -duplicate}}{\text{mean of sample \& duplicate}} \times 100 \right|$$

The RPD has been calculated for all the duplicate samples. The results are tabulated in Appendix A2 and an assessment of these results follows:

The minor ions and trace element duplicates that have an RPD value greater than 10% were B, Ba, Zn, Cu, and Ni. . With these elements, the concentrations are very low and of the same order of magnitude as the analytical resolution. Consequently, variation in duplicate results are magnified as a percentage difference.

In most duplicates, RPD of Mg, Na, K, Si and S were well below 10% except for K which also has concentrations just above the detection limit. However, these elements had disproportionately high RPD for duplicate samples of a surface water sample from Howard Springs. In this duplicate, additional to the relatively low concentrations of the analytes, the surface sampling procedure for each duplicate may have varied slightly but significantly in either the water depth or proximity to the spring efflux. Consequently either mixing or evaporation effects may account for these high RPD.
In the other duplicates, RPD of these cations were well below 10% except for K which also has concentrations just above the detection limit.

Some duplicate samples of total oxidised nitrogen, and total dissolved phosphorus. had RPD results greater than 10%. The higher RPD percentages are the result of very low concentrations close to limits of resolution of the analysis.
Of the duplicate samples for deuterium and oxygen-18, none of the RPD values exceeded 6%.

Overall, errors in precision in the sampling process, as reflected by RPD values, are considered to be minimal. The predominant RPD values greater than 10% were associated with very low concentrations close to resolution limits for the analyte.

Spikes

Major ions: No spikes were used for assessing contamination of the major ions. Various dilutions of seawater were used as a laboratory standard for AGSO analysis of major cations and anions.

The spike solutions contained the following concentrations:

Minor Ions: ACTEW Laboratory
2.5 mg/L of F and I

Trace Metals: AGSO Laboratory
0.25 mg/L of Al, Cu, Zn, Li, Ba, Fe, Mn

Trace Metals: ALS Laboratory
0.25 mg/L Al, As, Cu, Mn, Pb, Sn, U, V, Zn, Fe
(The two laboratories, AGSO and ALS, were used to cover a broader range of metals)

Nutrients: ACTEW Laboratory

DOC	5 mg/L
N (as NO_3)	5 mg/L
N (as Urea)	5 mg/L
P (as PO_4)	1 mg/L

P&W (NT) Lab

N (as NH_3)	1 mg/L

The Percentage Recovery of the spiked samples is determined by the following equation:

$$\% \text{ Recovery} = \frac{\text{Spiked Sample Result - Unspiked Sample Result}}{\text{Spike Concentration Added}} \times 100$$

The Percentage Recovery for the spiked samples has been calculated and the results are tabulated in Appendix A2.

Discussion:
The relative standard deviation (RSD) for Fe exceeds 20% because of a poor spike recovery in the third set. Fe is characteristically unpredictable because its solubility, and hence soluble concentration, alters rapidly with the changes in pH and Eh that may have occurred during the sampling process.

As and Sn have anomalously high RSD values because the percentage recovery for these trace elements was variably low. However, almost all trace elements are below detection limit and consequently, any detect gives a major deviation.

There were no excessive relative standard deviations in the spike results for the nutrients, except for dissolved organic carbon (DOC) which had a 64% RSD. As discussed on the basis of blanks, these DOC data are discarded. .

It was necessary to adjust the raw data for chloride and sulphate due to an apparent zero error in analytical instrumentation.

Any significant effects of contamination - as determined by the blanks - are noted in the interpretation.

4. HYDROCHEMICAL ANALYSIS

4.1 INTRODUCTION

The Data

The data derived from the September 1995 sampling program are tabled in Appendix A1, and documented digitally on disc (in the back pocket) (RAWDATA.xls). This digital data is in ®Excel 7 spreadsheet format with a separate spreadsheet for each of the following categories:

- •Field Measurements,
- •Physical Characteristics and Major Inorganic Chemistry,
- •Minor Inorganic Chemistry,
- •Fluoride and Iodide,
- •Metal and trace Elements,
- •Nutrients,
- •DOC (Dissolved Organic Carbon),
- •Stable Isotopes (δD and $\delta^{18}O$),
- •Tritium,
- •Microbiology.

Pesticide data and microbiology data are in hard copy format in Appendices A6 and A7 respectively

Appendix A3 contains data that has had QA/QC, and is classified by catchment. Where duplicate data existed, the mean value has been entered. For duplicate values below the limit of detection, a value equal to half the limit of detection was used to calculated the mean. QCDATA.xls contains the data in a format similar to the hard copy data.
All data has been verified.

Methods of Analysis and Presentation of Data

Various methods and approaches were employed in presentation and analysis to enable enhanced interpretation of and new perspectives on the hydrochemical data.

1) *Bar Graphs of Hydrochemical Parameters against Bore Number*

This method of data display (Appendices A4.1 to A4.45) clearly illustrates the variation in levels of a particular parameter in relation to the bores sampled. The ordering of the bores by catchment facilitates intra- and inter-catchment comparison. Histograms are applied on data for all parameters except for some of the environmental isotopes. The bore samples are categorised under four groupings, eastern and western Howard River, Adelaide River, and Berry Creek-Darwin River Catchments (eg. Table 3.2.1).

NHMRC (1996) Drinking Water Guideline values are superimposed on these histograms. The highest value detected for any parameter determines full range on the Y axis. Where a guideline limit is not apparent on the histogram, this indicates that all values are lower than the limit. Some of the parameters do not have a health or aesthetic guideline value; and in such cases there is no associated guideline information on the bar graph. Guideline values for other water uses were not selected because the levels are often not so well defined, ie. guidelines for irrigation water vary with different crops, soils and climate. Further information on guideline values for different water uses can be found in the National Water Quality Management Strategy document *Australian Water Quality Guidelines for Fresh and Marine Waters* (ANZECC, 1992).

The NHMRC Australian Drinking Water Guidelines (1996) and the WHO Guidelines for Drinking Water Quality (1993) provide detailed information for each of the parameters in terms of a general description, source, treatment and health considerations.

2) *Spatial distribution of key parameters*

For selected parameters, results were plotted on a schematic map to allow further spatial analysis The layout of the schematic map is similar to Figure 2.2.1. This approach defines spatial patterns in the parameter, patterns that may indicate controls or processes.

3) *X-Y Plots for selected parameters*

XY plots are used to identify significant relationships that may exists between the parameters. Interpretation of such plots may indicate dominant processes occurring ie. redox processes, natural vs anthropogenic processes, recharge processes. Parameter units vary mg/L or meq/L.

4) *Correlation coefficients between parameters*

Correlation coefficients offer a statistical measure of covariation between parameters. The Excel™ correlation function was used to generate the coefficients

Significant correlations do not necessarily imply causal relationships, and deduction of causal association requires supporting evidence from other methods. Correlation matrices of analytes (Appendices A5.1 to A.5) are given for 6 datasets; the total Darwin Rural Area, as well as for each catchment and subcatchment. For each dataset of sample number (n^1), coefficient values are listed for two levels of significance (P of 0.05 for >95% probability; **P of 0.01 for > 99% probability**). In each correlation matrix, significant values are indicated (P of <0.05 are highlighted; **P of <0.01** are in bold). In each of the eastern Howard River, Adelaide River, and Berry Creek-Darwin River catchments, the sample number is small ($n^1 \approx 6$) and very high coefficients are required for significance. With computation of the coefficients using the Excel formula, it is found that one chemically-anomalous groundwater in the sample strongly influences this coefficient. Accordingly in these catchments, the interpretation of correlation coefficients requires extra caution.

Interpretation of analyte concentrations and causal associations is based on information from a variety of sources, predominantly from Hem (1989), Stumm & Morgan (1979), Mazor, (1991), NHMRC (1996), WHO (1993).

5) *Discussion of Results*

In the following documentation and discussion of analytes, abbreviations are as follows:

n	sample number of dataset
n^1	sample number of dataset for correlation matrix
$P < 0.01$	probability of correlation >99%; highest level of significance
$P < 0.05$	probability of correlation >95% ;high level of significance
P_{10}	10th percentile of a frequency distribution
P_{50}	median, 50th percentile of a frequency distribution
P_{90}	90th percentile of a frequency distribution
σ	standard deviation of a frequency distribution

4.2 FIELD PARAMETERS

Total Dissolved Solids (TDS)

Total Dissolved Solids comprise inorganic salts and small amounts of dissolved organic matter. TDS is a good general indicator of water quality. Because of the very low concentrations. In Darwin groundwater, concentrations of TDS are low and the calculated TDS is used in this study in preference to laboratory-measured TD. Larger error margins are possible in the latter measure in low-TDS waters.

TDS in the Darwin groundwaters is very low, with a median of 139 mg/L within a range from 34mg/L (P_{10}) to 187 mg/L (P_{90}). This is good to excellent quality, well below aesthetic guideline limit of 500mg/L (NHMRC,1996). As expected, TDS has highly significant positive correlation with EC and most ions, and additionally with pH. Countering this trend are inverse correlations of TDS with Eh, Cu, Ni, Fe, and Al.

Each of the catchments varies in character with respect to TDS (see Appendix A4.1).

The western Howard River Catchment has a median TDS concentration of 122 mg/L (σ = 61mg/L, n = 20). In this catchment, pH increases with the log of TDS (Figure 4.2.1) (R^2 = 0.94). The significant correlation of most ions with TDS indicates an increase in pH with the uptake of salts in the recharge waters.

Of all catchments, the eastern Howard River Catchment has the lowest median TDS value of 80 mg/L, but largest standard deviation (σ = 77, n = 6). Here TDS has a significant negative correlation with tritium and Eh, that reflects the progressive increase of TDS of the groundwater with time and an associated depletion of dissolved oxygen.

The Adelaide River Catchment has groundwaters with the highest TDS median of 163 mg/L (σ = 40, n = 6). In this catchment TDS has significant positive correlation with EC, SO_4, S (all $P<0.01$), and Na, Cl, Br (all $P<0.05$).

Berry Creek-Darwin River Catchment also has a comparatively high median TDS (158mg/L) with low standard deviation (σ =14.5, n = 6). In this catchment, TDS has positive correlations with EC, alkalinity, dissolved oxygen (all $P<0.01$) and Cl, FE, FC, R2A, FEP, and *Clostridium* (all $P<0.05$). Because of the small sample size, caution is essential in the interpretation of the following observations. There is a significant negative correlation between TDS and tritium activity. Some of these correlations contradict the general pattern of increasing groundwater age with higher TDS and lower dissolved oxygen. In this catchment DO increases with TDS (see Figure 4.2.2) and this is unexplained. The high correlation of FIB with TDS is misleading, a result of the one very high sample at Berry Springs.

Jolly (1983) observed the classic pattern of lower hardness groundwater in upper catchments, where recharge is occurring, increasing to higher hardness waters as the groundwater equilibrates with the Dolomite aquifer as it moves down gradient towards river drainage. The spatial plot of TDS (Figure 4.2.3) supports this pattern in the Howard River Catchment.

pH

In the Darwin rural catchments, groundwater, as sampled at the boreheads, has a pH range from 4.1 to 7.6 (Appendix A4.2). Groundwater pH has direct relationships with TDS (Figure 4.2.1), EC, Ca, Mg, alkalinity, and HCO_3 . Both orthophosphate and total dissolved phosphorus also have significant correlation with pH. Eh, Al and Cu have significant negative correlation with pH.

In the western Howard River Catchment, in addition to the general correlations described above, dissolved oxygen (Figure 4.2.4) and *Clostridium* spore abundance have significant negative correlations with pH

In the eastern Howard River Catchment, as well as the above general trend, SO_4, Cl, and Cl/Br have positive correlations with pH. Tritium activity has a negative correlation with pH.
In the Adelaide River Catchment, Ba has a negative correlation with pH.

pH in the Berry Creek - Darwin River catchment is relatively constant between 6.6 and 7.0. However, within this small variation, there are significant negative correlations with temperature and Fe.

The spatial pattern of groundwater pH in the Howard and Adelaide River Catchments (Figure 4.2.5) follows closely those of TDS and is the inverse of TU (tritium activity).

Discussion:
Darwin rural groundwaters have a wide range of pH (4.1 to 7.6), within which acidity is the main problem. When pH is below 6.5, the water may corrode plumbing fittings and pipes. NHMRC (1996) recommends that the pH of drinking water should be between 6.5 and 8.5 on the basis of the need to reduce corrosion. The aquifer in the weathered Coomalie Dolomite provides acceptable pH levels and Jolly (1983) notes that in the borefield of the Howard River catchment, whilst equilibrium pH ranges from 7.6 to 7.8, the pH of the water at the borehead of existing McMinns production bores is 7.2, contrasting to the groundwater in the Cretaceous sediments in the recharge areas where it is acidic (usually <5) and very corrosive.

The origin of initially acidic groundwater is ascribed largely to acidic rainfall in the Darwin region, although uptake of organic acids from initial percolation into the soil is a possible additional contributor. Cloudwater was found to be highly acidic, pH <4 (Noller *et al.*, 1986; Gillett, 1988) with the organic acids, formic, acetic, and propionic acids, responsible for between 40% (Galloway *et al.*, 1982) and 74% (Gillett, *et al.*, 1990) of free acidity in rainfall. In rainfall analyses for the Alligator Rivers area, Keywood (1995) found strong correlations between H^+ and NO_3, as well as excess concentrations of SO_4 which could not be attributed to anthropogenic emissions. For this area, Gillett *et al.*(1990) established that monsoonal rain was less acidic than non-monsoonal rain.

The pH of groundwater is a useful index of the state of equilibrium reactions.
In the Darwin region, where pH exceeds 6, it is indicative of groundwater from the Dolomite aquifer. The correlation of pH with orthophosphate and total phosphate relates to the distribution of orthophosphate and condensed phosphate in solution being governed by pH. The predominant orthophosphate species over the pH range of 5 to 9 are $H_2PO_4^-$ and HPO_4^{2-} (Stumm & Morgan, 1970).
The negative correlation of Eh with pH in these groundwaters is seen as a reflection of decreasing oxygen and increasing reduction state with time, that is, age of the groundwater. The negative correlation of pH with Al and Cu directly reflects the reduced relative solubility of these ions with rising pH.

In the Howard River Catchment, the negative correlation between pH and DO (Figure 4.2.4) does not necessarily indicate any direct process, but rather reflects an evolution of groundwater with concurrent increasing pH and decreasing DO with time. The pH increase is from groundwater equilibration with the carbonates. Dissolved oxygen decreases as a result of consumption by biochemical processes.
Similarly, the negative correlation of pH with *Clostridium* spore abundance in the western part of the catchment probably reflects the dilution of abundance of this stable FIB spore with age of the groundwater.
In the eastern part of the catchment, the positive correlations of SO_4,Cl, and Cl/Br with pH suggest that in the Coomalie Dolomite aquifer, there is an increased salinity component relating to chlorides and sulphates, possibly from seawater intrusion. The tritium activity is expected to fall with increasing age, TDS, and pH.

In the Adelaide River Catchment, the decrease of Ba concentration with pH in the range of 6 to 7, is possibly controlled by either adsorption on oxides and hydroxides or replacement of Ca in the weathered Dolomite aquifer.
In the Berry Creek - Darwin River Catchment, negative correlation of pH with Fe reflects an apparent slight decrease of pH and increasing Fe concentration of groundwater eastwards across this region.

Electrical Conductivity (EC)

Field electrical conductivity (EC) of Darwin groundwaters ranges between 19 and 422 µs/cm with a median value of 281 µs/cm (Appendix A4.4). Field EC demonstrates a good correlation to calculated TDS (Figure 4.2.6), with an R^2 of the regression at 0.99 (n = 36), that indicates calculated TDS is a reliable measure.

Redox Potential (Eh)

The redox potential for Darwin groundwaters sampled at the borehead ranges from 52 to 483 mV, with a median value of 295 mV (Appendix A4.6). A scatter plot of dissolved oxygen versus Eh (Figure 4.2.7) shows a significant correlation for the Howard River Catchment. Neither the Adelaide River not the Berry Creek - Darwin River Catchments show any correlation between Eh and DO, but cluster around the median Eh value, and have relatively higher DO levels than for groundwaters of the Howard River Catchment.

Discussion:
The redox potential (Eh) is a measure of the oxidising/reducing conditions of the groundwater system. Darwin groundwaters are generally oxidising, as indicated by Eh. The regression of DO and Eh for the Howard River Catchment (Figure 4.2.7) indicates the predictive reliability of Eh for DO at values exceeding 100mV. The lack of correlation of these parameters in the other catchments is enigmatic.

Dissolved Oxygen (DO)

In the Darwin Rural groundwaters, dissolved oxygen has a range from below detection to 5.5 mg/L (Appendix A4.7) and as expected, has a strong positive correlation with Eh and tritium activity ($P<0.01$), significant positive correlation with NO_3, Na, Cl, Br, and significant negative correlation with borehead temperature and reactive dissolved phosphate.
Dissolved oxygen has differing median concentrations and statistical variance between catchments.

In the western Howard Catchment, dissolved oxygen ranges between 0 and 4.9 mg/L (median 1.8 mg/L ,σ =1.35, n =20). Dissolved oxygen shows the expected direct relationships to Eh and tritium, and inverse relationships to TDS (Figure 4.2.2) and pH, as demonstrated in figure (4.2.4). Nitrate has a significant positive correlation with dissolved oxygen.

In the eastern Howard Catchment, dissolved oxygen concentration ranges from 1.5 to 4.8 mg/L (P_{50} 3.4 mg/L, σ =1.35, n = 6). Here it has a negative correlation with R2A (Heterotrophic Bacteria plate count) ($P<0.01$).

The bores sampled in the Adelaide River catchment have the highest dissolved oxygen levels (P_{50} 4.1 mg/L, σ =1.01, n =6) where the range is between 2.4 and 5.5 mg/L. Inverse correlations with Mg and HCO_3 concur with the inverse relationship with TDS. A positive correlation of dissolved oxygen with Ca/Mg indicates calcium does not vary proportionally with magnesium as would be expected in a dolomitic aquifer.
In the Howard and Adelaide River Catchments, the spatial variation of dissolved oxygen has a broad similarity to the tritium 'age'(see Figures 3.2.4, 4.2.8).

In the Berry Creek -Darwin River Catchment, dissolved oxygen has a more uniform concentration range between 2.5 and 3.9 mg/L (P_{50} 2.9 mg/L, $\sigma = 0.49$, n = 6) and has an unexpected positive correlation relationship to TDS (Figure 4.2.2) and an inverse relationship to tritium activity. Here there is a very high count of FIB, Heterotrophic bacteria and iron-precipitating bacteria in the spring sample with the highest DO level of this region.

Discussion:

As a generalisation, groundwater will have a low dissolved oxygen content where there is a lack of direct contact with the air or where the existing oxygen has been utilised in chemical and microbiological processes. Oxygen is supplied to groundwater by recharge or by movement of air through the unsaturated material above the watertable. It is possible for recharge water to have DO concentrations as high as those for well-mixed surface waters. As groundwater migrates along the flow path within the aquifer, oxygen will react with any oxidisable material, ie. organic materials and reduced inorganic minerals. Depletion of DO can encourage microbial reduction of nitrate to nitrite, sulphate to sulphide and increase the amount of ferrous iron in solution (Hem, 1989).

In the Darwin region, the negative correlation of temperature with dissolved oxygen (Figures 4.2.9), is to be expected as a result of either gas solubility decrease, or increased oxidation reactions with rising temperature as suggested by the direct correlation with nitrate. The negative correlation of DO with orthophosphate concentration (dissolved reactive phosphorus)(Figure 4.2.10) may not be a causal correlation. Low dissolved oxygen concentrations are apparent throughout the groundwater temperature range; to be expected in older waters exhausted of oxygen from microbial or inorganic oxidation reactions.
Orthophosphate concentrations (Figure 4.2.10) may reflect normal TDS trends but most anoxic waters have higher orthophosphate.

The relative concentrations of dissolved oxygen and tritium, and their inverse relationship to TDS is apparent in the borewaters of the Howard and Adelaide River Catchments (Figures 4.2.2, 4.8.2). This demonstrates the gradual reduction of dissolved oxygen in the groundwater with time after recharge. The efflux at Howard Springs gave one of the lowest levels of dissolved oxygen. Nitrate concentration in groundwater has a positive correlation with both dissolved oxygen and tritium activity as a consequence of its input with recharge (generated in the atmosphere during electrical storms) and its gradual reduction in the subsurface with time, probably as a result of microbial consumption.

In the Berry Creek - Darwin River Catchment, the direct relationship of dissolved oxygen with TDS (Figure 4.2.2) and its inverse relationship with tritium (Figure 4.8.2) is anomalous and not currently understood. This may result from the Berry Springs efflux being recently oxygenated water, even though it has relatively low tritium and high TDS levels. The very high heterotrophic bacterial counts and the absence of anaerobic denitrifiers in this efflux water is compatible with the observed higher dissolved oxygen.

4.3 MAJOR AND MINOR INORGANIC CONSTITUENTS

Calcium

Calcium concentrations in Darwin groundwaters range from 0.03 to 36.5 mg/L (Appendix A4.9). Groundwater in the Howard River Catchment has this same range, with a median of 18 mg/L. Here calcium has an almost linear relationship with TDS but with two distinct modes; <7 mg/L and a more scattered upper range (Figure 4.3.1). In both the Adelaide River and Berry Creek - Darwin River Catchments, calcium levels are at the high end of the range, from 22 to 36 mg/L.

In the Howard River Catchment, groundwater calcium concentrations have correlate positively with EC, pH, TDS, alkalinity, HCO_3, and orthophosphate (all P of <0.01) as well as S and SO_4 (P of <0.05). Calcium has negative correlations with Eh, Fe, Al, and Cu. $\delta^{18}O$ and total phosphate also have positive correlation with calcium in the western part of the catchment, while DO and NO_3 have negative correlation with calcium.

