Technical Report

Adelaide Coastal Waters Study

***Stage 2** Research Program 2003 - 2005*

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Estimation of groundwater and groundwater N discharge to the Adelaide Coastal Waters Study area

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Estimation of groundwater and groundwater N discharge to the Adelaide Coastal Waters Study area

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Executive Summary

One of the suspected causes for the decline of seagrasses in the coastal waters of Adelaide (South Australia) is from an excess input of nitrogen (N) causing eutrophication (excess algal growth). As a component of the definition of N inputs for the Adelaide Coastal Waters Study (ACWS), this project aimed at determining the load of N from groundwater in the study area (from Port Gawler to Sellicks Beach in Gulf St Vincent). This load was assessed using a combination of approach, including 1) a review of groundwater flow nets for the three main groundwater systems in the study area, 2) a preliminary assessment of the potential for environmental tracers to measure groundwater discharge *in situ* in Gulf St Vincent and 3) a field study of nutrient loading by tidal pumping along a beachface combined with sampling of bores to determine the range in N concentration of groundwater and recirculated seawater.

There are at least three hydrogeological systems potentially contributing groundwater to the ACWS area. These are the Northern Adelaide Plains (NAP) to the North, the Metropolitan Adelaide area to the centre and the Willunga Basin to the South. While each of these systems is composed of several aquifers, an emphasis was given here to the ones most likely to contribute significant amounts of groundwater to the ACWS area – the Quaternary aquifers in the NAP and Metropolitan Adelaide area, and the Port Willunga Formation and Maslin Sands in the Willunga Basin. The review of flow nets for these aquifers suggested that <u>groundwater discharge was small, approximately 2020 ML year^{-1} (or $2.0 \cdot 10^6$ m^3 year^{-1}) for the whole study area</u>. However, this estimate is <u>highly uncertain</u> because existing bore monitoring networks poorly cover the coastal fringe across the study area. The flow net review also suggested that seawater intrusions may be more widespread than previously thought along the ACWS coastline.

A range of environmental tracers were tested to measure groundwater discharge *in situ* in Gulf St Vincent. This was achieved by sampling for these tracers in Gulf waters along two ~10 km onshore-offshore transects (near Henley Jetty and Port Willunga) in November 2003. This period was selected because it corresponded with the highest seasonal water levels in many aquifers in the region (which should translate into higher rates of groundwater discharge to the study area). The tracers tested included salinity and naturally occurring radioisotopes (^{222}Rn and the “radium quartet” – ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra). These radioisotopes have much higher activities in groundwater than surface water and are currently used across the world to quantify groundwater discharge to the oceans.

Inverse salinity gradients (higher salinities <u>nearshore</u>) were found at the transects at the time of sampling, which is a typical feature of the South Australian gulfs. In general, the activities of the environmental tracers in seawater were low in the study area. Radon-222 was at background levels throughout the transects, the short-lived Ra isotopes (^{223}Ra and ^{224}Ra) had logarithmically declining activities with distance offshore and the long-lived Ra isotopes were slightly above oceanic background (^{226}Ra) or had weak offshore gradients (^{228}Ra). Groundwater discharge estimated from Ra isotopes varied from <0.1 to 3.5 m^3 m^{-1} d^{-1}. However, this range probably overestimates groundwater discharge because the input of Ra isotopes from the seafloor could only be conservatively estimated. Furthermore, the lack of nearshore freshwater plumes, the absence of ^{222}Rn and the relatively higher activity of short-lived relative to long-lived Ra isotopes are all consistent with seawater recirculation (tidal pumping along beachfaces, porewater exchange with the sea floor, etc) as the principal source for Ra isotopes to the study area.

The beachface study showed that tidal pumping accounts for about 5 m^3 d^{-1} of recirculated seawater per metre of shoreline in the ACWS area, similar to what has been found in other studies. At the site chosen, the beachface was an active zone for mixing between fresh nitrate-rich groundwater derived from local sand dunes and nutrient-poor seawater. There was also evidence that vertical recharge during high tides adds significant quantities of dissolved organic carbon to beachface groundwater. These findings highlight that diffuse

discharge of groundwater to the sea is a complex process, with a large potential for the transformations of nutrients at the interface between groundwater and seawater.

There was a contrast in N concentration in groundwater between the Quaternary aquifers of the Metropolitan Adelaide area and the aquifers from the Willunga Basin. Total dissolved N (TDN) concentrations (principally as nitrate) averaged 7.4 mg N L^{-1} in the Quaternary aquifers, similar to values found in previous studies. These elevated N concentrations are thought to result from past agricultural activity, fertiliser use on lawns and leakage from sewers and septic systems. The average TDN concentration in the Willunga Basin aquifers was lower (1.6 mg N L^{-1}), possibly reflecting a lower urbanisation, relatively low rates of N fertilisation and a longer water residence time in the aquifers.

The N load from unconfined aquifers to the ACWS area was estimated at <50 ton N $year^{-1}$. In comparison the N load through seawater recirculation was estimated to range between 220 to 660 ton N $year^{-1}$. Likewise, the individual loads from other sources of N to the ACWS area (such as sewage treatment effluent, stormwater discharge and atmospheric deposition) all range above 250 ton N $year^{-1}$. How much groundwater N is discharged further offshore from confined aquifers is unknown but is also expected to be small. While N discharge from groundwater is a small source of N at the scale of the ACWS area, it could still be a significant input locally.

The key recommendations from this study are:

- To develop and implement a better groundwater monitoring program along the coastal margins of the ACWS area;
- To use selected environmental tracers to map zones of localised groundwater discharge across the ACWS area;
- To further investigate the use of Ra isotopes to quantify seawater recirculation and groundwater discharge to the Gulf;
- To investigate the seasonality of nutrient recycling by tidal pumping along beachfaces.

Table of Contents

Introduction

This report summarises the findings of Input Studies IS 1 – Subprogram 3: “Groundwater discharge to the coastal environment: Flow quantity and quality” of the Adelaide Coastal Waters Study (Ellis and Fox 2001). The goal of the input studies component of the ACWS is to characterise the input of nutrients (especially nitrogen) to Adelaide’s coastal waters, with the aim to identify the potential causes of seagrass decline and eutrophication in this environment.

The role that groundwater plays in the water balance, nutrient fluxes or the ecology of Gulf St Vincent is not known. Elsewhere, there is evidence that fresh groundwater discharge can influence the distribution of plant communities in coastal environments (Johannes 1980; Hatton and Evans 1998; Kamermans *et al*. 2002). In addition, groundwater can be a major source of nitrogen (N) to coastal areas (Rutkowski *et al*. 1999; Smith *et al*. 2003; Slomp and van Cappellen 2004). Unlike phosphorus, nitrogen has a very mobile form in groundwater (NO_3^-) which makes this source more problematic for eutrophication in N-limited coastal zones (as opposed to the more common P-limitation of inland waters). In addition, many coastal aquifers are now under increased risk of N pollution as leaking sewers, septic systems, leakages from some industries and the increase use of N fertilisers in agriculture all contribute to increased N concentrations in groundwater. As groundwater can have long residence times before discharging to surface waters (years to millennia), N pollution of aquifers can have long-lasting consequences on the N loads to downstream ecosystems (Lamontagne 2002).

Groundwater discharge to coastal environments is more complex than in the inland context due to the presence of strong density gradients between seawater and freshwater and the confounding effect of tides (Ataie-Ashtiani *et al*. 2001; Slomp and van Cappellen 2004). The presence of density gradients along the coastal zone tends to focus groundwater discharge along the shoreline, as denser seawater tends to intrude inland as a wedge under fresher groundwater. For example, at Cockburn Sound in Western Australia, most of the groundwater discharge from an unconfined sand aquifer occurred within 10 metres of the shoreline (Smith *et al*. 2003). Salt water intrusions under fresh groundwater can extend for kilometres inland, especially when pumping of freshwater occurs. Offshore groundwater discharge from confined aquifer can also occur when aquifers outcrop to the seafloor or when weaknesses in confining layers generate springs. One such example of submarine spring discharge in Australia is the “Wonky holes” of North Queensland (Stieglitz and Ridd 2000).