Discussion:
Calcium concentrations are a direct result of dissolution of dolomite (Figure 4.3.2) and probable minor gypsum (Ca correlation with S and SO_4) in the Howard River Catchment, as indicated by the positive correlations with EC, TDS, pH, Mg, Alkalinity and HCO_3. The positive correlation with orthophosphate (and total dissolved phosphate in the western catchment) is attributed to phosphate solubility changes in higher pH, and higher calcium levels (See 4.5 Nutrients). The correlation with $\delta^{18}O$ in the west of the catchment is indicative of a mixing of water types in the aquifer (see 4.8 Isotopes). The inverse correlation with DO and Eh indicates a progressive reduction of oxygen, hence lowering of Eh with age of groundwater and associated increase in Ca and TDS. In the eastern part of the catchment, this evolution is indicated by a negative correlation between tritium activity and Ca.

In the Adelaide and Berry Creek - Darwin River Catchments, a carbonate source of Ca is indicated by the positive correlation with HCO_3 (also alkalinity and Mg in the Adelaide River Catchment). A negative correlation of δ^2H with Ca in the Adelaide River Catchment suggests a possible mixing from estuarine-seawater which has intruded the aquifer.

Sodium

In the Darwin rural groundwaters, sodium concentration ranges from 1.1 to 31 mg/L, generally an order of magnitude lower than the aesthetic guideline of 180 mg/L NHMRC (1966). The Howard River and Berry Creek - Darwin River Catchments have groundwater with concentrations below 9 mg/L (Appendix A4.10). In the

Adelaide River Catchment, groundwater from two bores, RN 27743 and 25371 exceed 20 mg/L. Consumption of water with Na levels above 20 mg/L is a concern for medical patients with severe hypertension or congestive heart failure (NHMRC,1996).

In the Howard River Catchment, a slight but consistently higher Na concentration is delineated along the western topographic divide paralleling the Stuart Highway, and along the lower catchment, approximately north of Howard Springs (Figure 4.3.3). Although Na levels are very low, the Harrison Dam - Fogg Dam area of the Adelaide River Catchment has anomalously high levels for the region, with a progressive increase of Na eastwards towards the river.
In the Berry Creek - Darwin River Catchment, Na concentrations are very low but have a progressive rise northwards towards Berry Springs (Figure 4.3.3).

Considering the combined catchments, Na has the expected positive correlations with TDS, Cl, SO_4, Br, Cl/Br and as well as with NO_3 and Sr ($P < 0.01$). Correlations of lower significance exist with EC, DO, and Pb. Sodium has additional unique correlations in individual catchments:
positive correlation with Mn and NH_3 in the western Howard River Catchment ; and positive correlation with K in the Adelaide River Catchment, but negative with K in the Berry Creek-Darwin River Catchment.

Discussion:
Sodium concentrations in the regional groundwaters are extremely low. Scatter plots of Na vs Cl (Figure 4.3.4) indicate that all sodium can be derived from halite. The Cl/Br ratios of groundwaters with detectable bromide are close to that of seawater, indicating a direct marine source with little modification (Figure 4.3.5).
The slightly higher sodium levels on the western boundary of the Howard River Catchment may result from anthropogenic contamination, or a marine source from the Elizabeth River. In the lower catchment of the Howard River, the spatial distribution of both sodium (Figure 4.3.3) and chloride (Figure 4.3.7) indicate intermixture with a seawater source lower in the catchment. The positive correlation of sodium with ammonia in this catchment, and with nitrate in the combined catchments, may be indicative of an anthropogenic influence.
In the topographically lower Harrison and Fogg Dam area of the Adelaide River Catchment, higher sodium concentrations and their increase eastwards towards the tidal reaches of the Adelaide River most probably results from seawater intrusion into the Dolomite aquifer which is below river level. The mixing line on the Na vs Cl plot (Figure 4.3.6) is indicative of this phenomenon.
In the Berry Creek - Darwin River Catchment, the subtle increase of sodium northwards, comparable to that of chloride concentrations (Figures 4.3.3, 4.3.7) is consistent with the common trend of increasing TDS down catchment but equally consistent with seawater intermixture.

Magnesium

Magnesium concentrations in Darwin groundwaters range from 0.05 to 35.9mg/L (Appendix A4.11). Magnesium has an association with TDS (Figure 4.3.8) similar to that of calcium but is generally in excess of a 1:1 molar ratio with calcium in groundwaters where the pH is above 6.2 (Figure 4.3.9). The Howard River Catchment has a Mg concentration range from 0.05 to 35.4 mg/L, with a median of 17 mg/L. In both the Adelaide River and Berry Creek - Darwin River Catchments, magnesium concentrations are at the high end of the range, from 14 to 36 mg/L.

Magnesium has similar correlations to those of calcium. In the Adelaide River Catchment, δD and orthophosphate have positive correlations with magnesium and the orthophosphate correlation is also apparent in the Howard River Catchment data. In the Berry Creek-Darwin River Catchment, magnesium concentration has more significant positive correlations with chloride and sulphate ($P< 0.01$) than seen with sulphate in the Howard River Catchment ($P<0.05$).

Groundwaters with a molar excess of magnesium over calcium, when exceeding 0.3 milliequivalents, have positive correlations between (Mg-Ca) and orthophosphate , total dissolved phosphate, and counts of denitrifying bacteria. In the Berry Creek - Darwin River Catchment, the proportion of excess magnesium in the groundwater increases consistently northeast towards Berry Springs.

Discussion:
The spatial variation of magnesium concentration is very similar to that of calcium (Figures 4.3.8, 4.3.11). Magnesium is presumed to be sourced predominantly from dissolution of dolomite and magnesite in all catchments.
The cause of the correlation of excess magnesium (Mg>Ca) with orthophosphate is unresolved but may relate to a pH-controlled phenomenon within the aquifer rock type. In the Berry Creek - Darwin River Catchment, the correlation of magnesium with chloride and sulphate possibly reflects dissolution of relict evaporites, halite and anhydrite that have trace occurrence in the magnesite and dolomitic carbonates of the Coomalie Dolomite (Crick & Muir, 1980). In the Howard and Adelaide River Catchments, this magnesium excess may reflect magnesite abundance where groundwaters exceed pH 6 (Figure 4.3.10).

An alternative explanation of the magnesium excess is from the additional source from groundwater intermixture with seawater. In the Adelaide River Catchment, magnesium, like calcium, has a negative correlation with δD.

Potassium

Potassium occurs at very low concentrations in Darwin regional groundwater, with a range from below detection to 3.6 mg/L. Western Howard River Catchment has the greatest range, Adelaide River Catchment has the least variation, and potassium concentrations are almost entirely below detection in the other catchments (Appendix A4.12).

In the West Howard River catchment, K has positive correlations with Fe and F (P 0.01), and Ba (P 0.05). In the Adelaide River Catchment, potassium has significant positive correlation with Cl, SO_4, Br (P 0.01) and Na (P 0.05).

Discussion:
There are no prescribed health guidelines for potassium in drinking water (NHMRC, 1966; WHO, 1993) but the Darwin groundwaters have extremely low concentrations.

In the Adelaide River Catchment, the correlations of potassium with Cl, SO_4, and Br, as well as the Cl/Br ratios that have been shown to be at seawater values (Figure 4.3.5) are strongly indicative of seawater intrusion effects.
In the western Howard River Catchment, potassium has significant correlation with Fe, F and Ba but the reason for these correlations is unresolved. One groundwater from RN 27871 has 3.6 mg/L K in conjunction with high Fe, F, Ba, and higher Mn. This may indicate association with mineralisation in the aquifer.

Although potassium is quite abundant in rocks, it is not easily liberated into solution from minerals and it has a tendency to be reincorporated into minerals. It does not commonly occur in high concentrations in groundwater. Leakage of potassium from soils into groundwater and runoff can occur following burnoff in the dry season when vegetation sources are liberated as highly-soluble ash.

Chloride

Like sodium, chloride has very low concentrations in the various catchments of the Darwin Rural Area, ranging from 2.5 to 58.6 mg/L with a median of 3.1 mg/L (Appendix A4.17). Adelaide River Catchment is anomalous in its higher chloride levels, with a median of 31.8, and a range of 3.5 to 58.6 mg/L (Figure 4.3.12). Here chloride concentration increases significantly northwards and eastwards (Figure 4.3.7)

The other catchments have chloride levels below 10 mg/L except for one bore, RN 27525 (20.5 mg/L), in the western Howard River Catchment. In this catchment, chloride concentration increases slightly to the northwest, down the catchment; at the northernmost bores the increase is more significant (Figure 4.3.7). In the Berry Creek - Darwin River Catchment, the chloride concentration increases slightly but consistently northwards.

For the region, chloride concentration has significant correlations with EC, Na, S, SO_4, and Cl/Br. In the western Howard River Catchment, chloride has positive correlation with NH_3, δD, and Mn. In the eastern Howard River Catchment, chloride correlates positively with Ca, HCO_3, alkalinity, and negatively with tritium. In the Berry Creek - Darwin River Catchment, chloride also correlates with DO and Mg, and negatively with tritium.

Discussion:
The regional chloride levels are very low, an order of magnitude less than the aesthetic drinking water guideline level of 250 mg/L (NHMRC, 1966).
Chloride is predominantly attributed to a seawater origin by intermixture in the aquifer as demonstrated by Na vs Cl plots (Figure 4.3.4) and the Cl/Br ratios that are comparable to that of seawater (Figure 4.3.5).

In the eastern Howard River Catchment, the positive correlations with Ca, HCO_3 and alkalinity indicate higher levels in the older, deeper waters (negative correlation with tritium) of the Coomalie Dolomite aquifer.
Bore RN 27525 is situated in the lower area of the western Howard River Catchment. Groundwater of this bore has both higher sodium and chloride, as well as a Cl/Br ratio comparable to seawater (Figure 4.3.5), indicating a marine source. This may result from marine water intrusion and mixing within the tapped sand aquifer which is below sea level, and this phenomenon is also implied from the spatial patterns of Cl and SO_4 (Figures 4.3.6, 4.3.13).

In the Adelaide River Catchment, as with sodium, the higher chloride is attributed to seawater intrusion and mixing within the Coomalie Dolomite aquifer as indicated by spatial patterns of concentration, increasing towards the Adelaide River (Figures 4.3.14, 4.3.7), and from the Na versus Cl plot (Figure 4.3.6) that indicates a mixing line with seawater.

Chloride behaves very conservatively. It is not usually involved in common redox reactions, it is not adsorbed, has no biochemical role and most chloride salts have high solubility. It tends to be retained in solution and is affected mainly by physical processes.

Bicarbonate

In Darwin groundwaters, bicarbonate (as $CaCO_3$) (Appendix A4.16) has a concentration range from 2.5 to 206 mg/L. The Howard River Catchment has this full range of bicarbonate, with a median of 126 mg/L. The Adelaide River Catchment, has a comparable median of 106 mg/L, but with a narrower range, 88-141 mg/L. In the Berry Creek - Darwin River Catchment, is the highest median concentration of 175mg/L but with a narrow range from 161 to 183 mg/L.

Bicarbonate shows an almost linear increase with TDS except in the Adelaide River catchment where bicarbonate is lower for comparable TDS (Figure 4.3.15). In the Howard River Catchment there is a bimodal concentration distribution; one mode of very low TDS/bicarbonate groundwaters, and a low-kurtosis mode of higher concentration, overlapping with Berry Creek - Darwin River Catchment groundwaters. pH has a similar association with bicarbonate, except the trend changes in gradient at pH of 6 (Figure 4.3.16).

Bicarbonate has a near 1:1 relationship with (Ca+Mg) concentration in both Howard and Berry Creek - Darwin River Catchments. Any departure from this relationship is toward a slight excess of these cations (Figure 4.3.17). Groundwater in the Adelaide River Catchment has a greater departure from this 1:1 relationship due to excess Ca+Mg (and Mg>Ca), as does groundwater from Bores RN 26686 and 25917.

In all catchments, bicarbonate has significant positive correlations with EC, pH, TDS, Ca, Mg, Ca/Mg, alkalinity, orthophosphate, and negative correlation with DO, Eh, Fe, TU, Al, Cu, and Ni (Appendix 5.1). In the Howard and Adelaide River Catchments, there is also negative correlation with Cl/Br and δD. Additionally in the western Howard River Catchment, SO_4 and $\delta^{18}O$ have positive correlation, and NO_3 has negative correlation with bicarbonate. δD has a negative correlation with bicarbonate in the Adelaide River Catchment..

Discussion:
All groundwater except for that of RN 9225 lies below the recommended guideline of 200mg/L (NHMRC,1996) and shows the general trend of increasing bicarbonate with TDS.

In the Howard River Catchment, the evolution of waters from initial recharge to those equilibrated with the Coomalie Dolomite aquifer, is apparent in the progression from undetectable bicarbonate at *ca.*10 mg/L TDS and pH of 4, to 206mg/L HCO_3 at 200 mg/L TDS and pH 7 (Figures 4.3.16, 4.3.15). The positive correlations with SO_4 and $\delta^{18}O$ most probably indicate the mixing of the recharge water with a pre-existing groundwater that has acquired a signature from seawater intrusion within the Coomalie Dolomite aquifer. An alternative explanation is that this pre-existing groundwater had a more evaporated origin and which had dissolved traces of anhydrite/gypsum. These minerals have been documented in the host sequence by Crick & Muir (1980). In this catchment, nitrate (Figure 4.3.18), and dissolved oxygen levels have higher concentrations in younger waters, that is in low bicarbonate waters, and these levels diminish with time, shown to result from natural processes, probably microbiological. NO_3 has a lower significance of correlation, a result of point contamination sources (Figure 4.3.18). Al and Cu have negative correlation with bicarbonate (and increasing pH) as a result of their diminishing solubility with increasing pH.

The Adelaide River Catchment has lower bicarbonate concentrations for comparable TDS and pH levels observed in the other catchments, consistent with the identified seawater mixing within the Coomalie Dolomite aquifer (Figure 4.3.14).

In the Berry Creek - Darwin River catchment, bicarbonate is high and with little variation, indicating mature equilibrated waters.

Sulphate

Sulphate concentration ranges from 0.3 to 6.0 mg/L, with a median of 1.32 mg/L in the Darwin Rural Area (Appendix A4.18). The Adelaide River Catchment has the higher sulphate of the regional groundwater, with a median of 3.3 mg/L.

In the lower end of the Howard River Catchment, the northernmost bores show a marked gradient of sulphate increasing northwards. Additionally, sulphate shows a more complex spatial variation than other related ions in the western part of this catchment (Figure 4.3.13).

Here sulphate has significant positive correlations with EC, TDS, Ca, Mg, Na, S, Alkalinity, HCO_3, Cl, Br, and Mn , and negative correlations with Eh, DO, ^3H and NO_3.

Spatial patterns of sulphate concentration (Figure 4.3.13) in the Adelaide River Catchment show a marked increase northwards and eastwards towards the Adelaide River. In this catchment, sulphate has positive correlations with TDS, Na, S, Cl, and Br.

In the Berry Creek - Darwin River Catchment, sulphate has positive correlation with Mg, S, Cl, Cl/Br, U, FC, FE, Cp, HPC, and iron-precipitating bacteria; and negative correlation with Ca/Mg and NO_3. Spatially, sulphate concentrations increase slightly but consistently northeastwards.

Discussion:

Sulphate levels in the Darwin groundwater are extremely low, about two orders of magnitude below the aesthetic guideline for drinking water recommended by NHMRC (1996).

Groundwaters of the Howard River Catchment have apparent increased sulphate with progressive evolution (Figure 4.3.19) within the Dolomite aquifer (negative correlation with DO, ^3H; positive correlation with TDS, Ca, Mg, HCO_3). This could result from several processes: dissolution of trace relict evaporites in the host carbonate; mixing with a relatively sulphate-rich pre-existing water in this aquifer (see $\delta^{18}O$ section); or from oxidation of sulphides. As all dissolved sulphur is present as sulphate (Figure 4.3.20), the inverse relationship between sulphate and DO in this catchment (Figure 4.3.21) indicates sulphate increase with oxygen depletion with time, most probably from oxidation of sulphides. The gradient of this relationship indicates sulphate produced by this process would consume less than half of the DO initially available in the groundwater. The scatter plot of SO_4 vs dissolved Fe (Figure 4.3.22) indicates concurrent increase of sulphate and iron in this catchment. The spatial variation of sulphate concentration (Figure 4.3.13) delineates the inferred mixing with more saline water, probably diluted seawater in the lowest and northernmost part of the catchment. Elsewhere the more varied sulphate pattern has similarities to spatial variation of both F and Fe (Figures 4.3.23, 4.3.24), indicating the areas where sulphide oxidation is a probable source.

In the Adelaide River Catchment, both the relatively elevated concentrations and the spatial gradient of sulphate in groundwater can be attributed predominantly to intermixing with a blend of seawater/river water that has invaded the aquifer via the tidal river (SO_4 has positive correlations with Na, Cl, Br: see also Figures 4.3.13, 4.3.14).

In the Berry Creek - Darwin River Catchment, the positive correlation with Mg, Cl, Cl/Br, and U may indicate lithological variation within the host Dolomite aquifer. The similarity of spatial variations of sulphate and (Mg-Ca.), both with eastward gradients (Figures 4.3.13, 4.3.10) is compatible with lithological changes in the aquifer. However, this pattern could also be caused by seawater intermixture.

Iron

Dissolved iron concentrations range from 0.003 to 3.2 mg/L in the Darwin rural groundwater (Appendix A4.19). The Howard River Catchment has this full range with a median of 0.07 mg/L ($\sigma = 0.33$) in the western side of the catchment, and a median of 0.04 mg/L ($\sigma = 1.26$) on the eastern side. Elevated iron concentrations are spatially restricted to a central, NW-SE trending zone in the western catchment, and to the upper horizons of the piezometer nest (RN 22069, 22068) on the eastern side of the catchment (Figure 4.3.24).

Both Adelaide River and Berry Creek - Darwin River Catchments have much lower median values of 0.006 ($\sigma = 0.005$) and 0.008 ($\sigma = 0.003$) mg/L respectively. These analyses are based on water samples filtered at 0.45µm, which may include a component of colloidal iron (>0.22 to <0.45 µm). Consequently these results should be considered with this in mind.

In the Berry Creek-Darwin River Catchment, iron has a significant negative correlation with pH, while in the Adelaide River Catchment it has positive correlations with field temperature and denitrifying bacteria.

West Howard River Catchment has significant positive correlations between iron and K, B, Ba, and F. On the eastern side of this catchment, iron has positive correlations with NH3, Mn, Ni, FC, Fe- precipitating bacteria, denitrifying bacteria and *Clostridium* spore abundance.

Discussion:

No health guideline limit has been set for iron but NHMRC (1996) recommend an aesthetic limit of 0.3 mg/L. The Howard River catchment has groundwater that generally exceeds this aesthetic limit and the visual effects of high iron levels are frequently evident on the bore heads.

In surface water that is well aerated, iron concentrations are usually less than a few micrograms per litre while in groundwater it may commonly be 1-10 mg/L.

Dissolved iron in water is usually present predominantly as ferrous (Fe^{2+}) and possibly as ferric (Fe^{3+}) ions. Solubility is dependant on the redox potential (Eh), pH and availability of other ions - especially sulphide and carbonate. Microorganisms often assist in catalysing redox reactions involving iron. The source of iron can be minerals in igneous, metamorphic and sedimentary rocks, sulphides and organic waste. The occurrence of iron in solution is primarily an inorganic phenomenon although microbial activity can have an effect on the amount of iron.

In the Berry Creek - Darwin River Catchment, iron concentration has the expected inverse relationship with pH over a narrow range of pH (Figure 4.3.25). In the Adelaide River Catchment, although a small sample, correlations suggest the variation in iron concentration appears to be influenced by microbial activity and water temperature. In the eastern Howard River area (also a small sample) the significant correlations of iron with microbial abundance and ammonia, as well as increased manganese and nickel concentrations are atypical for the Darwin Rural Area. These associations are influenced predominantly by one bore RN 22068, which has probable anomalous contamination for this catchment.

In the western Howard River Catchment, the correlation of iron with F and K (Figures 4.3.26, 4.3.27), and less significantly with Ba and B, suggests a possible leaching of a mineral suite associated with sulphide mineralisation near bores RN 27871, 22387, 9421, 9225, 20780 and possibly 27374. Iron has a positive linear relationship with dissolved oxygen in RN 27871, 22387 and 9421 (Figure 4.3.28), and with sulphate in RN 27871 and 22387(Figure 4.3.22); relationships that would be expected with oxidation of pyrite. Interestingly, these bore locations have a general SE - NW alignment within the Coomalie Dolomite aquifer, paralleling its western limit, but intercepting fractured siliciclastics and sand within the Coomalie Dolomite. They are central to the spatial iron distribution (Figure 4.3.24).

Manganese

Manganese is below detection limits in groundwater from both the Adelaide and Berry Creek - Darwin River Catchments (Appendix A4.32). In the Howard River Catchment, manganese ranges from 0.5 to 53 μg/L, with a median of 2 μg/L in the western part of the catchment, and a median of 5 μg/L on the eastern side. Higher manganese concentrations are restricted to the northwestern end of the catchment and have a general coincidence with the higher iron concentrations (Figure 4.3.24).

In the western Howard River Catchment, manganese has significant positive correlations with S, SO_4 (Figure 4.3.29), Cl, Br, Na, and Cl/Br; and negative correlations with Eh (Figure 4.3.30), DO, and tritium activity.