There were four components to IS 1 - Sub-Program 3: 1) An estimation of groundwater discharge to the ACWS area through a review of existing flow net studies; 2) A survey of groundwater N concentration in regional groundwater; 3) A field study of N transformations at a beachface, where subsurface mixing between groundwater and seawater occurred; 4) An assessment of the usefulness of selected environmental tracers to estimate groundwater discharge *in situ* in Gulf St Vincent. The following report is divided in three sections: *Section 1* reviews the flow net studies; *Section 2* reviews the results of the regional groundwater water quality survey and of the beachface field experiment; *Section 3* reviews the environmental tracer study and presents the estimates of groundwater N discharge to the ACWS area. Finally, the main findings of the study and recommendations for future research and monitoring efforts are summarised under the section *Conclusions and Recommendations*.

1 Review of the hydrogeological setting and of past estimates of groundwater discharge to the ACWS area

1.1 *Introduction*

The Adelaide Coastal Water Study (ACWS) area stretches from the coast adjacent to the Northern Adelaide Plains prescribed wells area, north of Adelaide, to Aldinga Bay in the south. In terms of existing hydrogeological information, the study area can be divided into three main areas, Northern Adelaide Plains Prescribed Wells Area (NAP), Metropolitan Adelaide and the Willunga Basin (Fig. 1.1), with little or no information for any sites existing between these areas. The main aquifers in each system are primarily of Tertiary and Quaternary age, up to 600 m thick and contain multiple aquifer systems (Shepard 1975; Gerges 1997). The majority of these aquifers are recharged in the Mt Lofty Ranges and discharge is assumed to occur to the sea. The upper Quaternary aquifers are recharged from surface drainage and from lateral inflow from the fracture rock aquifer (Gerges 1999). The spatial distribution, quantity and quality of groundwater discharge along the Adelaide coastline from the upper sedimentary aquifers are not well known.

The main objectives of the hydrogeological review were to:

- To identify potential offshore groundwater discharge areas using stratigraphic information from existing bore records and ocean floor surveys.
- To identify the potential location of groundwater discharge zones along the coastline from the potentiometric surfaces of the upper aquifers.
- To estimate groundwater discharge rates for the three main hydrogeological systems contiguous to the ACWS area using past and re-evaluated flow net analyses.