The correlations calculated for the eastern part of the catchment are considered spurious and are not presented because of an anomalous borewater concentration of 53 mg/L from RN 22068.

Discussion:

Manganese concentrations are extremely low in Darwin groundwater, less than half of the aesthetic guideline level of 0.1 mg/L recommended by NHMRC (1996). Where detectable in the Howard River Catchment, manganese has median levels that are two orders of magnitude less than the recommended health limit of 0.5 mg/L.

For the western Howard River Catchment, the correlations indicate that higher concentrations of manganese are associated with older relatively-reducing waters elevated in SO_4, Na, Cl, and Br, in a groundwater that has been derived from intermixture. The spatial distribution of higher manganese levels in the northern, lower part of the catchment, is comparable to both SO_4 and Cl patterns (Figures 4.3.7, 4.3.13, 4.3.24). This and the correlation with sulphate (Figure 4.3.29) indicates that the groundwater mixing in the aquifer is probably with a diluted seawater.

Fluoride

Fluoride in Darwin Rural groundwater ranges in concentration from a maximum of 0.36 mg/L to below the detection limit at 0.03 mg/L (Appendix A4.26). Apart from the western Howard River Catchment where the median value is 0.06 mg/L within this full range, approximately half the analyses in each of the other catchments are below detection levels.
In the Howard River Catchment the spatial variation of fluoride concentration indicates an intersection of two probable linear trends of higher fluoride (Figure 4.3.23). Here fluoride has highly significant positive correlations with K and Fe. On the eastern side of the catchment, fluoride has significant positive correlation with TDS, Mg, Ca, S, Alkalinity, HCO_3, SO_4 and orthophosphate.

One of the linear zones of detectable fluoride appears to extend across drainage catchments to the southern sampled bores in the Adelaide River Catchment (Figure 4.3.23). Here fluoride correlates with Sr, total dissolved phosphate, condensed phosphate and Pb. In the Berry Creek - Darwin River Catchment, only the westernmost bore had detectable fluoride and this correlates significantly with Ca, Ca/Mg, NO3, total dissolved phosphate, and condensed phosphate (Appendix **A5.5**).

Discussion:
Based on the NHMRC (1996) health guideline limit of 1.5 mg/L, fluoride concentrations in the whole Darwin region are very low, an order of magnitude below the guideline limit.

Fluoride in the western Howard River Catchment has a probable genetic relationship with Fe, and K as indicated by both the XY correlations (Figures 4.3.27, 4.3.26) and the spatial coincidence of the highest iron concentration (Figure 4.3.24) at the intersection of linear trends of higher F groundwater concentrations (Figure 4.3.23). In the Adelaide River Catchment, fluoride has close association with probable contamination as indicated by the correlation with condensed phosphate in RN 27743. Similarly in RN 20319 in the Berry Creek - Darwin River region, the combined correlations of fluoride with condensed phosphate, total dissolved phosphate and NO_3 also indicate probable surface contamination of the aquifer.

Iodide

Iodide has been detected in only one at a concentration of 0.55 mg/L in RN 8825 in the western Howard River Catchment (Appendix A4.27). This bore also has a higher concentration of Ba in the groundwater.

Discussion:
The absence of detectable iodide in the Darwin Rural Area, except in one sample where the level was half that of the NHMRC (1996) health guideline limit of 0.1 mg/L, affirms the quality of this groundwater resource for human consumption. In RN 8825, the association of iodide with barium may indicate a common origin. This

site is adjacent to but not within the zone of seawater intrusion effects within this catchment.

Iodide is widely distributed in the environment but not in great abundance. It occurs in seawater, nitrate minerals, seaweed, in salt and mineral deposits, and is found in circulation in the atmosphere.

Silicon/Silica

Concentrations are expressed as silicon (Si) although the usual convention is to refer to dissolved silica as SiO_2 because Si occurs in water as hydrated silica, and does not behave like a charged ion.

Silicon is present in Darwin rural groundwater within the range of 4.5 to 20 mg/L Si (Appendix A4.13) The catchments have only small variation in median (P_{50}) concentrations:

western Howard River Catchment 6.3 - 11.8 mg/L range, (P_{50} 8.3);
eastern Howard River Catchment 4.5 - 20 mg/L range, (P_{50} 9.9);
Adelaide River Catchment 4.9 - 7.7 mg/L range, (P_{50} 8.2);
Berry Creek-Darwin River Catchment 6.6 - 7.8 mg/L range, (P_{50} 7.3).

In the eastern Howard River Catchment, silicon concentrations have positive correlation with K, orthophosphate, total dissolved phosphate, condensed phosphate, denitrifying bacteria and Cr.

In the Adelaide River Catchment, silicon has highly significant positive correlations with Li, Cu, sulphate reducing bacteria, and U; and negative correlation with DO, Cl/Br, and Ca/Mg.

Discussion:

In the Howard River Catchment, the groundwater is shown to quickly reach equilibrium with silicon saturation during its initial recharge while TDS is less than 30 mg/L (Figure 4.3.31), and while the pH is below 5 (Figure 4.3.32).

RN 25034 on the eastern side of the Howard River Catchment has an anomalous silicon concentration, 20 mg/L. On the basis of the correlations with Si on this side of the catchment, a common source of silicon, condensed phosphate and chromium is highly probable.

In the Adelaide River Catchment, the correlations indicate higher silicon levels in more reducing conditions, with mobilisation of U, Cu and Li in RN 24997. Here Sr and F are also in higher concentrations.

Most silica in water is derived from the chemical breakdown of silicate minerals during the weathering process. The amount in solution is controlled by kinetics, adsorption or secondary mineral precipitation. As a result of these processes the silica concentration tends to fall within a narrow range, usually 1 to 30 mg/L (0.5-14 mg/L Si) with the exception of RN 25034. Surface water concentrations are usually less than 10 mg/L (4.7 mg/L Si) (Stumm & Morgan,1979).

Total Sulphur

All sulphur is present as sulphate in the Darwin Rural groundwater as indicated in Figure 4.3.20. The difference between the regression and a 1:1 relationship between S and SO_4 is within the error limits of analytical procedures (ICP analysis for sulphur, IC analysis for sulphate).

4.4 TRACE ELEMENTS AND METALS

Recent interest in the toxic effect of trace elements on humans and the environment illustrates the importance of including these elements in groundwater quality assessments. The trace elements are given below with their detection limits.

Elements that were detected in this study are highlighted in the list below and the maximum concentration (µg/L) in each catchment is defined:

Category	Element	l.o.d.	**guideline**	WHRC	EHRC	ARC	BC-DRC
Alkali Metals:	**Lithium**	(10 µg/L)	?	20	14	12	-
Alkali Earths:	**Barium**	(5 µg/L)	**700**	41	8	12	-
	Strontium	(5 µg/L)	?	-	-	10	-
Metals:	**Aluminium**	(10 µg/L)	**200***	30	-	-	-
	Cadmium	(0.2 µg/L)	**2**	-	-	-	-
	Chromium	(1 µg/L)	**50**	-	1	-	-
	Cobalt	(1 µg/L)	?	1	-	-	-
	Copper	(1 µg/L)	**1000***	4	1	1	1
	Gold	(1 µg/L)	?	-	-	-	-
	Lead	(1 µg/L)	**10**	-	-	2	2
	Mercury	(1 µg/L)	**1**	-	-	-	-
	Molybdenum	(1 µg/L)	**50**	-	-	-	-
	Nickel	(1 µg/L)	**20**	6	2	-	-
	Silver	(1 µg/L)	**100**	-	-	-	-
	Tin	(1 µg/L)	-	-	-	-	-
	Vanadium	(10 µg/L)	?	-	-	-	-
	Zinc	(1 µg/L)	**3000+***	30	-	-	-
Non-Metals:	Antimony	(1 µg/L)	**3**	-	-	-	-
	Arsenic	(1 µg/L)	**7**	-	-	-	-
	Boron	(5 µg/L)	**300**	53	31	-	34
	Br as **Bromide**	(50 µg/L)	?	66	-	189	-
	Uranium	(0.1µg/L)	**20**	0.95	0.2	0.1	0.4

l.o.d.	limit of detection
guideline limit	health guideline limit NHMRC (1996)
	* aesthetic guideline limit NHMRC (1996)
?	no guideline limit specified, NHMRC (1996)
-	detectable concentrations absent in this catchment
WHRC	western Howard River Catchment
EHRC	eastern Howard River Catchment
ARC	Adelaide River Catchment
BC-DRC	Berry Creek-Darwin River Catchment

Concentrations were below detection limits in all sampled groundwaters: antimony, arsenic, cadmium, gold, mercury, molybdenum, selenium, silver, tin, and vanadium. These elements will not be discussed further.

For detected trace elements, bar graphs of concentration are given in Appendix A4 which illustrate variations within and between catchments. A brief description of detected elements and their distribution follows. The source references for most of the descriptive information in this section include Hem (1989), NHMRC (1996) and WHO (1993). Not all elements have associated NHMRC or WHO guideline values.

Lithium

Lithium was detected in the groundwater of 6 bores, at the order of magnitude of the detection limit (Appendix A4.22). The Howard River Catchment has the highest levels, up to 20μg/L in RN 21995, and lithium is detectable in five bores. In this catchment it has positive correlations ($P < 0.01$) with B, NO_3, Cu, Ni, and Zn and with condensed phosphate in the eastern side of the catchment. RN 24997 in the Adelaide River Catchment, with 12 μg/L has positive correlation with Si, and negative correlation with Cl/Br and Ca/Mg ratios..

Discussion:
Lithium is at relatively low concentrations in these groundwaters. The correlations in the Howard River Catchment indicate two probable associations; with Cu, Ni and Zn from mineralised areas, and/or with NO_3 and condensed P resulting from anthropogenic contamination. In the Adelaide River Catchment, in RN 24997, it appears linked with Si and Mg as probable weathering products of silicates.

No recommended guideline limit is available for lithium, possibly because it is not toxic at the concentrations it can normally reach in groundwater. Lithium is an alkali metal usually sourced from igneous minerals where it can substitute for magnesium. It is relatively rare but if leached, tends to remain in solution once there. High TDS waters can have lithium concentrations up to a few mg/L which can be toxic to plants.

Barium

Barium was detected at low concentrations in Darwin rural groundwater, but was highest in the Howard River Catchment (up to 41 μg/L) (Appendix A4.24). On the western side of the catchment, barium has significant positive correlation with I, Co, TU, K, B, Fe, and abundance of denitrifying and sulphate-reducing bacteria. Barium has negative correlation with TU on the eastern side of the catchment. The spatial distribution of barium generally follows that of iron concentration.
Barium concentrations have a narrower range up to concentrations of 12μg/L in the Adelaide River Catchment, and have negative correlation with pH. Barium concentration in groundwater apparently decreases across the pH range of 6 to 7. Barium is below detection in the Berry Creek - Darwin River Catchment.

Discussion:
Barium, an alkali earth metal like calcium, magnesium and strontium, exists in a divalent oxidation state in natural waters. Barium generally comes from natural

sources, existing in minerals in igneous rocks. Its concentration is usually controlled by the solubility of $BaSO_4$ and by adsorption on metal oxides and hydroxides.

Barium in the Howard River catchment may have association with oxidation of iron sulphides. In the Adelaide River catchment, Ba concentrations may reflect the influence of pH on baryte solubility or adsorption on oxides and hydroxides.

In other Australian reticulated water supplies, barium is usually present in concentrations of less than 5 µg/L but can be as high as 30 µg/L.

Strontium

Strontium was only detected at a very low concentration of 10 µg/L in RN 27743, in the Adelaide River Catchment (Appendix A4.21). This occurrence coincides with relatively elevated concentrations of condensed phosphate, fluoride, and R2A score.

Discussion:
The correlations of strontium in this bore indicate an association with anthropogenic contamination. However, with only one sample this is speculative. Strontium is another alkali earth metal with a chemical behaviour similar to calcium.
It is a common element in igneous rocks, replacing calcium and potassium in minerals, and strontium sulphates and carbonates are common in sediments. The solubility of strontium is controlled largely by strontium sulphate.

Aluminium

Aluminium concentrations are above detection limits in less than 15% of bores in the western Howard River Catchment where the highest level is 30µg/L (Appendix A4.28).
The plot of Si vs Al (Figure 4.3.33) shows decreasing aluminium concentration with increasing Si over a narrow pH range from 4 to 5 (Figure 4.3.34). Aluminium becomes undetectable above pH 5.

Discussion:
There is no current health guideline set for aluminium but NHMRC (1996) recommends that acid-soluble aluminium concentrations be kept as low as possible, preferably below 0.1 mg/L. In the west Howard River catchment, the highest level of 30µg/L is still well below the recommended maximum concentration.

Plots of Al vs Si and Al vs pH (Figures 4.3.33, 4.3.34) for the Darwin groundwater are compatible with documented observations that aluminium has a very low solubility in the range of most natural waters and that this solubility is further reduced in the presence of silica, probably owing to the formation of clay-mineral species.

Although aluminium is one of the more abundant elements in the earth's crust, in natural waters it is usually found at levels less than 1.0 mg/L. Aluminium gets into the natural water system by leaching of soils and rocks but the majority of weathered aluminium minerals usually remain as solid species.

Chromium

Chromium has only been detected at 1µg/L in RN 25034, on the eastern side of the Howard River Catchment (Appendix A4.30). This detect coincides with higher concentrations of total phosphate, condensed phosphate, orthophosphate and silicon.

***Discussion*:**
The source of chromium can be natural, from soil and rock minerals, or it can be anthropogenic, from industrial wastes. Natural chromium levels are commonly below 10 µg/L. Significantly higher levels would most likely be attributed to anthropogenic sources.
Although present at just above detection limit and well below health guideline limits, the association of chromium with phosphate, including anthropogenic phosphate supports a possible anthropogenic contamination source.

Cobalt

Cobalt has been detected at 1µg/L(on the detection limit) in groundwater from RN 22387, at the southern end of the western Howard River Catchment (Appendix A4.29). This detect is coincident with higher temperature, Ba, and abundance of sulphate-reducing and denitrifying bacteria, R2A. δ^2H in this groundwater is comparatively low for this catchment..

Discussion:
No health guideline limits have been set for cobalt and the extremely low concentration detected has no health significance. The association with a variety of bacteria and low deuterium ratio may indicate a link to recent recharge and possible bacterial contamination.. In uncontaminated natural groundwater cobalt concentrations are usually less than a few µg/L. The ion usually exists in the divalent state and its solubility is controlled by coprecipitation and adsorption.

Copper

Copper was present at very low concentrations, just above detection limits, in groundwaters in all catchments (Appendix A4.31). On the western side of the Howard River Catchment, copper concentrations above 3µg/L occurred in RN 22387 in the south, and in a northwest linear trend between RN27374, 25917, 21995, and

20780. This distribution overlaps the high iron concentrations in this catchment. Copper concentrations have significant positive correlation with Ni, Zn, Eh, Li, NO_3, and abundance of *Clostridium* spores; and negative correlation with EC, TDS, pH, Ca and HCO_3. In the eastern area of the catchment in RN21374 copper has co-occurrence only with higher $\delta^{18}O$. Groundwater from RN24997 in the Adelaide River Catchment has detectable copper associated with higher Si, and lower Cl/Br and Ca/Mg ratios. In the Berry Creek - Darwin River Catchment, one bore, RN 26779 has detectable copper associated with higher water temperature, denitrifying bacteria abundance, and lower pH.

Discussion:
Copper has very low concentrations in all catchments, and is two orders of magnitude below the NHMRC (1996) guidelines. Apart from the western Howard River Catchment, it was detected in one groundwater sample of each of the other catchments.

The correlations of copper indicate its concentrations in the western Howard River Catchment are linked to oxidising, more acidic conditions which have mobilised other trace metals (Ni, Zn, Li). The higher copper concentrations are in younger recharge waters which have higher nitrate.
In the Berry Creek - Darwin River Catchment, the copper is also associated with microbiota concentrations and lower pH.
Hem (1989) notes that copper usually exists in natural waters as Cu^{2+} or with complexes. It's solubility is primarily controlled by pH and Eh with adsorption and co-precipitation also playing a role. The average concentration in groundwater is 50 µg/L. In acidic waters, especially where acid drainage may be involved, levels of copper can rise to several hundreds of mg/L.
Copper in groundwater can also have anthropogenic sources linked with industrial activity or agricultural activity - ie. from inorganic copper compounds used extensively in pesticide (fungicide) sprays.

Lead

Lead was detected in only two groundwaters samples at 2 mg/L concentration, RN 26686 in the Berry Creek - Darwin River Catchment and RN 27743 in the Adelaide River Catchment (Appendix A4.34), where there are higher concentrations of condensed phosphate and fluoride.

Discussion:
These two bores have lead levels at a factor of five below the health guideline limit of NHMRC (1996). All other bores are at least an order of magnitude below this limit.
The RN27743 occurrence appears linked to traces of anthropogenic contamination with associated condensed phosphate and fluoride. Interestingly, both bores are sited on existing banana plantations, and this association raises the question of possible use in earlier years of 'old generation' insecticides such as lead arsenate or lead arsenite. No arsenic was detected in this survey but with the ICP scan analytical method used, arsenic detection has much lower precision.

Lead occurs naturally in minerals but can also be sourced from atmospheric fallout and runoff linked to vehicular emissions of tetraethyl lead. It can exist in solution as free Pb^{2+}, hydroxide, carbonate or form sulphate-ion pairs. Lead has a low solubility that is controlled by pH, alkalinity, adsorption and coprecipitation.

Nickel

Nickel was detected in 26% of bore groundwaters in the Howard River Catchment, but not in the other areas (Appendix A4.33). Nickel concentrations reach 6 µg/L in RN 21995 on the western side of the catchment. Here nickel has significant positive correlation with Li, Zn, B, Cu, NO_3, and abundance of *Clostridium* spores. On the eastern side of the catchment, nickel is detected in two bores, RN 21374 and 22068. In the latter groundwater, nickel detection is associated with elevated *Clostridium* and denitrifying bacteria counts, ammonia, manganese and iron.

Discussion:
Nickel in groundwater can result from leaching of ferromagnesian minerals where it can be a trace substitute for iron, or from anthropogenic sources such as fossil fuel burning or industrial waste disposal. In aqueous systems it usually exists in the form of Ni^{2+}. In natural waters, the concentration of nickel is commonly less than 20 µg/L.

Nickel concentrations in Darwin Rural groundwater are well below the health guideline limits of 20µg/L (NHMRC, 1996). The groundwaters with detectable nickel appear to indicate anthropogenic sources; for example RN22068 on the eastern side of the catchment has an anomalous signature of contamination indicators.
In the western Howard River Catchment, nickel has close association with other trace metals, and anthropogenic contamination of *Clostridium* and nitrate in RN 21995. It is unresolved whether the trace metals are sourced from mineralisation or are also derived from this anthropogenic contamination.

Zinc

Zinc was detectable in only three bores on the western side of the Howard River Catchment, RN 21995, RN 22387 (13.5 µg/L) and RN 27525 (9 µg/L) (Appendix A4.20).
In this catchment, zinc has highly significant correlation ($P<0.01$) with Ni, Li, B, NO_3 and Cu.

Discussion:
Zinc exists in solution as Zn^{2+} and in groundwater it is commonly in concentrations less than 50 µg/L. Its solubility is controlled by other ions in solution, adsorption, ion exchange and coprecipitation. A concern with zinc is not so much the levels detected at source, which are usually low, but 'pick-up' in water distribution systems.

Zinc is commonly found as sulphide in the earth's crust, comparable to copper and nickel, but zinc is much more soluble. Zinc can also have anthropogenic sources linked to paint, metallurgy, industrial processes, pesticides and fungicides.

Darwin Rural groundwaters have very low zinc concentrations. The highest detected concentration in the Howard River Catchment (30µg/L) is two orders of magnitude below NHMRC (1996) aesthetic guideline limits. Although at very low levels, where zinc was detected, its correlations indicate possible anthropogenic contamination as in RN 21995.

Boron

Boron was detected in 23% of Darwin Rural borewaters, detected only in the Howard River and Berry Creek-Darwin River Catchments, where concentrations ranged from below detection levels to 53 µg/L (Appendix A4.23). In the western Howard River Catchment, boron has significant positive correlation with Ni, Zn, Li, Ba, K, NO_3 and Fe. In the eastern part of this catchment, boron was negatively correlation with δ^2H.

Discussion:
Boron in groundwater can be derived from dissolution of minerals such as tourmaline, or from domestic and industrial effluents. Boron exists in many forms and complexes but in natural water it is predominantly available as boric acid. Concentrations are rarely above 1 mg/L in surface water or groundwater.
Darwin groundwater has very low boron concentrations, at least an order of magnitude lower than the NHMRC (1996) health guideline limit.

In the western Howard River Catchment, the correlations with other trace metals and nitrate indicate possible anthropogenic contamination and/or a link to oxidised sulphide mineralisation. The negative correlation between boron and deuterium in the eastern side of the catchment may indicate that in that area boron is predominant in direct recharge waters that have experienced minimal evaporative enrichment of deuterium.

Bromide

Dissolved bromide is above detection limits in only 13% of Darwin regional bores (Appendix A4.25). In the western Howard River Catchment, one groundwater in bore RN 27525 had a concentration of 66 µg/L. Four bores in the Adelaide River Catchment had bromide concentration up to 189 µg/L. In both catchments, dissolved bromide has positive correlation with Na, Cl, and SO_4, but additionally with TDS and EC in the Adelaide River area.

Discussion:
Dissolved bromide concentrations are very low. No health guideline limit has been established for bromide as this ion is not perceived to be toxic like bromate.
Where bromide is detected, it has significant associations with Na, Cl, and SO_4, indicating a seawater source. The Cl/Br molar ratios of all groundwaters with detectable bromide fall close to the seawater value of 648 (Figure 4.3.5).

Uranium

Uranium was detected at low concentrations in the regional groundwater, with median concentrations ≤0.1 µg/L in all catchments (Appendix A4.35). The highest concentration of 0.95 µg/L was determined in groundwater from RN27050 in the western Howard River Catchment. Uranium has no significant correlations in this area, but on the eastern side of the catchment, it has positive correlation with Na and DO. In the Adelaide River Catchment, it has positive correlation with Si, but negative with Cl/Br and Ca/Mg. In the Berry Creek - Darwin River Catchment, U has positive correlation with SO_4, and negative correlation with Ca/Mg, NO_3, orthophosphate and condensed phosphate.

Discussion:
Uranium in groundwater can result from leaching of natural mineral deposits or mill tailings, from fallout in the combustion of coal and fuel, as a product of the nuclear industry, or from phosphate fertilisers. Naturally-occurring uranium is a mixture of three radionuclides, predominantly ^{238}U, with less than 1% of combined ^{235}U and ^{234}U. Radiation from uranium is only a health concern if the element concentration exceeds 300 µg/L (NHMRC,1996).
In groundwater, uranium concentrations normally range from 0.1 to 10 µg/L.

Concentrations in the Darwin region are very low, frequently one but sometimes greater than two orders of magnitude lower than the NHMRC (1996) health guideline of 20 µg/L for chemical toxicity. The behaviour of uranium appears unpredictable on the basis of the varied correlations with uranium in the different catchments. In the western Howard River Catchment uranium has a general northwest-southeast spatial distribution which follows that of iron (Figures 4.4.1, 4.3.24). Uranium is below detection near anomalously high iron but otherwise has a similar north northwest-south-southeast aligned spatial pattern. It is possible that uranium has a similar lithological control to iron, but has differing geochemical behaviour. In the Adelaide River Catchment, only RN 24997 had detectable uranium in its groundwater which has the least seawater intermixture and highest silicon concentrations of this catchment.
In the Berry Creek - Darwin River Catchment, uranium correlates with sulphate and has a comparable spatial variation of concentration to that of Mg, Fe and SO_4, all with increasing concentration to the northeast (Figure 4.4.1).

4.5 NUTRIENTS

Nitrogen

The nitrogen cycle provides a framework for understanding the complex nature of nitrogen in the environment. Although it is nitrate that is often used as an indicator for contamination it is frequently other species of nitrogen (N) that are the initial source of contamination. The identity of this initial source is quickly lost in the cycling, as well as with the many inputs and sinks that may be involved.

Alley (1993) summarises the main processes of the nitrogen cycle:

Immobilisation of inorganic N to soil organic N;
Mineralisation of organic N to inorganic/mineral N (ie NH_4^+);
Nitrification - the microbial oxidation of ammonium to nitrite to nitrate; and
Denitrification - the return of N to the atmosphere.

Nitrification is the primary source of nitrate to the biosphere and is a process that occurs in the soil. Because nitrate is relatively mobile it can participate in leaching processes. Denitrification can occur in anoxic environments or where denitrifying bacteria exist. This process can reduce the quantity of nitrate available for leaching to groundwater.

Sources of nitrogen can be natural or anthropogenic. The main anthropogenic sources include fertiliser, plant residues, wastes (industrial, domestic and agricultural) and nitrogen adsorbed from the atmosphere. The risk of nitrate contamination is especially significant in areas of intense agricultural activity because of the combination of irrigation water recharge, and high levels of nitrogenous fertiliser application. Nitrate concentrations in pristine groundwaters are usually less than 2-3 mg/L NO_3 -N (Hallberg, 1989).

Large variations in nitrate levels are to be expected as there are many complex factors involved in the nitrogen cycle: the quantity of nitrogen available, the hydraulic conductivity of the unsaturated zone, recharge, depth to water table, denitrifying potential and seasonal variations.

Different Nitrogen Species

Nitrogen exists in nature in various oxidation states from N^{-3} to N^{+5}. In groundwater the most common forms are ammonia, nitrite, nitrate and dissolved organic nitrogen. The ammonium ion is readily adsorbed onto mineral particles and nitrite is unstable in aerated conditions. Nitrate is the most commonly determined of the nitrogen species. Total oxidised nitrogen-N is not discussed. For the Darwin Rural Area, it approximates nitrate-N because no other oxidised nitrogen species were found in the groundwaters.

Nitrite

Nitrite (NO_2^-) was not detected in any groundwater recovered during this survey in which detection limits were in excess of two orders of magnitude lower than the NHMRC (1996) health guideline of 0.9 mg/L N. Nitrite can be an indicator of contamination but is unstable under oxic conditions. Dissolved oxygen levels in Darwin regional groundwaters were relatively high and the redox conditions were not highly reducing - consequently nitrite was not expected to be present.

Ammonia-N

Groundwater of the Darwin Rural Area has very low ammonia content (Appendix A4.36). Less than 30% of groundwaters sampled had any detectable ammonia-N (detection limit of 0.01 mg/L); all detections were at concentrations less than 0.03 mg/L-N. The NHMRC (1996) recommended aesthetic guideline of 0.4 mg/L-N is an order of magnitude higher than the highest concentrations detected.

In the Howard River Catchment, the highest concentration of ammonia was found in bore RN 22068, in the piezometer nest on the eastern margin of the catchment. This anomalous ammonia level is complemented with an extremely high *Clostridium* spore count. In the western side of the catchment, ammonia was detected in an arcuate band that adjoins but rarely overlaps, only where there is anomalous nitrate occurrence (Figure 4.5.1: contours are in µg/L). Here in the western Howard River Catchment, ammonia has significant positive correlation ($P < 0.01$) with Na and Cl. Half of the bores in this area with detected ammonia also have detects of FIB (FC, FS, &/or Cp).

In the Adelaide River Catchment, ammonia is detected in only bore RN 25731 (20 µg/L -N), which has the highest nitrate concentrations in the Harrison Dam area. Ammonia has a highly significant positive correlation with iron-precipitating bacteria.

In the Berry Creek-Darwin River Catchment, ammonia is detected in only bore RN 21427 at 20 µg/L -N which also has modest nitrate (120 µg/L -N). In this region, ammonia has highly significant positive correlation with abundance of sulphate-reducing bacteria.

Discussion

In the Howard River Catchment, the spatial pattern of ammonia concentration shadows but does not coincide with the occurrence of nitrate (Figure 4.5.1: contours are in µg/L) and this pattern suggests a genetic association with nitrate, most probably as a precursor of it. This explains the more frequent association with FIB detects. In 50% of groundwaters where it was detected, ammonia is associated with FIB detects. In this region it may be possibly a more sensitive indicator of FIB contamination than the standard microbiological sampling. However, the association with Na and Cl may indicate concurrence with the area of probable seawater mixing in the aquifer.

Ammonia detection in both other catchments was limited to one strike in each area, in groundwater with modestly low nitrate levels but with no FIB.

Ammonia enters the groundwater system from fertilisers, plant residues, wastes and is adsorbed from the atmosphere. It is considerably less mobile than nitrate, has a tendency to be adsorbed onto mineral surfaces and is often nitrified before entering the groundwater system. For these reasons it is a less common indicator of groundwater contamination.

No correlation is apparent between ammonia and nitrate, however nitrate has a low but significant positive correlation with dissolved oxygen in all areas while ammonia has a non-significant negative correlation with dissolved oxygen. These give a weak indication of oxidation of ammonia in relatively oxygenated waters.

Nitrate

Although detected in all but one groundwater sample in the Darwin Rural Area (Appendix A4.37), nitrate levels are very low, almost entirely an order of magnitude lower than the NHMRC (1966) health guideline level of 11.4mg/L N (50mg/L NO_3). The Adelaide River Catchment has the highest levels, peaking at 2.1 mg/L N. All other groundwater samples from all catchments have nitrate concentrations < 0.9mg/L N.

In the Howard River Catchment, higher nitrate levels are in the upper catchment to the southeast, and in an arcuate zone in the western side of the river from Bore 21995 around to Bore 8825 (Figures 3.2.4, 4.5.1). There is a positive correlation of nitrate with tritium activity (Figure 4.3.18), that is with younger waters. Significant negative correlations in the western Howard River Catchment exist between nitrate and SO_4, Ca, TDS, HCO_3 and alkalinity.

In the Harrison Dam area of the Adelaide River Catchment, three bores have the highest nitrate levels detected in this survey and two of them, RN 27743 and 21343, also contain significant traces of condensed phosphate but with no FIB detects. In this catchment, significant positive correlations exist between nitrate and K, NH_3, and iron-precipitating bacteria but no FIB detects. Nitrate levels decrease to the northwest of the sampled area (Figure 4.5.1).

In the Berry Creek - Darwin River Catchment, nitrate concentrations are very low ($\leq$0.22 mg/L N) and there is a gradual decline in nitrate content from Bore 20319 northeastwards towards Berry Springs (Figure 4.5.1). Nitrate concentration has significant positive correlations with Ca/Mg, total P, and F.

Discussion

Nitrate concentrations in bores throughout the NT, with aquifer depths comparable to the Darwin Rural Area (between 12 and 70 m), are in the range 9 -12 mg/L NO_3-N (Childs & McDonald, 1993). In contrast, nitrate concentrations in the Darwin regional groundwaters are extremely low, predominantly below 0.9 but up to 2.1 mg/L NO_3 -N. Even with such low concentrations in Darwin Rural groundwater, well below NHMRC guideline levels, the combined evidence points to low-level indirect anthropogenic contamination in many bores.

The pervasive nitrate input with recharge may be predominantly due to the high levels of nitrogen compounds in rainfall. Galbally (1984) lists six major processes that contribute ammonia and oxidised nitrogen to the atmosphere. These have been quantified in their relative contribution to nitrogen content of rainfall for tropical Australia by Ayers & Gillett (1988a):

emissions from soil microbial processes	7%
lightning	<10% (Galbally, 1984)*
combustion of biomass	80%
anthropogenic fuel combustion	<5%
fertiliser application (10% of applied NH_3)	
volatilisation of ammonia from animal urine	10%

*No evidence was found by Likens *et al.*(1987) to suggest that lightning contributed to the nitrate concentration in rainfall at Katherine.

In the western Howard River Catchment, it has already been demonstrated that there is a chemical evolution of groundwater (Figures 4.2.1, 4.2.3, 4.2.5), becoming progressively higher in TDS, pH, and consequently in major ions. The negative correlation of nitrate with these parameters suggests that there is reduction of nitrate with age of the groundwater in the aquifer. This trend corresponds to the observed reduction of nitrate that follows the decline of tritium activity (hence apparent age) of the groundwater (Figure 4.3.18).

Nitrate variation is more erratic than the corresponding reduction in tritium activity in the groundwater (Figure 4.3.18). The nitrate variation is interpreted as being the combined result of a steady first-order reduction, comparable to that of tritium activity, with superimposed contamination spikes. The steady first-order reduction of nitrate concentration is most probably by natural biochemical processes. A surface contamination source of higher nitrate concentrations is inferred for groundwaters in bores RN 8825, 25917, 24728, and 21995, and confirmed by the co-occurrence of FIB (FS, FC and/or *Clostridium*) in these samples. These bore waters indicate a recharge component of contaminated surface water that was originally sourced from the aquifer via the bore, and hence retaining a lower tritium signature than would be expected from normal recharge (Figure 4.3.18). This pattern of nitrate contamination, superimposed on a progressive reduction in groundwater nitrate, has been observed in the Piccadilly Valley, SA (Ivkovic et al., 1998)

The combined presence of nitrate and condensed phosphate, as well as correlations with potassium and ammonia indicate very low anthropogenic contamination, probably from fertilisers in land use, around bores RN 27743 and 21343 in the Adelaide River Catchment. A similar pattern around bore RN20319 in the Berry Creek - Darwin River Catchment may also indicate recharge waters with minor dissolved contamination from a fertiliser source.

Nitrate has a low but significant positive correlation with dissolved oxygen in the Darwin region (Figure 4.5.2). In the western Howard River Catchment, both dissolved oxygen and Eh have positive correlation with nitrate concentration. This is seen to reflect the previously observed association of younger groundwater (generally with higher dissolved oxygen) with higher nitrate levels; a correlation also to be expected with the progressive exhaustion of both components by microbial processes within the aquifer.

Phosphorus/Phosphate

The parameters measured for this study are termed 'total dissolved phosphorus' and 'dissolved reactive phosphorus' but operationally include any particulate phosphorus forms that are smaller than 0.45μm:

Dissolved reactive phosphorus is largely a measure of orthophosphate (inorganic and organic) but with a small fraction of any condensed phosphate which is hydrolysed in trace amounts

Total dissolved phosphorus encompasses all inorganic condensed phosphates (pyro, meta and other polyphosphates), and organic condensed phosphates, in addition to orthophosphate (dissolved reactive phosphorus).

The difference between these parameters generally indicates the level of **condensed phosphate**. This component of the phosphates can result from the contribution of natural biomass within the groundwater, as well as anthropogenic contamination.

Phosphorus concentrations were very low in all catchments, with median values of 0.013 ± 0.001 mg/L reactive phosphorus (Appendix A4.39), and 0.015 ± 0.001 mg/L total dissolved phosphorus (Appendix A4.40).

Howard River Catchment groundwaters have the greatest range of phosphorus concentration, from 0.003 to 0.112 mg/L total dissolved P. Both the Adelaide River and Berry Creek Catchments have much narrower ranges, between 0.001 and 0.028 mg/L total dissolved P. Phosphorus is predominantly present as orthophosphate, seen in a close 1:1 relationship between total dissolved and dissolved reactive phosphorus (Figure 4.5.3). Significant departure from this 1:1 relationship indicates the presence of condensed phosphate species of presumed anthropogenic origin.

In all catchments except Berry Ck-Darwin River Catchment, P as orthophosphate has significant positive correlations with Ca, Mg, HCO_3, alkalinity and pH, indicating their higher concentration in the Coomalie Dolomite aquifer.

In the western Howard River Catchment, 37% of sampled bores (n =19) indicate presence of P(total-reactive), that is, condensed phosphate. RN 25619 (a palm grove and nursery) has the highest condensed phosphate at 0.023 mg/L P and adjoining bore

RN 8825 (on a nursery) has 0.006 mg/L P. Three other sites, RN 27687(domestic bore with surrounding mango plantation), 27050 (open paddock near orchards), and 21995(earlier land usage for poultry, pigs, and horses) have condensed phosphate levels of 0.004 mg/L P (Figure 4.5.4). Condensed phosphate shows significant positive correlation with tritium activity, dissolved oxygen, Eh and TDS, but negative correlation with SO_4.

In the eastern Howard River Catchment, 33% of sampled bores (n = 6) have low levels of condensed phosphate; RN 25034 on an orchard (at 0.017 mg/L P) and RN 21374, the site of an earlier poultry farm (at 0.006 mg/L P). Orthophosphate, total phosphate and condensed phosphate have significant positive correlation with K and Si.

In the Adelaide River Catchment, 50% of sampled bores (n = 6) have detectable condensed phosphate; RN 27743 on an orchard has 0.017 mg/L P, and RN 21343 (a banana plantation) and RN 24997 (a nursery) have 0.006mg/L P. Here total phosphate and condensed phosphate correlate with fluoride, and condensed phosphate also with Sr. Orthophosphate has a negative correlation with δD.

In the Berry Creek-Darwin River Catchment, Bore RN 20319 (a domestic bore on a mango plantation) has detectable condensed phosphate at 0.006 mg/L P. Total phosphate has significant correlation with K, Ca/Mg, NO_3, F and δD.

Discussion

Phosphorus has both natural and anthropogenic origins. It is found in the dissolved form in natural waters as a result of natural weathering and solution of phosphate minerals (such as apatite), soil erosion, soil fertilisation, biological transfer, the use of soluble phosphate compounds found in detergents and domestic and industrial waste waters (Stumm and Morgan, 1979). Anthropogenic sources include fertilisers, sewage, animal waste, detergents and organic phosphate species.

Phosphorus exists in natural waters primarily as orthophosphate because of its chemically stability but biological lability in that form. Phosphate has a low solubility that is controlled by pH and redox conditions, by adsorption onto mineral particles, co-precipitation and uptake by biota. Its concentration in natural waters would usually be less than 0.5 mg/L (Stumm and Morgan, 1979). Only one site, RN 25619, approached this concentration of total phosphate (0.112 mg/L) with an inferred concentration of 0.023 mg/L P as condensed phosphate, and adjoining bore RN 8825 may reflect the diffused signature of this component (Figure 4.5.4). These two bores and RN 21995 also contained FIB, believed to be sourced from domestic septic contamination. All other sites in all catchments had less than half of the RN 25619 level of total dissolved phosphorus.

Phosphorus levels in groundwater differ markedly with aquifer type in the Darwin Rural Area. Bores with screened intervals within siliciclastics , common in the Howard River Catchment, have groundwaters significantly lower in total dissolved phosphorus (below 0.025 mg/L P) than in the Coomalie Dolomite aquifer. In groundwaters sourced from this aquifer, there is positive correlation between phosphate concentrations, TDS and pH (Figures 4.5.5, 4.5.6).

Groundwaters from the Dolomite aquifer show a wider spread from 0.004 to 0.112 mg/L P in the Howard River catchment. Groundwater from the Dolomite aquifer in all catchments is clearly delineated by pH >6 and a comparable though not as distinct differentiation is made by TDS (Figures 4.5.5, 4.5.6). Apart from the FIB-contaminated RN 25619, small subpopulations of groundwater exhibit an apparent inverse relationships between total dissolved phosphorus and both TDS and pH. The pathway of recharge for the Dolomite aquifer is via infiltration through the overlying clays and siliciclastics of the Cretaceous sequence. Given the higher phosphate levels in the Dolomite aquifer, and the apparent trends of decreasing levels of phosphate with both increasing TDS and pH, it would appear that there is initial dissolution of phosphate from the Dolomite aquifer when the recharge waters first interact with the unit, and when pH is below 6. As the recharge waters equilibrate with the Dolomite, with a consequent rise in both pH and TDS, it appears that this dissolved orthophosphate is re-precipitated (Figures 4.5.5, 4.5.6).

The highly significant correlations of phosphate concentration with K and Si in the eastern Howard River Catchment, and with F in the Adelaide River Catchment, and with K and F in the Berry Creek-Darwin River Catchment may indicate a component of sources is from dissolution of silicates and apatite. In the Berry Creek area, the aggregate of significant correlations of total phosphate with K, NO_3, and δD may indicate a source from fertiliser that has infiltered with more evaporated waters, such as with irrigation effluent during the dry season. An alternative interpretation is that this phosphate component is introduced with the intrusion blend that includes some seawater.

N-P relationship

Where nitrate and condensed phosphate (P total - P dissolved reactive) have a combined presence, anthropogenic contamination is suspected, especially where faecal indicator bacteria are also detected. Of 11 bores with detected FIB (Table 4.5.1), RN 25619, 21995, and 8825 have above background nitrate and condensed phosphate levels. An additional 7 bores have groundwater with above background nitrate and condensed phosphate. The majority of these bores are sited on horticultural activities.

Dissolved Organic Carbon (DOC)

All natural waters contain organic material, generally in low concentrations. This organic matter can affect metal solubility, participate in redox reactions and provide nutrients for biota that participate in subsurface biogeochemical processes. The naturally occurring organic compounds are considered to be similar to those found in soil.

Dissolved organic carbon (DOC) concentrations in natural waters can be variable and tend to be lower in groundwaters, where it is more likely to be affected by adsorption, than in surface waters. High DOC concentrations are often, though not invariably, an indicator of contamination from, for example, sewage, animal wastes, or industrial chemicals. On the other hand the inhibition of microbial degradation processes by local physico-chemical conditions, and/or the resistance to breakdown conferred by chemical structure, may enable the accumulation of eg. dissolved humic and fulvic compounds originating from higher plants.

It is possible to make only general comments about DOC in Darwin Rural Area groundwaters. QA/QC protocols indicate that the data are unreliable. The data do, however, suggest very low DOC concentrations, even from sites where faecal contamination is evident, consistent with the generally very dilute character of these groundwaters. Among the many (highly speculative) explanations for this are the possibilities that DOC may be substantially consumed before it can transit from the source to the casing screen and/or the particulate FIB may move ahead of soluble materials such as DOC as a consequence of size exclusion and hydrodynamic chromatographic effects (Harvey *et al.*, 1989).