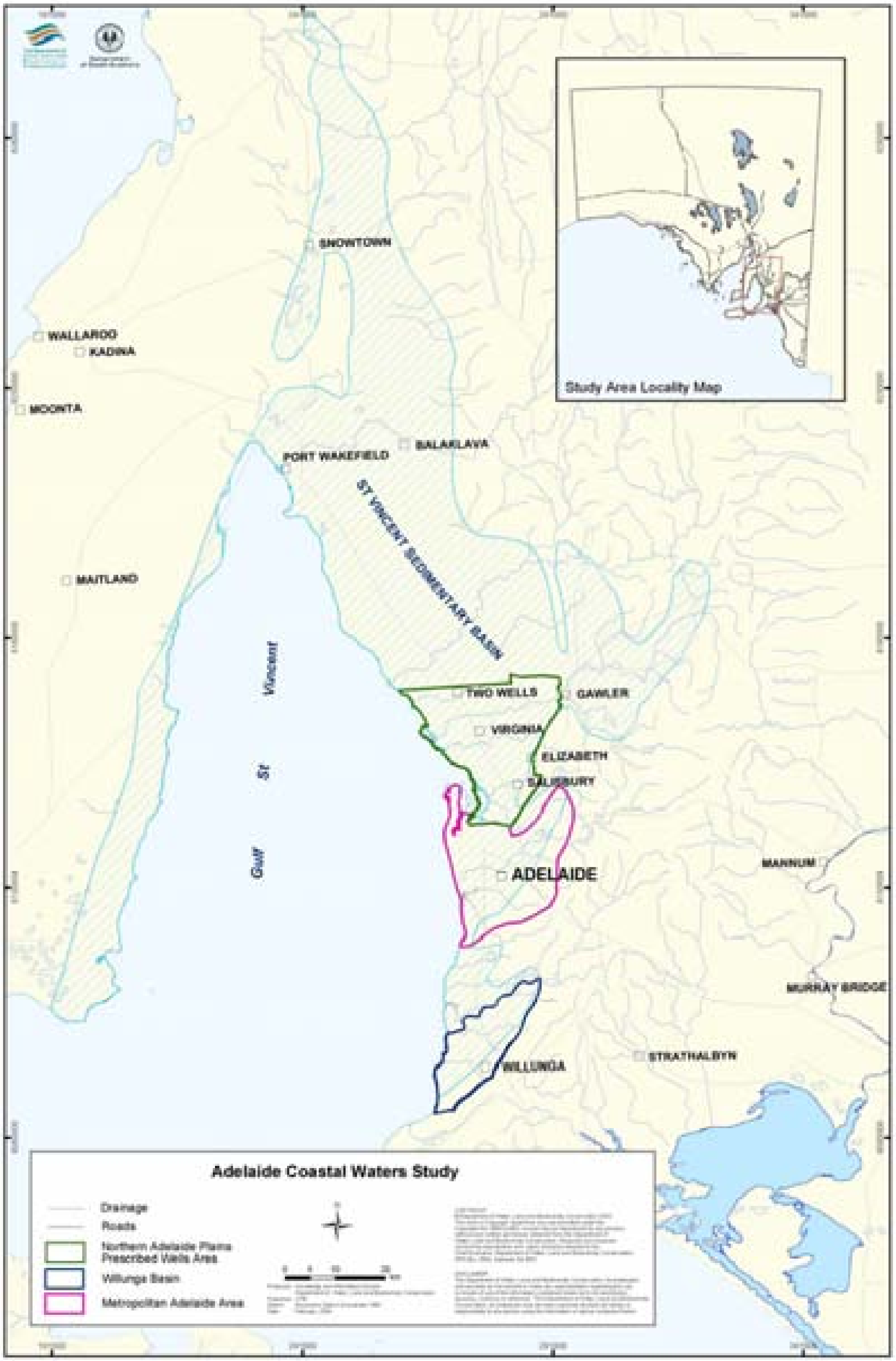

Fig. 1.1. Location of the three main hydrogeological systems contributing to the Adelaide Coastal Water Study area.

1.2 *Bore networks and observation wells*

For accurate estimates of groundwater discharge to the sea, it is important to have a good network of observation wells. Within the NAP area there are 16 observation wells located in the first Quaternary aquifer (Q1), seven of these wells are situated on the coastward side of the Redbank Fault. All the wells are situated at a distance greater than 5km from the coast. In the Metropolitan Adelaide area, 28 observation wells exist within the Q1 aquifer. However most of the wells are located more than 2 km inland from the coast.