Bore	Land Use Comments	NH_3	NO_3	Pcond	Portho	FC	FS	*Clost.*
West Howard River Catchment								
RN 7071	adjacent to orchards, mangoes				0.02	4	270	
RN 9225	scattered orchards, open woodland				0.02	1		
RN 6310	open woodland	0.02			0.03			
RN 20255	domestic use, septic nearby,	0.02			0.03		5	
RN 27525	domestic and orchard	0.03						
RN 25917	orchard of tropical fruits	0.02	0.33			1		
RN 25619	domestic use, palm grove	0.02	0.15	0.023	0.09		1	
RN 21995	unused, some poultry; prev. horses,pigs	0.02	0.71	0.004	0.02	1	3	1
RN 8825	open cleared land, domestic use		0.21	0.006	0.05	2	2	
RN 27871	domestic use; mango orchard							
RN 28032	mango & tropical fruit orchard							
RN 24728	mango orchard		0.28		0.04		1	
RN 27374	mango orchard							
RN 27050	open paddock near orchards			0.004	0.04			
RN 8450	open padock with surrounding gardens		0.37					
RN 20780	nursery with surrounding mango orchard							3
RN 27687	open woodland, domestic use, surr. mangoes		0.27	0.004				
RN 9421	rainforest	0.01						
RN 22387	domestic use; mango orchard		0.19					
East Howard River Catchment								
RN 22069	open woodland							
RN 22068	10m from RN 22069, open woodland	0.02				1		TNTC
RN 26455	mangoes, woodland; no house		0.12					
RN 21374	old poultry farm site; surrounding bush		0.49	0.006				
RN 25034	cane & flower farm, domestic crops		0.36	0.017	0.03			
RN 21398	close to RN 22069, RN 22068							
Adelaide River Catchment								
RN 25371	Mango & banana orchard	0.02	2.08					
RN 29733	Banana orchard				0.02			
RN 24997	nursery		0.36	0.006	0.02			
RN 21343	adj. banana plantation		0.87	0.006				
RN 4223	open woodland; sev hundred m to bananas		0.16				7	
RN 27743	banana plantation		0.93	0.017				
Berry Ck - Darwin River Catchment								
RN 21427	open woodland	0.02	0.12					
RN 26686	Banana Plantation & natural woodland		0.11					
RN 26779	mango orchard							
RN 25232	school supply & fire tank supply							
RN 20319	domestic use, mangoes		0.22	0.006	0.02			

Nutrients in mg/L
Pcond, Porth condensed & ortho Phosphate
FC, FE/FS, *Clostridium* -Faecal indicators

Table 4.5.1 Summary of potential contaminant indicators in bores, Darwin Rural Groundwater

Bore	Land Use Comments	Li	F	Cu	Ni	Zn	Co	Cr	Pb	Br	Other
West Howard River Catchment											
RN 7071	adjacent to orchards, mangoes										
RN 9225	scattered orchards, open woodland		150								
RN 6310	open woodland										
RN 20255	domestic use, septic nearby,										
RN 27525	domestic and orchard					9				66	
RN 25917	orchard of tropical fruits			3							
RN 25619	domestic use, palm grove										
RN 21995	unused, some poultry; prev. horses,pigs	20		4	6	30					
RN 8825	open cleared land, domestic use				1						I
RN 27871	domestic use; mango orchard		360								
RN 28032	mango & tropical fruit orchard										
RN 24728	mango orchard	11									
RN 27374	mango orchard			3							
RN 27050	open paddock near orchards										U
RN 8450	open padock with surrounding gardens										
RN 20780	nursery with surrounding mango orchard			3	2						
RN 27687	open woodland, domestic use, surr. mangoes										
RN 9421	rainforest										
RN 22387	domestic use; mango orchard		170	3	2	14	1				
East Howard River Catchment											
RN 22069	open woodland										
RN 22068	10m fromRN 22069, open woodland				2						
RN 26455	mangoes, woodland; no house										
RN 21374	old poultry farm site; surrounding bush	12		1	1						
RN 25034	cane & flower farm, domestic crops	14						1			
RN 21398	see RN 22069, RN 22068										
Adelaide River Catchment											
RN 25371	Mango & banana orchard									189	
RN 29733	Banana orchard									136	
RN 24997	nursery	12		1							
RN 21343	adj. banana plantation										
RN 4223	open woodland; sev hundred m to bananas									86	
RN 27743	banana plantation		110						2	186	Sr
Berry Ck - Darwin River Catchment											
RN 21427	open woodland										
RN 26686	Banana Plantation & natural woodland								2		
RN 26779	mango orchard			1							
RN 25232	school supply & fire tank supply										
RN 20319	domestic use, mangoes										

Table 4.5.1 Summary of potential contaminant indicators in bores, Darwin Rural Groundwater

4.6 PESTICIDES

Introduction

Pesticide contamination of groundwater is becoming an increasingly important global issue. Little is known of contamination levels in rural areas of Australia. The groundwater quality in this study area may be influenced by residential expansion into areas which were previously farmed lands. The dominant land uses of the Howard River Catchment are tropical fruit plantations (bananas, mangoes, custard apples, star fruit and other exotics), rural residences and open bushland (Northern Territory Department of Lands and Housing, 1990).

The NHMRC (1996) Australian Drinking Water Guidelines state that pesticides should not be detected in drinking water. The detection of pesticides in groundwater is of health significance as many exhibit toxic properties.

Some insecticides, such as the organochlorine group, are persistent and not readily mobile in the soil and vadose zone. They tend to accumulate through the food chain, concentrating in body fat. In recent years organochlorines have been linked with cancer, reproductive and fertility disorders, hence their deregistration for most agricultural applications in the 1980's. Despite application restrictions, organochlorines remain a common contaminant of soils due to their widespread historical use and persistent nature (Bouwer, 1978), with half-lives ranging from moderate to long (eg. $t_{1/2}$ of: endosulfan = 50 days, lindane = 180 days; Weber and Keller, 1994). In addition to half-lives, other chemical properties influence their environmental fate. Water solubility and volatility play a part, as does K_{oc} (distribution coefficient between soil organic carbon and water). K_{oc} measures the capacity of a chemical to bind to organic carbon. Low K_{oc} indicates a low capacity to bind to organic carbon and, therefore, high mobility, whilst a high K_{oc} indicates the compound is more likely to bind to soil, hence low mobility. Organochlorines tend to have moderate to very high K_{oc} values (eg. K_{oc} of: endosulfan = 10000, lindane = 1100) and are therefore more likely to be found in the vadose zone than in groundwater.

Organophosphorous insecticides are acutely toxic, but break down in the environment more rapidly than organochlorines. Half-lives of this group are generally very short to moderate (eg. $t_{1/2}$ of: malathion = 2 days, Ethion = 90 days). Organophosphorous insecticides also have moderate to very high tendencies to bind to soil (eg. K_{oc} of : Malathion = 1800, Ethion = 10000).

Triazine herbicides, on the other hand, are relatively mobile and have often been found in Australian groundwater from rural regions (Bauld, 1994b). Half-lives of *s*-triazines range from very short to moderate ($t_{1/2}$ of: anilazine = 1 day, simazine = 90 days) and they have a very low to low ability to bind to soils (eg. K_{oc} of: anilazine = 1000, simazine = 200), which contributes to their mobility in the environment.

Thirty-six groundwaters were collected during AGSO's field survey of the Darwin Rural Region, all of which were processed in the field using solid phase extraction methodology (Appendix A6.5) and later analysed by Gas Chromatography-Mass Spectrometry (GC-MS) for pesticides from Schedule A (see Appendix A6.2). Three replicate samples, three field-spiked samples and two field equipment blanks were extracted and analysed alongside the bore samples. Two spring water samples were collected to compare with nearby groundwater.

In addition, all 36 groundwater samples were extracted and analysed for pesticides from Schedule B (See Appendix A6.3) using slightly different extraction and analytical methods (Appendix A6.5). This schedule consists of compounds unsuitable for Schedule A extraction and analytical procedures, due to their acidic nature. Three field-spiked samples and two field equipment blanks were extracted and analysed using these altered procedures alongside the groundwater samples. Two surface water samples were also collected and analysed for Schedule B compounds, to compare with nearby groundwaters.

The detection limits of analytes from Schedule A and B are, generally, two orders of magnitude lower than the NHMRC Health Guideline Values. Previous analyses of groundwater from this area (Wilson, 1992) had lower detection limits for most analytes, but a narrower range of compounds were screened.

Previous Work

In 1981-1982 the Power and Water Authority conducted a groundwater investigation in the McMinns-Benham Lagoon area (Jolly, 1983). This study contained limited water quality data but did not include organic analyses. Aquifers in the Darwin Member and Coomalie Dolomite were described as uncontaminated. Only one bore from the McMinns-Benham Lagoon area was sampled in the present study (Bore 21398).

The Power and Water Authority conducted a subsequent surface and groundwater investigation (Wilson, 1992). A trace of carbaryl (<1µg/L) was detected in surface water from runoff in the Howard Springs area. Atrazine and prometryn were detected at trace concentrations (<0.01µg/L) in a groundwater sample from the Berry Springs area.

The present groundwater survey extends earlier studies, covering a more comprehensive range of pesticides. The majority of chemicals identified as being commonly used in the Darwin Rural Area (Alcock, personal communication) were screened (eg. endosulfan, dimethoate, chlorpyrifos, malathion, carbaryl, chlorothalonil, metalaxyl, chlordane, heptachlor, dieldrin, aldrin, fluroxypyr, picloram, triclopyr, hexazinone, diuron and 2,4-D). Historically insecticide and termiticide application in the area has been high, though some of these compounds (dieldrin and aldrin) have been de-registered for use (Alcock, personal communication).

Results and Discussion

Pesticides from Schedule A and B (Appendices A6.2, A6.3) were not detected in any of the thirty-six groundwater and two surface water samples. This survey represents only one time slice at the end of the dry season. It is expected that groundwater is more vulnerable to contamination during the monsoon season as recharge accelerates and water tables rise. In addition other prevailing conditions, such as temperature and soil pH, may have influenced degradation rates in this region.

Conclusion

Groundwater sampled in this study of the Darwin Rural Region was free from pesticide contamination. The potential for organic contamination of groundwater of this area is high, as evidenced by the presence of microbiological contamination and previous reports of contamination. Intensive use of insecticides and termiticides, in particular, appears not to have affected groundwater quality, most probably due to the immobile nature of many of these compounds.

4.7 MICROBIOLOGY

Background

Like natural habitats everywhere the subsurface environment, including groundwater, has been found to contain a broad spectrum of microbial types similar to those found in surface soils and waters, encompassing bacteria, fungi and protozoa, and representative of most physiological types. On occasion pathogenic viruses, bacteria and protozoans of gastrointestinal origin from domestic, agricultural and other anthropogenic activities, may infiltrate through soils, sediments and rocks to the underlying groundwaters. There they may survive for sufficient time to be available for ingestion with the drinking of extracted groundwater.

Faecal Indicator Bacteria (FIB) are used as surrogates for pathogenic microbes of gastrointestinal origin (including bacteria, viruses and protozoa) since the difficulty and cost of routinely enumerating the latter remains significant. Their presence in a water sample indicates that the water has received faecal contamination from humans and/or other warm-blooded animals. FIB are generally present in the gastrointestinal tract (GIT) in large numbers and their public health utility is based on the assumption that they survive in aquatic environments at least as long as GIT-borne pathogens. Many pathogens (e.g. *Salmonella, Leptospira, Campylobacter, Giardia,* and *Cryptosporidium*) found in warm-blooded animals will also infect humans ingesting contaminated water.

Three classes of FIB were target indicators for our groundwater quality assessment of the Darwin Rural Area - faecal (thermotolerant) coliforms (FC), faecal streptococci (FS) [also referred to as faecal enterococci (FE), a closely similar but not identical group], and spores of *Clostridium perfringens* (Cp). FC and FS are "normal" bacterial cells whose survival outside the GIT is commonly reported to range from hours to days (but see below). In contrast, Cp spores are dormant cells which survive indefinitely under a wide range of environmental conditions providing a long-lived indicator of faecal contamination.

Most public health and/or regulatory agencies set standards/guidelines using FC (i.e. FC should not be detectable in any sample; minimum volume 100mL). FS provide an additional indicator because they may be present in faecal material in considerably higher numbers than FC, appear to be more persistent in aquatic environments than FC (*eg* McFeters *et al.*, 1974), and are resistant to drying (thereby surviving episodic transport through the vadose zone). Cp, as a consequence of their longevity (of the order of years), may accumulate and be detected long after and far away from contamination event(s) and thus indicate intermittent and/or remote contaminant sources.

Interpretation of FIB data

The presence of FIB at any subsurface location is contingent upon processes such as transport and/or retention of FIB, their survival as entities capable of growth (and hence detection) after reaching ground water, and the magnitude and frequency of contamination events.

Bacteria are usually of colloidal dimensions (i.e. of diameter < 10 μm, commonly as small as 1-2 μm) enabling them to be transported with other particles from the soil surface into the subsurface by recharge events. Considerable lateral distances may be traversed in the subsurface before FIB succumb to the relatively hostile world outside the GIT. Depending on the surface properties of both bacteria and sediment particles and the surrounding aqueous medium bacterial cells may adsorb reversibly or irreversibly to solid phase material in the subsurface environment.

Survival times for both FC and FS are dependent on environmental constraints and are variously reported in the range hours to days (occasionally weeks) depending on environmental conditions; they are sufficiently variable as to be no more than a general guide. Cp spores are stable over long periods as a consequence of their resistant structure and metabolic dormancy, and thus provide a long-lived signal of faecal contamination.

Survival of gastrointestinal bacteria and viruses in the (subsurface) environment appears to be promoted by low temperature, saturated conditions, and sufficient amounts of organic matter (but compromised by sunlight, low pH, and indigenous microbes which are antagonistic or predatory).

Most investigations of FIB survival have been carried out in temperate zone climates. These studies suggest that survival time is increased markedly at lower temperatures and at temperatures below 4°C survival for months or years has been reported. At higher temperatures (5-30°C) the die-off rate approximately doubles for each 10°C temperature increase. Survival would be enhanced during cooler months when shallow unconfined water tables would decrease in temperature.

The relevance of such data to tropical environments is unclear - not only are environmental temperatures substantially higher, but they are also much more stable. FC and FS are reported to survive for longer periods in tropical (surface) waters than in temperate waters. Further, it has been suggested that FC and FS are inappropriate indicator organisms in tropical waters because they can be found in the absence of (human) faecal contamination (Hazen and Toranzos, 1990; and references therein). However, the possibility that faecal contamination of these tropical waters originated from warm-blooded animals could not be excluded by the investigators.

FIB in Darwin Rural Area Groundwaters

General

Thirteen of the 38 samples contained one or more groups of FIB (i.e. 34%; Tables A3.11 & 4.5.1); two of the FIB-positive samples were surface expressions of underlying groundwaters (Howard and Berry Springs) reducing the proportion of FIB-positive bores to 11/36 (ie. = 31%). If FC only are used as the criterion for contamination, as is the case with most regulatory agencies, the proportion of FIB-positive samples falls to 8/38 (21%) [6/36 (17%) for bore samples], and is thus an underestimate of the actual frequency of contamination.

Inspection of the FIB data, together with those physico-chemical parameters which might be associated with human or animal faecal contamination (eg. DOC, other nutrients), does not reveal any obvious correlations. Analysis of the data is thus presented on a sample by sample basis.

Low-level FIB Contamination

With the exception of three samples (one spring and two bores) FIB levels were low (1-7 FIB/100mL), though exceeding drinking water standards [should be < 1 CFU/100mL for FC]. Of the 9 bores in this category, contamination in 5 (55%) can reasonably be attributed to domestic sources (via inferred septic tanks) - in each of these cases [RN 9225, RN 20255, RN 25619, RN 8825, RN 20780] houses are situated within approximately 10-20 m of the bore.

Plausible explanations can be advanced for another three bores -

RN 21995 is situated ca 70-80m from the house but only ca 25m from domestic poultry. Investigation of two FS cultures recovered from the sample was inconclusive and either location could be the source.

RN 4223 is located in natural bush and the nearest house is ca 200-300m away. The most likely source of FIB appears to be from native animal faeces infiltrating to the water table in the vicinity of the bore as a result of constant leakage from the (then) diesel pump which may attract wildlife to the site. At the time of sampling the owners were beginning to install a replacement electrical pump so this may no longer be a problem.

RN 25917 is located ca 300m from the nearest house and contained FIB (FC) at the detection limit. It is possible that preferential flow from the (inferred) septic tank at the house/packing sheds may have carried some FIB to the bore intake. Another possibility is the infiltration of run-off (or septic tank leakage) from the stormwater drain which is adjacent (ca 10-20m) to both the house and the bore.

On the other hand, RN 24728 is located in a mango orchard, there are no houses within 500m, and no obvious source of faecal contamination.

The low FIB populations recovered from these bores might be attributable to one or more of the following; faecal contamination reaching the sampling point took place as a single event some time prior to sampling and most of the FIB have died i.e. an earlier sample would have measured higher levels and a later sample lower levels; contamination occurs continuously (eg.leaking septic tank) but the sample point is sufficiently remote from the contamination source that transport distance/travel time is close to the limit for FIB survival time and attenuation by adsorption to soil or sediment.

Three of the contaminated samples in this category have low pH waters which would be inimical to FC and FS survival (RN 20780, pH 4.05; RN 21995, pH 4.48; RN 25917, pH 4.48). This suggests that input contamination might be greater than would be inferred for higher pH samples (other factors being equal).

Substantial-level FIB Contamination

Samples from Berry Springs (see below) and two bores showed substantial FIB contamination.

RN 7071 contained only slight FC contamination but FS were present at levels two orders of magnitude higher. Concentrations of DOC, and other nutrients likely to accompany faecal contamination, were low as was the population of heterotrophic bacteria naturally present in the aquifer. Land use was recorded as "rural sub-division adjacent to orchard, treed, mainly uncultivated" and therefore not flagging any obvious activity likely to be a source of faecal contamination. However, houses are located within 50-100m and one may well be up-gradient from the bore. The septic tanks at these houses are a probable source of the contamination and the presence of mostly FS is consistent with their higher survival compared with FC.

The other bore (RN 22068) in this category not only has barely detectable FC but lacks FS (ie.< 1 CFU/100mL). However, the sample had the highest NH_4-N concentration of any sample recovered from the study area, and contained high levels of *Cl perfringens* spores, consistent with either a large one-off contamination event or sustained low level contamination. The groundwater was of low pH (5.25), which would decrease FC and FS survival but would have little impact on Cp spores. The source of contamination remains conjectural since the site is in open woodland, is not settled, there are no agricultural activities and RN 22069, a mere 10m away and shallower (also lower pH), did not provide an FIB-contaminated sample.

FIB Contamination in Springs

Howard Springs and Berry Springs were sampled as close as possible to their sources. These springs are in nature reserve areas and, in both cases, the most probable source of faecal material would be from wildlife, principally (water)birds which appeared to be present in high numbers. Both samples were contaminated with FIB (Table A3.11; FC & FS; Cp only in Berry Springs), though the level of contamination in the Berry Springs sample was about two orders of magnitude higher than in the Howard Springs sample. This is probably due to two factors: the Howard Springs sampling site was almost at the spring source whereas at Berry Springs it was ca 30m downstream from the source, increasing the likelihood of contaminant input from wildlife. Further, the Berry Springs site was less accessible for people, and hence more attractive to animals. Subsequent laboratory investigation of FS strains recovered from these samples revealed the presence of *Enterococcus faecalis* and *E. gallinarum*, the latter consistent with the presence of abundant birdlife.

Discussion

The overall incidence of faecal contamination was 31% of bores sampled as determined by the presence of one or more classes of FIB. The incidence falls to about half (ie. 17%) when the standard regulatory indicator class for drinking water quality (FC; Australian Drinking Water Guideline Value < 1 CFU/100 mL) is used as the sole criterion of faecal contamination. However, FS are also valid indicators of faecal contamination and may even be somewhat more persistent in the natural environment than FC ie. a more sensitive indicator class. Previous work (summarised in Jolly, 1983) reported that, while groundwaters from the lateritised profile of the Cretaceous sediments were contaminated, groundwaters from the sandstones of the Darwin Member and the weathered Coomalie Dolomite aquifers did not appear to be contaminated.

Concentrations of FIB in groundwaters were generally low (ie.< 10 CFU/100 mL). In some instances low groundwater pH may be a contributing factor to the low numbers, since low pH is known to diminish FIB survival times. In contrast, the relatively high groundwater temperatures could conceivably extend survival times relative to those pertaining in more temperate subsurface environments. While the foregoing is speculative it seems that the interaction of temperature and pH is likely to play an important role in FIB survival in the Darwin Rural Area and that a clearer understanding of this would provide a useful interpretative tool for resource management from a public health perspective.

Substantially higher concentrations of various FIB classes were found in two groundwater samples and in runoff from Berry Springs. Contamination in the latter case is attributable to wildlife, principally waterbirds. Attribution of contaminant sources in the case of groundwater samples is less clear cut but most plausibly due to leaking domestic septic tanks which are, in many instances, within reasonably close proximity to the bores sampled.

FIB released from leaking septic tanks would be most unlikely to be exposed to UV light, thus enhancing their survival, and could move by infiltration and/or preferential flow through the vadose zone to the water table. However, our data do not preclude the possibility that FIB gain access through damage or corrosion at or near the borehead, or as a result of design, construction or completion inadequacies. It would be important that such problems that may exist be remedied ahead of further monitoring activities to ensure unambiguous interpretation of FIB data is possible.

Naturally-Occurring Microbial Populations

In view of the relatively limited information available regarding the naturally occurring (indigenous) microbial populations of the Darwin Rural Area aquifers all samples were routinely screened for a variety of heterotrophic bacteria. Heterotrophic bacteria, requiring an exogenous source of utilisable organic carbon for cellular synthesis and energy generation, generally respond to increasing concentrations of

DOC. In addition to enumerating general heterotrophs, specific metabolic types sought included those with nitrate-reducing, sulfate-reducing, iron-precipitating and cellulose-degrading capabilities.

Overall heterotrophic microbial populations (aerobes and facultative aerobes), as estimated using R2A medium, vary over more than 3 orders of magnitude (range 0.6-1228 CFU/mL) in groundwater samples (Table A3.11). Only 19% (7/36) of groundwater samples contained more than 50 CFU/mL R2A heterotrophs. The high heterotrophic microbial population in Berry Springs (5900 CFU/mL) was consistent with the substantial extent of faecal contamination (see above) and the associated organic input. However, less than half of those groundwater samples exceeding 50 CFU/mL R2A heterotrophs contained detectable FIB and, in the absence of reliable DOC data (see section 4.5), it is not possible to be more specific about this association.

The activity, and population level, of heterotrophic bacteria is also dependent on the availability of appropriate electron acceptors. Molecular oxygen is the most energetically favourable and is used by obligate and facultative aerobes such as those enumerated by R2A medium. Other electron acceptors include nitrate and sulfate - nitrate is used by some aerobes when dissolved oxygen concentrations fall below bulk readings of ca 2 mg/L; such microbes are capable of removing nitrate by reducing it to nitrite and the nitrogenous gases including dinitrogen; sulfate-reducing bacteria are obligate anaerobes and will be inactive in the presence of dissolved oxygen. Iron-precipitating bacteria deposit ferric iron as rust-coloured deposits - ferrous iron can oxidised by direct enzymatic processes or by indirect processes. During the latter microbial cells alter the surrounding environment sufficiently to instigate iron oxidation and/or precipitation. Cellulose digesting bacteria are common in soil but little is known of their occurrence in groundwaters, though they might reasonably be expected to be more prevalent in unconfined aquifers where cellulose, an insoluble source of organic carbon, might find easier access than to semi or fully confined aquifers.

Populations of nitrate-reducing heterotrophic bacteria ranged over about 5 orders of magnitude (10 - 330,000 MPN/100mL) and there was very little correspondence with R2A heterotrophic populations. Heterotrophic iron-precipitating bacteria (range < 1 - 4700 CFU/100mL) showed a similar lack of correspondence with other physiological groups. Sulphate-reducing bacteria were detectable in only about 20% of samples and, as with other microbial groups, at very low populations (< 10 - 100 SRB/mL). Correspondence with the concentrations of chemical components (e.g. nitrate-N, sulphate, or Fe) essential for the various metabolic processes is poor and possibly masked by the low concentrations of both microbes and required chemical substrates. Cellulose-degrading microbes were not detected.

Burkholderia pseudomallei in Darwin Rural Area groundwaters

The bacterium *Burkholderia pseudomallei* is the infectious agent responsible for melioidosis, an illness characterised by pneumonia, with or without septicaemia but with a range of symptoms including fever, fatigue and urinary and neurological problems. The organism appears to be an opportunistic pathogen of humans whose resistance to disease is compromised by risk factors such as excessive alcohol intake or diabetes. While death is rare in patients with no risk factors the severity of the illness and the mortality rate appear to be determined by the underlying risk factors (Currie *et al.*, 1993; Merianos *et al.*, 1993; Currie, 1995). However, understanding of the pathogenesis of melioidosis is poor and quantification of the risk is not possible with current information (Currie, 1995).

Melioidosis is predominantly a wet-season problem, with most cases due to subcutaneous inoculation with *B. pseudomallei* from surface waters, soils, or muds. *B. pseudomallei* appears widespread in the Darwin region and has been isolated previously from 4% of soils samples and 9% of surface water samples (Merianos *et al.*, 1993). A serious outbreak occurred in 1990-91 when 33 people contracted melioidosis. Groundwater samples were filtered and the filters were placed in an enrichment medium before being transferred to appropriate pathogen containment facilities at the Menzies School of Health Research. Soil samples and surface muds adjacent to surface waters were also collected for screening.

Confirmed positive cultures of *B. pseudomallei* was recovered from 5 groundwater samples (H. Smith-Vaughan, pers comm). The groundwaters samples (RN 27871, RN 26455, RN 27050, RN 31374 and RN 8450) from which the causative agent of melioidosis was recovered exhibited no other distinguishing characteristics. None were contaminated with FIB or contained unusually high populations of other, indigenous microbes. There were no notably higher concentrations of naturally-occurring chemical constituents and neither landuse nor aquifer lithology coincided in any obvious way.

4.8 ENVIRONMENTAL ISOTOPES

Environmental isotopes are those that occur naturally in the hydrological cycle (Lloyd and Heathcote, 1985) and they are suited to providing information on type, origin, processes and age of water. Their usefulness is maximised by correlating isotope data with other hydrogeological/hydrochemical data and by using multiple isotope studies.

In this study, the environmental isotopes selected for inclusion in the September 1995 sampling project included chlorine-36 (^{36} Cl) and the constituent isotopes of water molecules: oxygen-18 (^{18}O), deuterium (D or ^{2}H) and tritium (^{3}H).

Tritium (^{3}H)

In the Darwin Rural Area, the Howard River Catchment has the greatest range of tritium activity in groundwater, from 0.2 to 2.3 TU. Spatial variation (Figure 4.8.1) in the Howard River Catchment reflects significant positive correlation of TU with Eh and DO, and negative correlation with the major ions TDS, Ca, Mg, alkalinity, HCO_3. Additionally, TU has significant negative correlation with SO_4 in the western side of the catchment, and with pH, Cl, Ca/Mg and Ba on the eastern side (Figures A5.2, A5.3).

The Adelaide River Catchment has a narrow range of groundwater TU from 1 to 1.5. In the Berry Creek- Darwin River Catchment, TU has a comparable range but with a weighting to the upper value. In this latter catchment, TU has negative correlation with TDS, Mg and Cl, relationships comparable to the Howard River Catchment. There is no consistent recognisable pattern in the Adelaide River area.

Discussion- Processes:
Tritium exists naturally but, as a result of the atmospheric nuclear weapons testing during 1952-1963, levels were increased by up to three orders of magnitude over the natural levels. Peak tritium levels, or 'bomb pulses', mark the occurrence of particular events like the 1962-63 atmospheric tests. International agreements in the 1960's curbed the tests and since then, tritium activity has been declining towards its natural levels.

Tritium (^{3}H) in waters of the hydrological cycle arises from both natural and man-made sources. Once tritium infilters the ground surface, it is generally considered to move as an integral component of the water molecule in the same way that ^{1}H does (Lloyd and Heathcote, 1985). Tritium has a half-life of 12.43 years and is a decay product of Helium-3. Tritium activity is measured as Tritium Units (1 TU = one atom of ^{3}H in 10^{18} atoms of hydrogen). The most widespread use of tritium (^{3}H) is for verification of modern recharge for waters less than 45 years old. Because of its half-life, tritium is useful in studying pesticide and other recent anthropogenic contamination (Alley, 1993).

The application of tritium as an environmental isotope in the southern hemisphere is becoming less useful as the bomb pulse levels fall to the level of pre-1952 tritium. Whilst the northern hemisphere peaks were 500 to 10,000 TU and will therefore be useful into the 2030's, the southern hemisphere peaks were comparatively low and ranged from 50 to 100 TU (Calf, 1988).

Discussion -Results:

The Darwin groundwater data indicate the expected trend (Figure 4.8.2) of decreasing tritium activity with evolution of the groundwater after recharge, and the associated general increase of dissolved ions and hence TDS. In the Howard River Catchment, two paths of groundwater evolution are apparent:

- a slight increase in TDS up to 100 mg/L with concomitant decrease of TU to 0.25, and
- a consistent increase of TDS to 200 mg/L with the same decrease of tritium activity.

These trends of chemical evolution are interpreted to reflect the differing spatial association of aquifer types (Figure 3.2.2) in relation to groundwater flowpaths within the catchment as inferred from the potentiometric surface (Figure 3.2.5), spatial patterns of groundwater age (Figure 3.2.4) and salinity (Figure 4.2.3).

- Recharge through the Cretaceous sequence and residence in a noncarbonate aquifer, either still within the Cretaceous sequence, or into a noncarbonate Proterozoic equivalent of the Coomalie Dolomite where there is minimal increase in both TDS and pH with time (Figure 4.8.3). Subsequent groundwater migration is then laterally into the Coomalie Dolomite Aquifer.
- Recharge through the Cretaceous sequence into the Coomalie Dolomite aquifer where pH increases beyond 7, and TDS concentration increases by a factor of two.

Both DO and Eh decline with age of the groundwater (Figures 4.8.4), confirmed by their positive correlation with TU.

Additionally, the mixing phenomenon due to intrusion of either seawater or estuarine riverwater, as inferred already from major ion chemistry, produces groundwaters with higher TDS concentrations and TU levels ≥ 1. These form a distinct group that plots with partial overlap with groundwater recharging direct to the Coomalie Dolomite aquifer (Figures 4.8.2, 4.8.3).

The absence of significant correlations with tritium in the Adelaide River Catchment is also thought to be a consequence of this varying intermixture of seawater within the aquifer. Five of the six groundwaters of the Berry Creek - Darwin River Catchment have comparable TU and major element characteristics (Figures 4.8.2, 4.8.3).

Variations of nitrate with tritium activity (Figure 4.3.18) are discussed under the section on nitrate (in section 4.5)

Discussion-Tritium age

Even within Australia, tritium has significant spatial and temporal variability.
Data for tritium activity in Darwin rainwater is used to establish recharge input concentrations for the local groundwater system. Recharge in the Darwin region is predominantly a wet season phenomenon, and transit time through the unsaturated zone is minimal. Although fractionation of tritium is possible by a number of processes in this zone (Lloyd & Heathcote,1985), little if any fractionation of tritium is expected before recharge reaches the saturated zone. Tritium activity in Darwin rainfall is the lowest of the Australian data due to both its low latitude and proximity to the ocean (Calf, 1988). This significantly reduces the resolution and hence usefulness of apparent tritium ages except for a general overview of groundwater movement with time.

Dating with tritium activity in the Darwin Region is attempted even though a unique solution cannot be derived. The minimum apparent ages of water in table 4.8.1 have been derived from TU weighted mean data for Darwin rainfall, sourced from IAEA (1981, 1990), and Calf (1988). The age of groundwater would approach the minimum calculated age on the assumption that mixing of groundwaters within aquifers is assumed to be negligible. This has been demonstrated not to be the case but a necessary assumption for its application. Apparent tritium ages for the Darwin Rural Area are presented spatially in figure 3.2.4. The compatibility of this solution with TDS distribution in the Howard River Catchment demonstrates the applicability the method, even within its limitations.

In each catchment, there is a significant reduction in tritium activity down catchment. The Howard River Catchment has the greatest range of tritium concentration, from 0.2 to 2.3 TU, indicating a range of apparent groundwater ages from <20 to 60 years.
Adelaide River Catchment has a narrow TU distribution of 1 to 1.5 indicating apparent ages of between 25 and 40 years, while the Berry Creek- Darwin River Catchment has a comparable TU range to the Adelaide River Catchment but with a weighting to the upper value.
These age estimates are consistent with an apparent CFC-12 groundwater age of between 30 and 40 years for the eastern Howard River Catchment (Cook *et al.*, in press).

Table 4.8.1
Age Interpretation of Tritium Activity in Darwin Groundwater

Year of recharge	TU Activity (wt. Mean) (Ao)	Calculated TU Activity at 1995 [4] (A)	Interpreted minimum age (yrs) (at 1995) (t)
		<0.12	approx. > 60 [5]
		<1.25	approx. > 37 [5]
1963	24.7 [1]	3.9	32
1964	24.5 [1]	4.1	31
1965	32.8 [1]	5.8	30
1966	15.1 [1]	2.8	29
1967	13.2 [1]	2.6	28
1968	13.9 [1]	2.9	27
1969	18.5 [2]	4.1	26
1970	14.2 [2]	3.3	25
1971	11.1 [2]	2.8	24
1972	11.4 [2]	3.0	23
1973	7.4 [2]	2.1	22
1974	6.2 [2]	1.8	21
1975	6.2 [2]	1.9	20
1976	5.5 [2]	1.8	19
1977	5.3 [2]	1.8	18
1978	6.6 [2]	2.4	17
1979	5.5 [2]	2.1	16
1980	4.0 [2]	1.6	15
1981	3.7 [2]	1.6	14
1982	4.6 [2]	2.1	13
1983	4.1 [2]	2.0	12
1984	3.2 [3]	1.6	11
1985	3.3 [3]	1.8	10
1986	3.6 [3]	2.1	9
1987	2.8 [3]	1.7	8

1 IAEA (1981)
2 Calf(1988)
3 IAEA (1990)
4 using $A = A_o 2^{-t/T}$ where T= 12.43
5 extrapolated from Calf (1988)

Deuterium-Oxygen

The abundance of naturally-occurring deuterium (D) and heavy oxygen (^{18}O) is expressed as a departure from the isotopic composition of standard mean ocean water (SMOW), as parts per mil (‰) deviation from this standard. Isotopically lighter waters, that is relatively deficient in deuterium and/or ^{18}O, have negative values compared to SMOW.

Rainwater of the Darwin region has a very wide isotopic range (IAEA, 1983, 1986, 1990) as shown in Figure 4.8.5). This distribution closely follows the global meteoric water line of Craig (1961)

$\delta D = 8\delta^{18}O + 10$.

Darwin experiences distinct wet and dry seasons. Stable isotope data (IAEA, 1983,1986,1990) indicates that although the wet season usually commences in October and extends to April, there is a distinct change of the isotopic character of rainfall which commences during November/December and continues to March/April, compared to the rest of the year *ie*. the dry season and the onset of the wet season. Throughout the dry season and into November, and sometimes into December, rain is predominantly from storms and has extremes of δD and $\delta^{18}O$ from light to heavy (Figure 4.8.5). In the November/December to March/April period, that coincides generally with the monsoon, rain is always isotopically light. This distinct isotopic differentiation is apparent on the local meteoric water line which lies between the regression lines,

$\delta D = 7.97\, \delta^{18}O + 9.25$ for the monsoon, and

$\delta D = 7.93\, \delta^{18}O + 9.38$ for the dry to early wet season.

The δD and $\delta^{18}O$ ranges for Darwin Rural Area groundwater lies on the meteoric water line at the approximate median values of δD and $\delta^{18}O$ for monsoon rain, confirming that groundwater recharge is during this time of the year (Figure 4.8.5). In an expanded plot of the groundwater signature in figure 4.8.6, groundwater in the Howard River Catchment shows two weak trends that border on acceptable significance. In the catchment, the δD- $\delta^{18}O$ linear regressions of groundwater on either side of the river show departure from the global meteoric line; $\delta^{18}O$ variation is increasing relative to changes in δD. On the western side of the catchment, this variability of $\delta^{18}O$ is greater ($\delta D/\delta^{18}O$ slope of 3) than on the eastern side ($\delta D/\delta^{18}O$ slope of 5.5). In both the Adelaide and Berry-Darwin River catchments there are no significant trends.

Discussion:

By comparing the δD and $\delta^{18}O$ groundwater values with the meteoric line it is possible to determine whether the isotopic composition of this precipitation has been modified by other processes during and after recharge to the saturated zone.

A significant secondary process that would affect the isotopic signature in this region would be evaporation from surface water bodies such as lakes, rivers, spray irrigation, mud and upper soil layers. This involves non-equilibrium processes and a resultant shift in slope of the regression line (Figure 4.8.6). If evaporation from the soil capillary zone is a dominant process, the $\delta D\, /\delta^{18}O$ slope will be between 2 and 3; and if evaporation from a free surface water body is dominant, then $\delta D\, /\delta^{18}O$ slope is usually between 4 and 6 (J. Ferguson, *pers. comm.*). The $\delta D\, /\delta^{18}O$ signature can reflect a mixture of these processes. The $\delta D\, /\delta^{18}O$ gradient of 3 suggests that recharge on the plateau on the western side of the catchment has its isotopic modification predominantly by soil capillary evaporation. On the eastern side of the catchment ($\delta D/\delta^{18}O$ slope is 5.5) where groundsurface slopes are greater and runoff would be expected to be more immediate, recharge may possibly have had less modification by soil capillary evaporation. However, the comparatively low R^2 values, although just significant, can be interpreted as indicating that surface evaporation is not the only process causing departure of groundwater from the local meteoric water line.

Oxygen -18

On the western side of the Howard River Catchment, $\delta^{18}O$ has significant positive correlation with EC , TDS, alkalinity, HCO_3 ,Ca, Mg, and pH (in decreasing significance). The plot of $\delta^{18}O$ vs TDS (Figure 4.8.7) shows this increasingly heavier oxygen with increasing TDS. $\delta^{18}O$ ranges from -5.9 to -4.4‰. This trend indicates the possibility of an additional post-recharge process during migration of the groundwater within the Coomalie Dolomite aquifer. These trends and correlations suggest a mixing of the recharge water with pre-existing groundwater which must have much heavier oxygen isotopic character. It has been demonstrated using Na/ and Cl/Br ratios that in the northernmost sampled area of this catchment, seawater has intruded the Coomalie Dolomite aquifer and mixing has occurred.

In the Adelaide River Catchment, $\delta^{18}O$ is highly variable between -5 and -5.9 ‰ with no relationship to TDS (120-220 mg/L range). Seawater constitutes a calculated 0.28% of the mixed groundwater within the Coomalie Dolomite aquifer but the intrusion component is in all probability much greater as it is more likely to comprise an intermixture of riverwater and seawater within the tidal reaches of the river. Intrusion is a phenomenon that would be expected to occur when the groundwater table is deepest and when bore abstraction is greatest, that is, in the late dry season. At this time of the year, riverwater would be a blend comprising seawater, dry-season stormwater runoff, and some groundwater discharge. With this composition, the intrusion waters would have a much heavier δD /$\delta^{18}O$ signature that could approach SMOW as dry season rainfall is isotopically heavier than monsoonal rainfall (Figure 4.8.5). Such an intrusion water would be expected to raise groundwater $\delta^{18}O$ slightly, through intermixture.
The other catchments show no significant trends with $\delta^{18}O$.

In the eastern Howard River Catchment, all groundwaters ($n = 6$) are very light ($\delta^{18}O$ below -5.3 ‰) even though there are two distinct groups of salinity: those less than 30mg/L TDS and the other 148-206 mg/L TDS (Figure 4.8.7).

Groundwater sampled in the Berry Creek-Darwin River Catchment, like that in the Adelaide River Catchment, has considerable random variation in both $\delta^{18}O$ and TDS; $\delta^{18}O$ with a range from -4.8 to -6.0 ‰ in a limited TDS concentration field between 150 to 190 mg/L.

Deuterium

In the western Howard River Catchment, δD has significant positive correlation with Cl, Br, Cl/Br, NH_3, and *Clostridium* spore detects. δD has negative correlation with heterotrophic bacteria (R2A), denitrifying bacteria, sulphate-reducing bacteria, and cobalt. On the eastern side of the catchment, the only significant correlation of δD is negative with boron. In the Adelaide River Catchment, δD has significant negative correlations with Ca, Mg, HCO_3, alkalinity and orthophosphate, and a near-significant positive correlation with condensed phosphate ($P<0.1$).

In an apparent converse situation, dissolved orthophosphate and total dissolved phosphate have positive correlation with δD ($n^1 = 6$) in the Berry Creek - Darwin River Catchment.

Discussion:
As a generalisation, most data is inconclusive as all regressions computed between δD and TDS (Figure 4.8.8) are below significance. The positive correlation of Cl and Br with δD in the western Howard River Catchment indicate some deuterium concentrations may be related to increased salinity, to seawater intrusion. Positive correlations of δD with NH_3 and *Clostridium* suggest that nutrient and microbiota may also be introduced by this mechanism. An alternative explanation is that contamination pathways also allow evaporated meteoric or irrigation waters access to the aquifer groundwater.

In the Adelaide River Catchment, there is no significant trend between TDS and δD (Figure 4.8.8) but possible negative correlations exist between δD and Ca, Mg, Ca/Mg, alkalinity, HCO_3 and orthophosphate. There are several possible explanations. The greater range of TDS concentrations indicate that there is more deuterium in groundwater at the end of the dry season and there has probably been continued isotopic modification of the groundwater by mixing. Such mixing is compatible with the observed intrusion into the aquifer of a seawater-blend. However, the detection of condensed phosphate and nitrate, as well as significant correlations between NH_3 and K could also be explained by a probable fertiliser source introduced with the local recharge of evaporated irrigation waters.
A plausible explanation for the association of increased δD with orthophosphate and total dissolved phosphate in the Berry Creek - Darwin River Catchment is that there is landward transport of these phosphate species with probable seawater-blend intermixing in the aquifer.

Chlorine-36

The chloride concentrations in Darwin Rural groundwater are very low, with a median of 3.1 mg/L. Six groundwaters from the Howard River Catchment have been analysed for ^{36}Cl, together with one spring, to help elucidate the origins and movement of water in the region. The simple hydrochemistry, high solubility and conservative behaviour of chloride in groundwaters and the natural occurrence of ^{36}Cl in the environment make this isotope useful for studying salt, and thus water, transport within an aquifer system (Bentley *et al.*, 1986). Data are shown in the table below and graphically in figures 4.8.9 and 4.8.10.

Bore ID	Cl (mg/L)	$^{36}Cl/Cl$ ($x10^{-15}$)	^{36}Cl ($x10^6$ atoms/L)	Depth to screen (m)
western Howard River Catchment				
RN7071	3.2	79 (5)	4.2	40
Howard Springs	4.3	49 (6)	3.6	0
RN6310	3.1	119 (9)	6.2	63
RN21995	4.2	63 (5)	4.4	27
RN8450	5.2	146 (5)	0	20
eastern Howard River Catchment				
RN22069	2.5	248 (25)	10.7	11
RN21398	3.0	66 (7)	3.4	56

Discussion:

Chlorine-36 (half-life of 301,000 years) is produced naturally in the atmosphere and lithosphere via various reactions. In the atmosphere, production is predominantly by cosmic-ray spallation of argon, though detonation of thermonuclear devices in the marine environment in the 1950's and 1960's generated considerable quantities via neutron capture of stable chlorine-35 in seawater. This was injected into the atmosphere as essentially a single pulse (Schaeffer *et al.*, 1960) that has today decayed almost to pre-bomb test levels. Lower levels of ^{36}Cl are produced in the surface of the earth through spallation of potassium and calcium, while neutrons produced from U and Th decay result in a low background of ^{36}Cl produced via neutron capture on any local chlorine-35. Production of ^{36}Cl from neutron capture on chlorine in sea-salt results in 30 atoms/m^2/s being produced. However, this amount is swamped by the vast quantity of inactive or "dead" chloride in the oceans, resulting in an oceanic $^{36}Cl/Cl$ ratio of $<1x10^{-15}$.