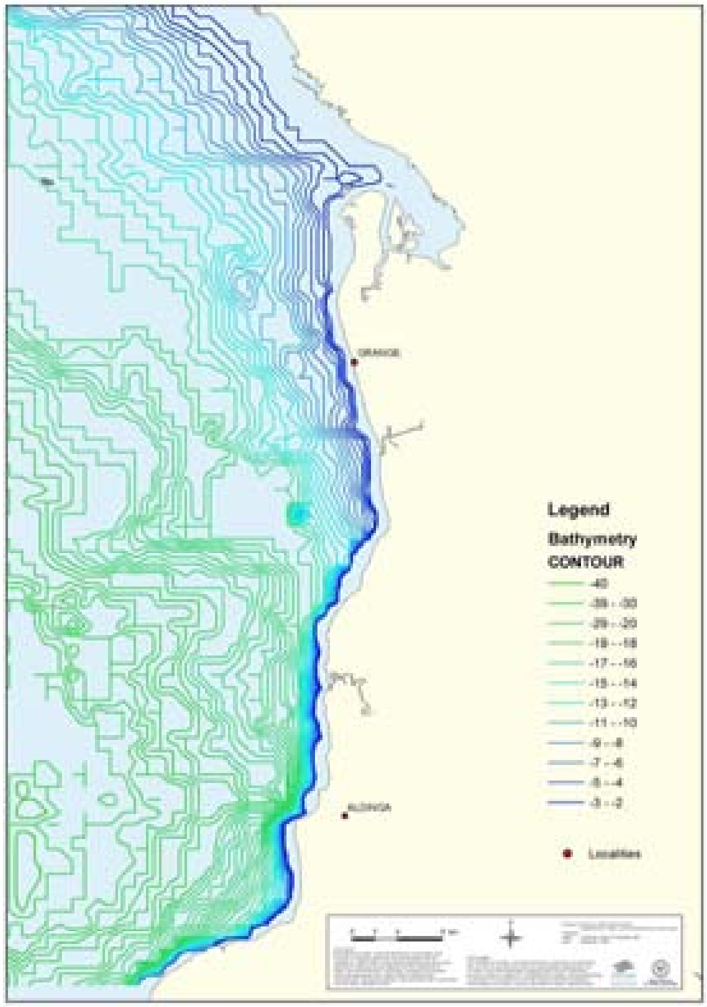

Fig. 1.2. Bathymetry of the ACWS area.

In the Willunga Basin, the Port Willunga Formation and the Maslin Sands aquifers were targeted in this study. As part of the current observation network, 33 wells are monitored within the PWF and 30 wells are monitored in the Maslin Sands. Ten of the PWF observation wells are located within 5 km of the coast. Only one Maslin Sands well is within 5 km of the coast. Thus, while the three hydrogeological systems have fairly extensive monitoring networks, the coverage near the coastline is limited.

Offshore, there are some 448 wells. According to the Department of Water, Land and Biodiversity Conservation database, most are shallow, less than 5 m, and generally backfilled/abandoned. Overall for the offshore wells, there is a distinct lack of information pertaining to the stratigraphy/ hydrogeology beneath the ocean floor; hence depths to the different aquifer system cannot be identified. Bathymetry was the only offshore information available. The bathymetry is constructed from the Australian Bathymetry and Topography grid from over 900 surveys obtained by Geosciences Australia since 1963 (Fig. 1.2). Off the coast of Grange the contours are reasonably well spaced suggesting there is a gradual increase in depth. In contrast, off the coast of Aldinga there is a sharp increase in depth.

1.2.1 Hydrogeology Literature Review

1.2.1.1 General

St Vincent Basin was formed in the Eocene period during the continental separation of Australia and Antarctica (Cooper 1979). Deposition began in the Adelaide Geosyncline approximately 1000 million years ago. During the Tertiary, older structures were reactivated and led to the formation of half grabens (St Vincent Basin) and high relief topography (Mount Lofty Ranges). Sedimentation was initiated by further subsidence and was followed by marine transgression. Renewed tectonism during late Tertiary/early Quaternary resulted in basement uplift, gentle folding of Tertiary sediments and later marine regression. This was followed by the deposition of Quaternary and Recent fluviolacustrine and alluvial sediments, with interruptions by minor marine events (Gerges 2001).