In the atmosphere, approximately 60% of production occurs in the stratosphere, and follows latitudinal dependence due to the influence of the earth's magnetic field, with greater production near the poles. Fallout to the earth's surface is strongly influenced by stratosphere-troposphere transfer, resulting in enhanced fallout beneath the troposphere, at about 40 degrees north and south of the equator (Lal and Peters, 1967). This ^{36}Cl rapidly mixes with atmospheric chlorine derived mainly from sea-spray and reworking of terrestrial salts, and the derived $^{36}Cl/Cl$ ratios can be estimated for chloride washed out in rainfall, or falling as dry deposition anywhere on the globe.

Keywood *et al.* (1998) have measured recent fallout of ^{36}Cl in rain across western Australia, and find that measured fallout exceeds theoretical estimates by about 30%. In addition, enhanced fallout was observed over northern Australia, up to10 times the expected level, possibly due to stratospheric scavenging during the monsoon (Keywood *et al.*,1998) or possibly from reworking of bomb-pulse ^{36}Cl from vegetation burn-offs (R. Cresswell, *pers.comm.*).

The weighted mean annual ^{36}Cl fallout for Kapalga, near Darwin, was determined to be 20 atoms/m^2/s. Annual accession of chloride is about 4 kg/ha, resulting in a mean $^{36}Cl/Cl$ ratio of 90-100 x 10^{-15}. Up to 40% of the chloride may be supplied as dry deposition; the bulk of the ^{36}Cl arriving in monsoonal rains, where $^{36}Cl/Cl$ ratios in excess of 300 x 10^{-15} were observed from seasonal (winter) rains (Keywood, 1995).

Deuterium and ^{18}O signatures indicate that groundwater recharge is almost exclusively monsoonal in origin (Figure 4.8.5), combined with some evaporation at the surface prior to infiltration (Figure 4.8.6). Geochemical signatures also indicate that seawater intrusions contribute to the groundwater system, albeit at low levels (<0.3%) (Figures 4.3.6, 4.3.7, & 4.3.14). The presence of CFC compounds (Cook *et al., in press*) and tritium in groundwaters of the regional aquifers indicate that the system is dominated by recently-recharged waters, and the long half-life of ^{36}Cl thus means that this species acts essentially as a stable isotope in this system. The vast difference in ^{36}Cl ratio between rainfall and seawater mean that it can be an effective measure of mixing of these 2 end members within the aquifers.

Figure 4.8.9 shows a plot of $^{36}Cl/Cl$ ratio for the 6 groundwater samples, together with a series of theoretical mixing curves for the postulated end-members (seawater, monsoon rain, evaporated monsoon rain and rainfall with an assumed mean ^{36}Cl concentration for 1992-1993). All samples can be explained by either evaporation of recent rains, or a mixing between monsoon rains and seawater, where seawater contributes between 0.01 and 0.1% to the total water budget.

The Cl vs ^{36}Cl plot in figure 4.8.10 suggests increased seawater mixing down the flowpath within the aquifer underlying the Howard River Catchment. Within the limitations of the small dataset and with flowpaths inferred from both the dry-season potentiometric surface (Jolly, 1983) and hydrochemical evolution of the groundwater, Howard Springs is considered to being fed laterally from more evolved waters.

5. GROUNDWATER EVOLUTION

5.1 GROUNDWATER CHARACTERISATION

Hydrochemical variation between catchments of sampled groundwater is outlined in table 5.1.1.
Three aquifers need consideration in this region, the lateritised profile of the Cretaceous sediments, the brown sandstone at the top of the bottom unit of the Cretaceous Darwin Member, and the weathered Coomalie Dolomite (Jolly, 1983).
As only operational bores were sampled in this study, waters are primarily from the weathered Coomalie Dolomite. However recharge into this aquifer should not be very fast via the upper aquifers. Younger waters in the weathered Dolomite aquifer can be differentiated by their signature of low TDS, low pH, and higher Tritium activity.

All catchments in the Darwin Rural Area have comparable aquifer regimes, and the Howard River Catchment has the largest diversity of samples in varying lithologies and in different aquifers (Table 3.2.1). Because of this diversity of aquifer level and lithotype within the aquifers, this catchment demonstrates a wider geochemical variation of groundwater from which the evolutionary stages of all Darwin groundwaters is made apparent.

5.2 GROUNDWATER EVOLUTION

Groundwater evolution is seen in five stages;

rainfall character,
soil infiltration,
recharge through Cretaceous and some other Proterozoic aquifers,
infiltration to and equilibration with the Coomalie Dolomite aquifer, and
in the lower catchments, closer to estuaries, seawater intrusion and consequent mixing with meteoric waters.

The origin of initially acidic groundwater (pH 4) is ascribed largely to acidic rainfall in the Darwin region (Galloway *et al.*, 1982; Gillett *et al.*, 1990), although uptake of organic acids from percolation into the soil is a probable additional contributor (as well as fermentative and other microbial processes operating under aerobic to semi-aerobic conditions on the organic matter in the soil zone). Evolution of groundwater from recharge shows initially a slight increase in TDS and pH (Figures 4.8.2, 4.8.3).

Parameter		All catchments		West Howard River catchment		East Howard River catchment		Adelaide River catchment		Berry Ck - Darwin R catchment	
		P_{50}	σ	P_{50}	σ	P_{50}	σ	P_{50}	σ	P_{50}	σ
TDS	mg/L	139.0	63.0	122.0	61.0	80.0	77.0	163.0	40.0	158.0	14.5
pH		6.8	1.1	6.3	1.1	6.1	1.3	7.0	0.5	6.9	0.2
DO	mg/L	2.6	1.5	1.8	1.4	3.4	1.4	4.1	1.0	2.9	0.5
Ca	mg/L	25.1	12.8	8.4	13.3	15.4	17.3	25.6	3.4	29.4	3.7
Na	mg/L	1.6	6.8	1.6	1.7	1.4	0.2	14.6	11.8	1.7	0.5
Mg	mg/L	19.8	11.0	17.9	11.6	10.3	12.4	17.8	4.4	26.5	4.1
K	mg/L	0.2	0.6	0.2	0.8	0.1	0.1	0.7	0.4	0.1	0.1
Cl	mg/L	3.1	13.7	3.1	3.9	2.8	1.2	31.8	1.4	2.9	1.4
HCO_3	mg/L $CaCO_3$	140.0	67.0	126.6	69.6	78.1	87.1	106.0	21.3	175.0	8.6
SO_4	mg/L	1.3	1.5	0.8	0.6	0.6	0.3	3.3	2.3	1.2	0.6
Fe	mg/L	0.0	0.6	0.1	0.3	0.0	1.3	0.0	0.0	0.0	0.0
Mn	μg/L	0.5	15.0	2.0	16.5	5.0	20.6	0.0	0.0	0.0	0.0
Si	mg/L	8.1	2.5	8.3	1.7	9.9	5.1	8.2	1.8	7.3	0.4
NO_3	mg/L (N)	0.100	0.380	0.066	0.180	0.080	0.200	0.060	0.750	0.100	0.070
NH_3	mg/L (N)	0.005	0.030	0.007	0.008	0.005	0.070	0.005	0.006	0.005	0.006
P diss. reactive	mg/L (P)	0.010	0.020	0.017	0.020	0.008	0.010	0.013	0.005	0.012	0.005
P condensed	mg/L (P)	0.001	0.001	0.001	0.006	0.000	0.007	0.004	0.007	0.003	0.003

Table 5.1.1 Summary of Hydrochemical Character of Darwin Rural Groundwater

If the groundwater remains within siliciclastic aquifers, such as the Cretaceous Darwin Member or the Proterozoic Whites Formation and Wildman Siltstone, significant change is only apparent with the decrease in tritium, nitrate, dissolved oxygen, and Eh. TDS and pH increase only slightly with time (Figures 4.8.2, 4.8.3). Where groundwater migrates into the Proterozoic Coomalie Dolomite and its weathered upper surface, TDS and pH increase significantly with uptake of Ca, Mg, bicarbonate and total alkalinity as the acidic water equilibrates with the magnesitic-dolomitic aquifer. When recharge waters first interact with this aquifer, and when pH is less than 6, dissolved orthophosphate concentration rises considerably over a small pH range of 6 to 7.3, but appears to lower again at higher pH (Figure 4.5.6). At lower ends of some catchments, close to tidal reaches of the river, intermixture of meteoric waters and seawater is apparent from the $^{36}Cl/Cl$ data (Figure 4.8.9). Ionic ratios in these waters are comparable to seawater (Figure 4.3.14) as a result of increasing Na, Cl, Br, K, Mn and Mg, independent of any carbonate-derived signature.

In both the Adelaide River Catchment and lower region of the Howard River Catchment, the Coomalie Dolomite aquifer is down to 20 metres below sea level. Seawater intrusion has occurred and although seawater mixing was minimal in 1995, constituting less than 0.23% of the groundwater at the time of sampling, it has produced a distinctive hydrochemical overprint with concentration gradients diminishing away from intrusion fronts.

Groundwaters are at a relatively juvenile stage of evolutionary development, covering a hydrochemical spectrum from recent recharge to equilibration with the host aquifer. The groundwaters are young, 12 to 50 years old as indicated from both tritium activities and chlorofluorocarbon dating (Cook *et al.*, in press). Characteristically the waters are initially acid (pH<5) and of very low salinity (<50 mg/L TDS) at recharge, but pH rises to 7-8, and TDS increases to 225 mg/L on interaction with the Coomalie Dolomite aquifer.

The Darwin groundwater data indicate the expected spatial trend of decreasing tritium activity and the associated general increase of dissolved ions and hence TDS with evolution of the groundwater after recharge (Figure 4.8.2).

Howard River Catchment

In the Howard River Catchment, two pathways of groundwater evolution are apparent: a slight gain of TDS up to 100 mg/L for reduction of TU to 0.25, and a consistent gain of TDS to 200 mg/L with the same reduction of tritium activity. These two pathways of chemical evolution relate to recharge into: a noncarbonate aquifer where there is minimal increase in both TDS and pH which remains below 6 (Figure 4.8.3), and recharge into the Coomalie Dolomite aquifer where pH increases beyond 7, with a relative doubling of TDS concentration. In this fractured and weathered aquifer $\delta^{18}O$ increases, indicating mixing of isotopically lighter recharge waters with isotopically heavier pre-existing water. Seawater intrusion is considered an important process in altering this isotopic signature.

Adelaide River Catchment

Within the Fogg and Harrison Dam area, there is a progressive seawater influence on the groundwater eastwards towards the Adelaide River which is still tidal in this area (Figure 4.3.14). The seawater influence on the groundwater may result from either windblown spray and/or evaporated salts, but most probably, by seawater invasion of the Coomalie Dolomite aquifer which lies below sealevel in this area. This latter process is preferably indicated by scatter plots of Na vs Br and Na vs Cl (Figures 4.3.6, 5.2.1) which show the mixing lines of these groundwaters with seawater. Based on the maximum sodium levels in these groundwaters and assuming the sodium is sourced solely from seawater, then the maximum seawater component of the groundwaters is approximately 0.23%. This dilution factor predicts the concentration of K, Cl, SO_4, and Br observed in the groundwater. For these salts to access the aquifer waters via aerosol transport, resolution by rainfall, and recharge through the Cretaceous aquifer without any modification of ionic ratios is highly unlikely. Groundwater in this catchment has a distinctive mixing trend from meteoric water that has equilibrated with a dolomite aquifer, towards seawater. The Ca - Mg - HCO_3 system, resulting from equilibration of recharge waters with the dolomite, appears almost entirely independent of the Na - K - Cl - SO_4 - Br component of the groundwater. There is anomalous high sodium in bore RN 21343, and lower K relative to Na than expected in RN 297133.

The westernmost bore, RN 24997, that furthest from the river, has a Cl/Br value of 140, comparable to that expected from Monsoonal rain recharge (J. Ferguson, pers. comm.; Keywood, 1996).

Berry Creek - Darwin River Catchment

Characteristics of this catchment are relatively uniform compared to the Howard River catchment, with TDS and pH characteristics indicating groundwater equilibration with the Coomalie Dolomite aquifer. Down catchment to the northwest., Cl increases. An additional chemical gradient exists across the catchment from southwest to northeast, with increasing SO_4, U, Fe, Mg and decreasing F, NO_3. The comparability of concentration and relationships of many ionic species in groundwater from this and the Howard River Catchment may indicate that subtle seawater intermixing has occurred in the aquifer in this region as well.

6. SUMMARY

A selected sample of groundwaters of the Darwin Rural Area covered areas of the surface drainage catchments; the Eastern and Western Howard River Catchment, the Fogg Dam area of the Adelaide River catchment, and the Berry Creek - Darwin River Catchment.
This study documents the water quality characteristics of groundwater from 36 bores and the efflux of two springs, sampled in the late dry season of 1995.
In the Darwin Rural Area, groundwater is utilised by PAWA for the regional reticulated water supply, and by private rural-domestic, horticultural, and agricultural users. For the reticulated water supply, groundwater abstracted from borefields in the Howard River Catchment is blended with reservoir water from the Darwin River Dam to both ameliorate the acidic corrosive quality of the surface reservoir water, and to meet consumption demand.

Host aquifers

The hydrogeology of the three catchments is similar. The main utilised aquifer is composite and comprises upper unconfined sandstones of the Cretaceous Darwin Member, that directly overlie the weathered zone of the Proterozoic Coomalie Dolomite- a silicified, fractured, and karstified semi-confined zone.

The Cretaceous Aquifer has characteristically high specific yield but low permeabilities, contrasting with the underlying Coomalie Dolomite aquifer of low specific yield and high permeabilities. Hydrochemistry is similarly contrasting between the aquifers and the Dolomite aquifer is the preferred abstraction zone because of its higher flow-rates and superior chemical characteristics. Groundwaters sampled in this survey are predominantly from the weathered Coomalie Dolomite aquifer.

The overlying Cretaceous sediments are also utilised for groundwater supplies, but only out of necessity because of lower yields and higher acidity. The water quality of this aquifer is dependant on whether the bore is located in a discharge or recharge area of the Dolomite aquifer. Water quality from areas of immediate recharge through Cretaceous sediments can be summarised as low hardness (usually <10 mg/L), acidic (approx pH 5 at the borehead) and very corrosive (Jolly, 1983).
For both the Comalie Dolomite aquifer and Cretaceous sediments within a discharge area of the Dolomite aquifer, groundwater is of excellent quality chemically, with near neutral pH, low TDS, very low trace metals, low nutrient levels, and no detected pesticides.

Groundwater evolution of recharge waters

Groundwaters are at a relatively juvenile stage of evolutionary development, covering a hydrochemical spectrum from recent recharge to equilibration with the host Coomalie Dolomite aquifer. The groundwaters are young, 12 to 50 years old as indicated from both tritium activities (this study) and chlorofluorocarbon dating (Cook *et al.*, in press).

The origin of initially acidic groundwater is ascribed largely to acidic rainfall (pH 4) in the Darwin region. Uptake of organic acids from percolation into the soil is a probable additional contributor. Characteristically the waters are initially acid (pH<5) and of very low salinity (<50 mg/L TDS) at recharge.

While the groundwater remains within siliciclastic aquifers such as the Cretaceous Darwin Member or the Proterozoic Whites Formation and Wildman Siltstone, significant change is only apparent with the decrease in tritium, nitrate, dissolved oxygen, and Eh. TDS and pH increase only slightly with time. Where groundwater migrates into the Proterozoic Coomalie Dolomite and its weathered upper surface, pH rises to 7-8 and TDS increases up to 225 mg/L with the uptake of Ca, Mg, bicarbonate and total alkalinity as the acidic water equilibrates with the magnesitic-dolomitic aquifer. When recharge waters first interact with this aquifer, when pH is less than 6, dissolved orthophosphate concentration increases briefly and drops again as pH rises above 7 with subsequent equilibration with the carbonate.

Seawater intrusion

At lower ends of catchments, close to tidal reaches of the river, intrusion into the aquifer by seawater-blends causes mixing with the existing groundwater. This phenomenon is indicated by Na, Cl, Br, K, Mn and Mg ionic ratios which approach those of seawater, and supported by 36Cl/Cl data which also indicates a rain-seawater mixing system . In both the studied portion of the Adelaide River Catchment and lower region of the Howard River Catchment, the Dolomite aquifer may be as deep as 20 metres below sea level. Although seawater mixing was minimal in 1995, constituting less than 0.23% of the groundwater at the time of sampling, it has produced a distinctive hydrochemical overprint with concentration gradients diminishing away from intrusion fronts.

The identification of intrusion of seawater or a seawater-blend into the Coomalie Dolomite aquifer, and its intermixture with meteoric groundwater in the aquifer, adds complexity to prediction of watertable variations resulting from both natural evapotranspiration by vegetation, and groundwater abstraction in bores. Situations could occur where abstraction rates exceed local recharge, and the schizohaline boundary of the freshwater lens could migrate significantly in response. This could expose deeper bores to increased salinisation, especially in the currently-delineated mixing zones in the lower end of catchments. Presently there is a wide latitude for increasing salinity without exceeding NHMRC hydrochemical guideline values but seawater intrusion may constitute a significant limit to future groundwater abstraction when its exploitation is commensurate with the anticipated longer-term development of the region.

The phenomenon of seawater intrusion is a potential mechanism for transport of contaminants landwards into the Darwin Rural Area, with ramifications for landuse zoning in areas downstream and seaward of the study area.

CONTAMINANTS

Inorganic ions

Darwin Rural Area groundwater is generally of excellent quality chemically in each of the Howard River, Adelaide River, and Berry Creek - Darwin River Catchments. Almost all ionic concentrations are well below NHMRC health and aesthetic guideline values, and many trace elements are below detection limits.

Acidity, with groundwater below a pH of 6.5, is one undesirable characteristic in the shallower aquifers; the lateritised Cretaceous sediments, and the lower sandstone of the Cretaceous Darwin Member. In the Coomalie Dolomite aquifer, groundwater pH lies acceptably between 6.5 and 7.6.

Groundwaters have low major-ion and extremely low trace element concentrations, well below health guideline limits. Within some areas of the Howard River Catchment, iron is close to or exceeds the aesthetic guideline limit of 0.3 mg/L (NHMRC, 1996)
In one bore (RN 8825) in the western Howard River Catchment, iodide was a factor of 5 above the NHMRC guideline limit, and had associated high barium.

However, even at these low concentrations, the combined presence of several trace elements was sometimes associated with either FIB, nutrient, or both forms of contamination (Figure 4.7.7). This indicates that even in low concentrations, specific trace elements may be used to indicate possible contamination.

Nutrients

The groundwaters have extremely low levels of dissolved organic carbon, phosphorus, and nitrogen (as nitrate, nitrite, and ammonia), well below health guideline limits.
Phosphate levels are very low. Condensed phosphate, which could arise through biological and/or anthropogenic contamination, is detectable in approximately 37% (n=19) of bore sites in the west Howard Catchment. Traces of condensed phosphate were detected in 33% of bores in the east Howard River Catchment, and 50% of bores

in the Adelaide River Catchment. One bore in the Berry Creek-Darwin River catchment had detectable condensed phosphates.

Although present at low concentrations, the combined presence of nitrate and condensed phosphate indicate an anthropogenic source. In the western Howard River Catchment, three of four groundwaters with observed combined detects of nitrate and condensed phosphate coincided with FIB contamination (Figure 4.5.1). The tritium vs nitrate plot (Figure 4.3.18) also shows that where nitrate concentrations depart from a direct relationship with tritium activity, the excessive nitrate is linked to FIB contamination.

Microbiota

The aquifer in the lateritised profile of the Cretaceous Sediments is primarily recharged through solution channels which enable surface water to reach this aquifer rapidly with little or no purification from filtration. This profile is bacteriologically contaminated in developed areas in the Darwin Rural Area (Jolly,1983). By comparison, he noted that the brown sandstone in the top of the bottom unit of the Cretaceous Darwin Member, and the underlying weathered Coomalie Dolomite were not contaminated. He concluded that microbiological contamination in the weathered Dolomite aquifer was not possible if bore heads were properly constructed. The majority of domestic and supply bores in the Darwin Rural Area obtain their water from this aquifer. He concluded that the Cretaceous aquifer could be potentially contaminated if industrial development or garbage disposal sites were located over this area (Jolly, 1983).

Contamination of groundwater by FIB was detected in 31% of bores sampled in 1995 (Figures 4.7.6, 4.7.7). Low-level FIB (Faecal Indicator Bacteria) contamination was detected in nine of the 36 bores. Five bores with FIB contamination are situated within 10-20m of domestic septic tanks. Two of the bores have detectable *Clostridium perfringens* spores, a long-lived bacterial spore which implies either chronic long-term contamination or a pre-existing but discontinued contamination event. The balance are enigmatic. With the exception of three samples (one spring and two bores) FIB levels were low (1-7 FIB/100 ml), though exceeding drinking water standards [should be <1 CFU/100ml for FC (Faecal coliforms) (NHMRC, 1996)].
Substantial-level FIB contamination was detected at both springs, and in two bores where a proximal domestic septic source is likely.

FIB contamination pathways are presumed to follow those of natural recharge but our data does not enable preclusion of malfunctioning bores. Such malfunction may result from either inadequate bore completion during their construction, or subsequent damage to the boreheads or casing of these bores. The cause of contamination needs thorough assessment as bore malfunction can be remedied, whereas if microbiological contamination of the aquifers is via natural recharge, including accelerated recharge into the groundwater via highly permeable conduits that bypass the slower infiltration process, the issues of incompatibility between rural development and exploitation of underlying aquifers has major implications with regional planning.

Howard and Berry Springs, sampled as close as possible to their sources, have FIB contamination. Both springs are in nature reserve areas, and contamination is considered to be from faecal material from wildlife, especially abundant waterbirds.