The oldest rocks are the Precambrian crystalline ‘Barossa Complex’, consisting of schist and micaceous gneiss. These rocks are unconformably overlain (that is, some erosion occurred beforehand) by younger Precambrian cover (Adelaidean), which extends northward to include the Mount Lofty and Flinders Ranges and forms part of the Adelaide Geosyncline (Fig. 1.3). The Adelaidean is preserved as rocks of various lithologies including tillite, quartzite, felspathic quartzite, dolomite, phyllite, slate and siltstone. The Adelaidean is unconformably overlain by Tertiary and Quaternary sediments up to 600 m in thickness. Willunga Basin is a thin wedge of mainly mid to late Tertiary and Quaternary sediments deposited on the downthrown western side of the Willunga Fault. The sedimentary sequence has not been strongly deformed; however, the sediments dip toward the southwest. All major aquifers outcrop at the surface. Sediments of Permian age are also known to occur in the north eastern and western areas of the basin. The basin is underlain and bounded to the north, south and east by Late Precambrian and Cambrian age rocks of the Adelaide Geosyncline. The basement rocks are interbedded slates, quartzites and dolomites.

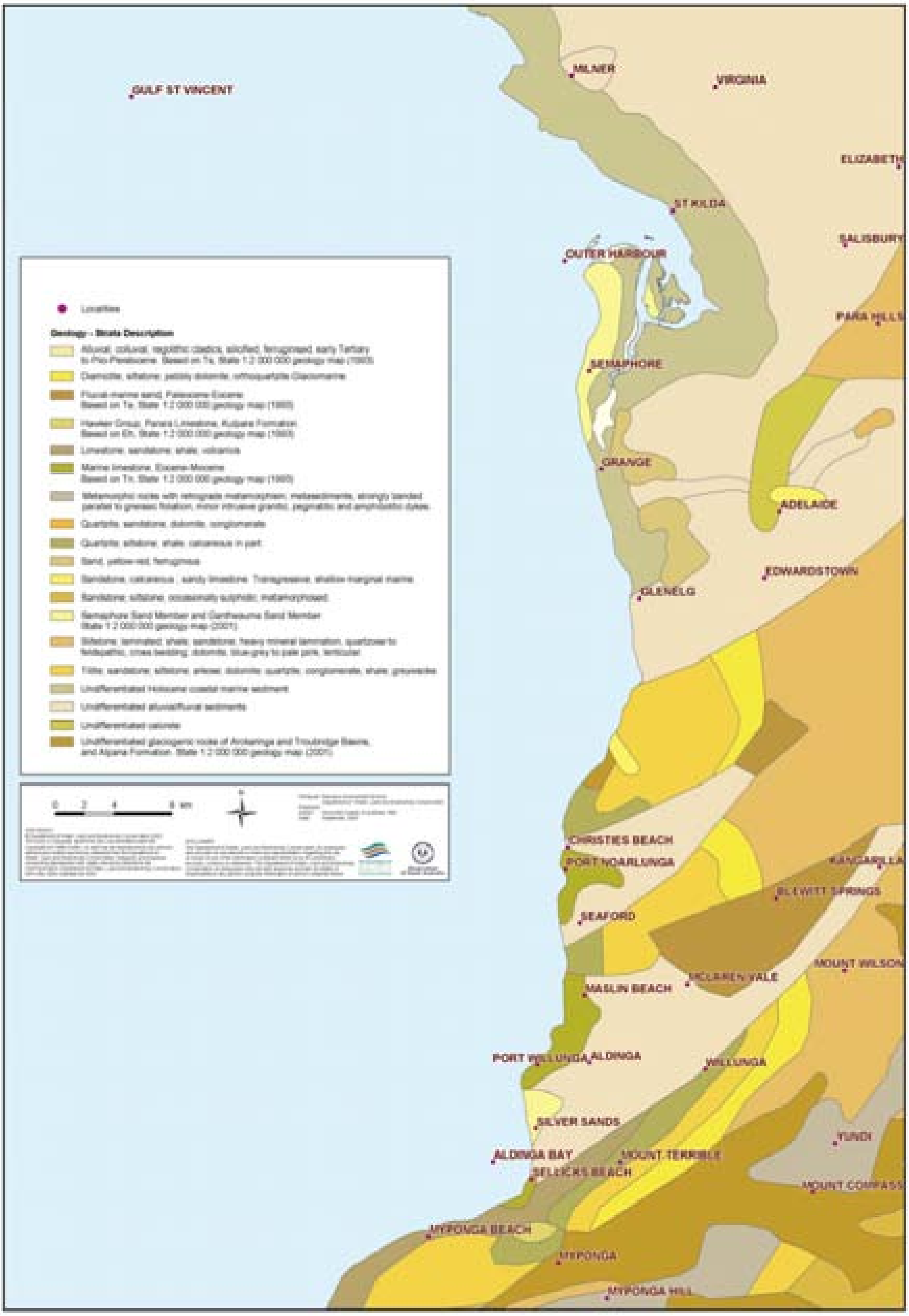

Fig. 1.3. Outcrop geology for the Greater Adelaide region.

1.2.1.2 Willunga Basin

The Willunga Basin is a complex multi-aquifer system (see detailed review in Martin 1998). Groundwater is withdrawn from aquifer layers within the Quaternary and Tertiary sediments, and from the basement rocks (Fig. 1.4). The groundwater system has been divided into four aquifer systems, Basement, Maslin Sands, Port Willunga Formation and Quaternary (Aldam 1989). Marls and marly limestones of the Blanche Point Formation aquitard separate the Maslin Sands and Port Willunga Formation aquifers. The most important sources of groundwater within the basin are the Maslin Sands and Port Willunga Formation aquifers (Aldam 1989), which are the focus of this study.

Recharge to the sedimentary aquifers of the Maslin Sands and Port Willunga Formation occurs via direct rainfall infiltration where the aquifers outcrop on the western slope of the MLR (Sellicks Hill Range), recharge from streams and outflow from the basement rocks. Groundwater flows toward the coast from the north-east corner of the basin. From pumping tests, the broad scale transmissivity of the Port Willunga Formation aquifer typically ranges between 150 and 200 m d^{-1}. Higher values have been measured but these are interpreted to reflect smaller scale local variations within the aquifer matrix. The transmissivity of the Maslin Sands aquifer typically has values ranging between 35 and 50 m d^{-1}.

Analysis of hydrographs show that more than half of all monitored wells have a declining water level trend. The maximum rate of decline is 0.8 m a^{-1}. Declines in the potentiometric surface for both the Port Willunga Formation and Maslin Sands correspond to the areas of greatest intensity of extraction. These declining water levels indicate that the groundwater systems are not in equilibrium with respect to hydraulics as groundwater outflow through pumping extraction is greater than groundwater inflow.

Salinity is increasing in the centre of the basin, in both the Maslin Sands and Port Willunga Formation aquifers, by approximately 20 EC units per year. Along the northern and coastal margin of the basin, salinity is increasing at a significantly higher rate. Observation well WLG 88 completed in the Port Willunga Formation aquifer, 1.25 km inland from the coast has an annual increase in salinity of 30 mg L^{-1}. This increase may be an early indication of seawater intrusion into this part of the aquifer. Along the northwestern margin of the basin, salinity within the Port Willunga Formation is increasing at similar levels, 30 mg L^{-1} per year. Along the same margin, salinity within the Maslin Sands is increasing at around 50 mg L^{-1} per year.