Burkholderia pseudomallei has also been detected in the regional groundwater aquifer. No relationship is apparent with detected FIB contamination or any other parameter, consistent with it being indigenous in this tropical environment.

Anthropogenic organic compounds

No pesticides were detected in any groundwater from the 1995 September-October period at the end of the dry season.
Analytes for this study were 112 commonly-used anthropogenic organic compounds including most locally-used herbicides, insecticides, and their decay products. Detection limits of these analytes vary considerably, but generally two orders of magnitude below NHMRC health guideline values where these values have been specified. Exceptions to this analyte list were the herbicides paraquat, glyphosate, and glufosinate, and the fungicide mancozeb. Although these compounds have a history of use in the region, the three herbicides are readily adsorbed and immobilised in soils (very high K_{oc}). Mancozeb is an organometallic fungicide with both a very short half-life (DT_{50} 6-15-70 days) and an affinity with soil particulates (moderately-high K_{oc}).

A previous study in 1992, with the use of a more sensitive analytical procedure, a trace of carbaryl was detected in the Howard Springs area; and atrazine and prometryne were detected in groundwater of the Berry Springs area. In a repeated survey, these contaminants were not detected (Wilson, 1992). Atrazine has an apparent rapid degradation to desethylatrazine (DEA). In a comparable climatic region, Bauld (1996) documents a 50% reduction in detected triazines concurrent with a 100% increase of DEA in one year, in Burdekin River Delta groundwaters.

Contamination by organochloride and organophosphate insecticides would be unlikely via normal percolation recharge because of probable adsorption on soil organic matter and on sesquioxides and clays in the lateritic soils. Additionally degradation rates of other relatively mobile compounds may be increased with high ambient temperatures during recharge. However, all anthropogenic compounds have differing characteristics in the processes of their degradation or immobilisation by adsorption and it is misleading to make generalisations. Additionally, the depth to the watertable varies dramatically between seasons and it is probable that in the wet season, when the watertable can be as close as 2 metres from the ground surface, the potential for pesticide access to the groundwater is much higher. Unfortunately, there is no temporal comparison currently available to identify possible seasonal variability.

The detection of FIB microbiological contamination in groundwater indicates that colloidal particles are being effectively transported from surface to groundwater, even in the dry season. Such particles are known to facilitate the transport of adsorbed organic contaminants like pesticides.

Groundwater of the Darwin Rural Area has the positive attribute of very low ionic concentrations. With this characteristic, chemical and nutrient contamination can be detected and identified at an early stage well before contamination by these species approaches NHMRC health guideline limits, and consequently temporal latitude is available for adjustment of management practices before any contamination anomaly approaches serious levels.

7. CONCLUSIONS AND MANAGEMENT IMPLICATIONS

1. Darwin Rural Area groundwater is generally of excellent quality chemically in each of the Howard River, Adelaide River, and Berry Creek - Darwin River catchments. All ionic concentrations (except iron) and nutrient levels are well below NHMRC health and aesthetic guideline values, and many trace elements are below detection limits.

2. Within some areas of the Howard River catchment, iron is close to and exceeds the aesthetic guideline limit of 0.3 mg/L (NHMRC, 1996).

3. Acidity, with groundwater below a pH of 6.5, is one undesirable characteristic in the shallower aquifers; the lateritised Cretaceous sediments, and the lower sandstone of the Cretaceous Darwin Member. In the Coomalie Dolomite aquifer, groundwater pH lies acceptably between 6.5 and 7.6.

4. No pesticides were detected in any of the borewaters. Analytes for this study were 122 anthropogenic organic compounds that included most pesticides currently used locally, and their decay products. Detection limits of these compounds vary considerably between a factor of three and four orders of magnitude below NHMRC health guideline values where they have been specified.

5. Microbiological contamination by Faecal Indicator Bacteria has been detected in 31% of bores sampled. Contamination pathways are presumed to follow those of natural recharge, but the results do not preclude the possibility that FIB contamination may access aquifers via bores with inadequate bore construction, damaged boreheads, or casing defects. The cause of contamination needs thorough assessment as bore malfunction can be remedied, whereas if microbiological contamination of the aquifers is via natural recharge, the issue of incompatibility between current and future landuse has major implications with regional planning.

6. *Burkholderia pseudomallei*, the causative agent of melioidosis, was detected in some groundwater samples. There was no obvious association with either FIB or other possible contaminants, consistent with its being indigenous in this tropical environment.

7. Evolution of groundwater from recharge shows initially a slight increase in TDS and pH with recharge. If the groundwater remains within siliciclastic aquifers, such as the Cretaceous Darwin Member or the Proterozoic Whites Formation and Wildman Siltstone, significant change is only with the decrease in tritium, nitrate,

dissolved oxygen, and Eh. Here TDS and pH increase only slightly with time. Where groundwater migrates into the Proterozoic Coomalie Dolomite and its weathered upper surface, TDS and pH increase dramatically with uptake of Ca, Mg, bicarbonate and total alkalinity as the acidic water equilibrates with the magnesitic-dolomitic aquifer. When recharge waters first interact with this aquifer, and when pH is less than 6, dissolved orthophosphate concentration increases over a small pH range, and decreases once the groundwater has equilibrated with the carbonate aquifer.

8. The Ca - Mg - HCO_3 system, resulting from equilibration of recharge waters with the dolomite, appears almost entirely independent of the Na - K - Cl - SO_4 - Br component of the groundwater.

9. At lower ends of some catchments, close to tidal reaches of the river, seawater intrusion into the aquifer causes mixing with the existing groundwater, and there is an increase in $\delta^{18}O$, Na, Cl, Br, K, Mn and Mg independant of the carbonate-derived signature. In both the Adelaide River catchment and lower region of the Howard River catchment, the aquifers lie below sea level and there has been seawater intrusion. Although the detected seawater mixing is minimal, constituting less than 0.2% of the groundwater at the time of sampling, it has produced a distinctive hydrochemical overprint that showed concentration gradients diminishing away from intrusion fronts.

10. Seawater-blend intrusion into, and subsequent intermixture with meteoric groundwater in the aquifers, is an added complication to prediction of watertable variations resulting from both natural evapotranspiration by vegetation, and groundwater abstraction in bores. Situations may arise when abstraction rates exceed annual recharge, and the gradational boundary of the freshwater lens moves dramatically in response. This would expose deeper bores to increased salinisation, especially in the currently-delineated mixing zones at the lower end of catchments. Presently there is a wide latitude for increasing salinity without exceeding NHMRC hydrochemical guideline values. Seawater intrusion may constitute a significant limit to future groundwater abstraction.

11. The phenomenon of seawater intrusion is a mechanism for transport of contaminants landwards within the Darwin Rural Area and has ramifications for landuse zoning in areas seaward and downstream of the study areas.

12. The Darwin regional groundwaters have very low ionic concentrations. With this characteristic, chemical and nutrient contamination can be detected and identified at an early stage well before contamination approaches concentrations of NHMRC health guideline limits.

8. RECOMMENDATIONS FOR FUTURE WORK

1. This survey has detected microbiologically-contaminated groundwater, caused by FIB, in over 30% of bores sampled. Given the projected growth anticipated by the local planning authority in this region in the coming decades, the causes of this contamination need to be identified and remedial measures taken. If this contamination is shown to come, in part, from natural recharge, then detailed monitoring and a study of local hydrostratigraphic effects on recharge rate and FIB attenuation during recharge is necessary. Such research would help to define regional stratigraphic-geomorphic parameters essential for modifying development guidelines.

2. The field sampling program underpinning this project occurred in 1995 during the late stages of the dry season. A second, repeat, sampling program, following major recharge in the catchment during the wet season, would help delineate temporal variation of groundwater quality, and the processes affecting groundwater quality in the area.

3. Groundwater is more vulnerable to pesticide contamination during the wet season when water levels are high and close to the surface. It is recommended that the pesticide sampling and analysis program is repeated during the wet season even if on a selected smaller group of bores in each of the areas.

4. Although within currently acceptable levels, the detected anthropogenic sources of nitrate and heavy metals should be monitored several times during one annual cycle to document seasonal fluctuations.

5. The phenomenon of seawater intrusion needs to be incorporated into modelling of the effects of groundwater abstraction in the coastal margins of the region. Given the added complexity of apparent preferential flowpaths in the Coomalie Dolomite aquifer, as well as the large tidal range experienced around the Darwin coast, the mixing zone between the seawater intrusion and the meteoric water mass may be diffuse and extensive.

6. Further ^{36}Cl data is required before firm estimates of seawater mixing and connectivity across the area can be given a quantitative basis. This would complement the spatial delineation of seawater intrusion that has been made with the use of major ion ratios.

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Table A1.1 RAW DATA: Darwin Rural Area: **Field Measurements**

Boreid	WQ Number	Date Sampled	Pump Type	Field EC (μS/cm)	Field pH	Field Eh (mV)	Field DO (mg/L)	Field Temp (^{o}C)	Comments
RN7071	95-145	05.09.95	I/P	280	7.07	323	1.40	30.0	
Howard Springs	95-146	06.09.95	Surface	337	6.38	254	0.05	32.1	
Howard Springs	95-147	06.09.95	Surface	337	6.38	254	0.05	32.1	Duplicate
Howard Springs	95-148	06.09.95	Surface	337	6.38	254	0.05	32.1	Spike
RN9225	95-149	07.09.95	I/P	372	6.92	204	0.61	30.5	
RN6310	95-150	07.09.95	I/P	281	6.81	283	1.71	30.6	
RN20255	95-153	12.09.95	I/P	292	7.01	274	0.42	30.6	
RN27525	95-154	12.09.95	I/P	370	6.96	121	0.00	31.0	
RN25917	95-159	15.09.95	I/P	40.1	4.48	465	3.54	30.4	
RN25619	95-160	17.09.95	I/P	311	7.06	320	0.99	29.9	
RN21995	95-161	17.09.95	I/P	46.3	4.68	421	2.86	31.1	
RN8825	95-162	18.09.95	I/P	239	6.31	218	1.67	30.2	
RN27871	95-163	18.09.95	I/P	170	5.98	205	2.19	30.9	
RN28032	95-165	19.09.95	I/P	74.1	5.23	336	2.47	30.7	
RN24728	95-166	20.09.95	I/P	271	7.28	260	1.95	30.9	
RN27374	95-167	20.09.95	I/P	35.1	4.60	401	3.44	30.4	
RN27050	95-168	21.09.95	I/P	256	6.97	221	1.90	31.4	
RN27050	95-169	21.09.95	I/P	256	6.97	221	1.90	31.4	Duplicate
RN27050	95-170	21.09.95	I/P	256	6.97	221	1.90	31.4	Spike
RN8450	95-177	27.09.95	I/P	31.5	4.16	483	4.92	29.8	
RN20780	95-178	27.09.95	I/P	31.3	4.05	475	3.64	29.9	
RN27687	95-181	29.09.95	I/P	137	6.20	234	1.85	29.9	
RN9421	95-187	04.10.95	G	311	6.98	52	0.00	31.0	
RN9421	95-188	04.10.95	G	ND	ND	ND	ND	ND	"Before" Blank
RN9421	95-189	04.10.95	G	ND	ND	ND	ND	ND	"After" Blank
RN22387	95-190	05.10.95	I/P	62.1	5.13	321	1.07	33.3	
RN22387	95-191	05.10.95	I/P	62.1	5.13	321	1.07	33.3	Duplicate
RN22387	95-192	05.10.95	I/P	62.1	5.13	321	1.07	33.3	Spike
RN22069	95-155	13.09.95	G	ND	ND	ND	ND	ND	"Before" Blank
RN22069	95-156	13.09.95	G	ND	ND	ND	ND	ND	"After" Blank
RN22069	95-157	13.09.95	G	19.2	4.41	386	3.74	29.9	
RN22068	95-158	14.09.95	G	30.5	5.25	332	1.49	30.5	
RN26455	95-164	19.09.95	I/P	314	7.05	164	1.70	30.7	
RN21374	95-171	22.09.95	I/P	35	4.66	427	4.29	30.9	
RN25034	95-175	26.09.95	I/P	312	6.95	252	3.07	30.5	
RN21398	95-186	03.10.95	G	264	7.14	305	4.80	30.7	
RN25371	95-172	24.09.95	I/P	422	6.26	325	3.94	30.0	
RN29733	95-173	25.09.95	I/P	390	7.18	267	3.60	31.8	
RN24997	95-174	25.09.95	I/P	306	6.46	303	2.37	30.2	
RN21343	95-179	28.09.95	I/P	228	7.35	328	4.30	29.9	
RN4223	95-180	28.09.95	I/P	264	7.58	295	5.45	30.0	
RN27743	95-182	29.09.95	I/P	340	6.87	276	4.81	30.0	
RN21427	95-151	08.09.95	I/P	282	7.01	271	2.86	30.5	
Berry Springs	95-152	10.09.95	Surface	373	6.77	311	3.90	30.8	
RN26686	95-176	26.09.95	I/P	303	7.02	252	2.90	30.8	
RN26779	95-183	01.10.95	I/P	287	6.62	296	2.44	31.9	
RN25232	95-184	02.10.95	I/P	329	6.93	295	2.75	30.9	
RN20319	95-185	02.10.95	I/P	322	6.91	272	2.91	30.6	

I/P = Installed Pump
G = Grundfos (Govt bore)
ND = Not Determined

Verified: Nerida Steel 11/08/97

Table A3.1 Darwin Rural Area: **Location Data**

Boreid	WQ No.	State	Study Area	Latitude	Longitude	Location description	Useage Comments	Yield	SWL	Top slots	Base slots	Aquifer sampled	Other comments
RN7071	95□145	NT	W. Howard R.C.	12 31.637	131 06.121	Girraween Lagoon	adjacent to orchards, mangoes	25	9.1	41	52	mdst., sltst., dol	
Howard Springs (surface)	95□146	NT	"	12 27.561	131 02.985	Howard Springs	origin of springs, Rainforest						
Howard Springs (surface)	95□147	NT	"	"	"	Howard Springs	origin of springs, Rainforest						duplicate
Howard Springs (surface)	95□148	NT	"	"	"	Howard Springs	origin of springs, Rainforest						spike
RN9225	95□149	NT	"	12 29.874	131 01.944	Howard S. Caravan Park	scattered orchards, open woodland	6.25	6.4		47	qtz, sandstone	
RN6310	95□150	NT	"	12 30.549	131 04.438	Girraween Lagoon	open woodland	70	11.6	63	67	cavitous dolomite	
RN20255	95□153	NT	"	12 28.163	131 04.297	Gunns Point Road	domestic use, septic nearby	?	12		25		
RN27525	95□154	NT	"	12 27.372	131 04.266	Lot 4183, Bronzewing Av.	domestic and orchard	8	6	30	34	sand, gravel, qtz	
RN25917	95□159	NT	"	12 31.112	131 03.689	Lot 90, Hillier Rd.	orchard of tropical fruits	0.75	?		87	siltstone	unknown casing; low yield
RN25619	95□160	NT	"	12 28.432	131 04.196	Lot 36, Callistemon Rd.,	domestic use, palm grove	6	7	27	38	dolomite	fluid sand above dol.
RN21995	95□161	NT	"	12 30.500	131 02.765	30 Lacy St., Howard Springs	unused, some poultry; prev. horses,pigs	1.8	11	27	36	sandstone	
RN8825	95□162	NT	"	12 28.322	131 03.994	Lot 4, Melaleuca Rd.	open cleared land, domestic use	6.3	9.1	42	55	clay, sd., qtz., dol	unknown perf. zone
RN27871	95□163	NT	"	12 30.335	131 03.056	70 Barker Road	domestic use; mango orchard	3	9	44	71	fractured siltstone	
RN28032	95□165	NT	"	12 31.252	131 03.674	65 Dichondra Rd.	mango □ tropical fruit orchard	2	8	53	56	qtz breccia, sst.	
RN24728	95□166	NT	"	12 30.050	131 03.692	63 Whitewood Rd.	mango orchard	5	6	28	30	sst brecc, qtz, dol.	sample after 5 filter units
RN27374	95□167	NT	"	12 31.145	131 03.831	Lot 3811, Geodoran Rd.	mango orchard	3	?	41	52	frac.sst, sand	
RN27050	95□168	NT	"	12 32.921	131 05.367	107 Power Rd.	open paddock near orchards	10	12	64	66	cavity in dolomite	sand screen unit
RN27050	95□169	NT	"	"	"	107 Power Rd.	open paddock near orchards	10	12	64	66	cavity in dolomite	dupl.;sand screen unit
RN27050	95□170	NT	"	"	"	107 Power Rd.	open paddock near orchards	10	12	64	66	cavity in dolomite	spike; sand screen unit
RN8450	95□177	NT	"	12 32.900	131 04.633	Lot 40, McMinns Drive	open padock with surrounding gardens	1.25	6.4	21	25	gravel; qtzite	unsure of upper limit of perforations
RN20780	95□178	NT	"	12 29.779	131 02.311	Lot 235, Whitewood Rd.	nursery with surrounding mango orchard	10	6	45	61	sltstone □ blk shale	
RN27687	95□181	NT	"	12 31.941	131 05.983	Lot 2661, 34 Zill Rd.	open woodland, domestic use, surr. mangoes	4	?	40	43	dolomite □ cavities	
RN9421	95□187	NT	"	12 27.649	131 02.959	Howard Springs Reserve	rainforest	1	4	16	21	sand	
RN9421	95□188	NT	"	"	"	Howard Springs Reserve	rainforest	1	4	16	21	sand	before blank
RN9421	95□189	NT	"	"	"	Howard Springs Reserve	rainforest	1	4	16	21	sand	after blank
RN22387	95□190	NT	"	12 35.448	131 07.657	Lot 34, Strangways Rd.	domestic use; mango orchard						
RN22387	95□191	NT	"	"	"	Lot 34, Strangways Rd.	domestic use; mango orchard						duplicate
RN22387	95□192	NT	"	"	"	Lot 34, Strangways Rd.	domestic use; mango orchard						spike
RN22069	95□155	NT	E. Howard R.C.	12 29.030	131 07.614	McMinns, off Gunn Pt. Rd.	open woodland	0.3	4.2	12	18	clay □ laterite	before blank
RN22069	95□156	NT	"	"	"	McMinns, off Gunn Pt. Rd.	open woodland	0.3	4.2	12	18	clay □ laterite	after blank
RN22069	95□157	NT	"	"	"	McMinns, off Gunn Pt. Rd.	open woodland	0.3	4.2	12	18	clay □ laterite	
RN22068	95□158	NT	"	12 29.033	131 07.609	McMinns off Gunn Pt. Rd.	10m from 155 to 157, open woodland	0.3	5.5	34	36	cavitous dolomite?	no circulation
RN26455	95□164	NT	"	12 33.021	131 08.469	Humpty Doo, 65 Ridley Rd.	mangoes, woodland; no house	6	10	38	41	gravel □ dolomite	
RN21374	95□171	NT	"	12 33.407	131 08.747	Humpty Doo, Lot 5 Pioneer Drive	old poultry farm site; surrounding bush	8	5.5	32	40	cl. gravel, sil. dolomite	2 aquifers tapped
RN25034	95□175	NT	"	12 33.126	131 09.868	Lot 2293, Dodson Rd.	cane □ flower farm, domestic crops	5.5	14.9	62	72	dolomite	
RN21398	95□186	NT	"	12 29.041	131 07.614	off Gunn Pt., Rd.	see RN 22069	40	9.7	56	63	qtz., frac. dol., cavity	also 48.4-50.5;chert
RN25371	95□172	NT	Adelaide R.C.	12 33.492	131 19.876	Sect. 1553, Middle Pt. Rd.	Mango □ banana orchard	23.5	9.3	33	35	dolomite, cavity	
RN29733	95□173	NT	"	12 33.825	131 15.111	"Top Bananas", Alphtonia Rd.	Banana orchard	5	?	48	60	sst, qtz, frac. dol.	bore collapsed subseq.
RN24997	95□174	NT	"	12 34.428	131 14.994	Lot 3 Miniata d., Lambells Lagoon	nursery	10	?	45	45	qtz., frac. dolomite	
RN21343	95□179	NT	"	12 34.323	131 19.167	Sect. 1548, Middle Pt. Rd.	adj. banana plantation	25	7	29	39	porcell., fr.dol., cavity	recycled down adj. collapsed bore
RN4223	95□180	NT	"	12 34.150	131 18.837	Sect. 1560, W, Middle Pt. Rd.	open woodland; sev hundred m to bananas	37.9	5.7	36	45	dolomite	
RN27743	95□182	NT	"	12 33.927	131 19.423	Sect. 1544, Middle Pt. Rd.	banana plantation	18.8	10	51	53	qtz., dolomite	
RN21427	95□151	NT	Berry Ck - D.R.C.	12 42.852	130 59.352	Berry Springs	open woodland	6.9	13	20	26	qtz gravel, sand, gravel	
Berry Springs (surface)	95□152	NT	"	12 42.383	130 59.731	Berry Springs	origin of springs						
RN26686	95□176	NT	"	12 43.270	130 59.508	Sect. 2352, Berry Springs	Banana Plantation □ natural woodland	40	13.6	42	?	dolomite, cavity, sst	
RN26779	95□183	NT	"	12 44.719	131 00.866	Berry Spr., Hopewell□Kentish Rds	mango orchard	6	17	68	70	dolomite	
RN25232	95□184	NT	"	12 42.943	130 59.179	behind Berry Springs School	school supply □ fire tank supply	10	?	61	65	qtz gravel;fr. dolomite	
RN20319	95□185	NT	"	12 44.658	130 57.050	20 Southport Rd., Berry Springs	domestic use, mangoes	2.5	10.5	21.6	23		