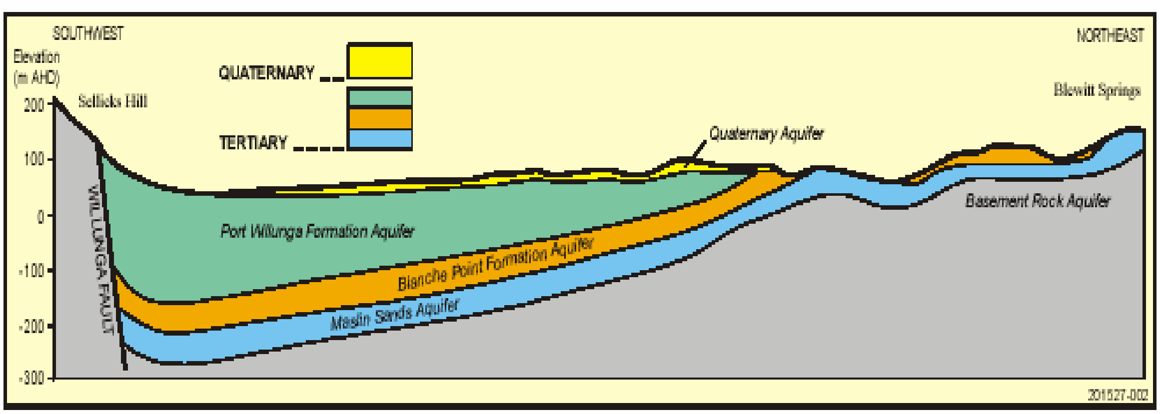

Fig. 1.4. Cross-section of the Willunga Basin

1.2.1.3 Metropolitan Adelaide Area

Gerges (1997) reviewed the hydrogeology of the Metropolitan Adelaide area. Two major fault zones, along the Eden-Burnside Fault and the Para Fault, control the topography of the Metropolitan Adelaide area. They are responsible for most of the major dislocation and tilting of the Precambrian rocks and for formation of the two embayments, the Golden Grove-Adelaide Embayment and the Adelaide Plains Sub-basin (Fig. 1.5). The Basin consists of Tertiary and Quaternary sediments up to 600m thick which overly a Precambrian fractured rock aquifer (Fig. 1.5). The basin contains up to 10 aquifer systems with groundwater of varying quality, with the Quaternary sediments containing up to six aquifers and the Tertiary sediments up to four aquifers (Gerges 2001). The different Quaternary, Tertiary and Precambrian aquifers have been designated by combining the prefix of the geological formations (Q, T or P) with the number of the aquifer in order of increasing depth:

- Quaternary aquifers — Q1 to Q6
- Tertiary aquifers — T1 to T4
- Precambrian fractured rock aquifer — P.

Despite the fact that the aquifers are identified with letters indicating their age, they remain relatively independent of stratigraphic units.

The main lithology of the Quaternary sediments is mottled clay and silt with inter-bedded sand, gravel and thin sandstone. The present withdrawal from these aquifers is negligible. The Quaternary aquifers vary greatly in thickness (from 1 to 18 m), lithology and hydraulic conductivity. Generally, grain size decreases towards the coast, and with increasing distance from surface drainage and major structures such as the Para Fault. The confining beds between the Quaternary aquifers consist of clay and silt and range in thickness from 1 to 20 m. These confining beds are absent in some areas, allowing hydraulic connection between aquifers.

The Q1 aquifer is the focus of this study in the Metropolitan Adelaide area. Q1 is well distributed over the area and is located at depths between 3 and 10 m below ground level with an average thickness of 2 m. In the proximity of major structures and surface drainage, aquifer materials tend to be coarser and thicker and therefore more transmissive. This aquifer was previously regarded as unconfined, but careful examination of water cut data has revealed that, in the majority of wells, confined conditions exist. This observation is important as it implies that, as long as the aquifer is fully saturated, changes in head are elastic responses (that is large changes in head for small changes in volume of water in storage).

Greater recharge rates (i.e. low salinities) in the Q1 are believed to be due to active recharge from surface drainage and from lateral inflow from the fractured rock aquifer. On the LeFevre Peninsula area, where Q1 is overlain by dune sands, shallow groundwater is quite fresh due to significant local recharge on sand dunes. However, groundwater deeper in the Q1 along the coastline as a poor water quality (salinities up to 21,000 mg L^{-1}). It is suspected that over-pumping of good quality water from this area is either promoting seawater intrusion or upward leakage from the underlying salty aquifer.

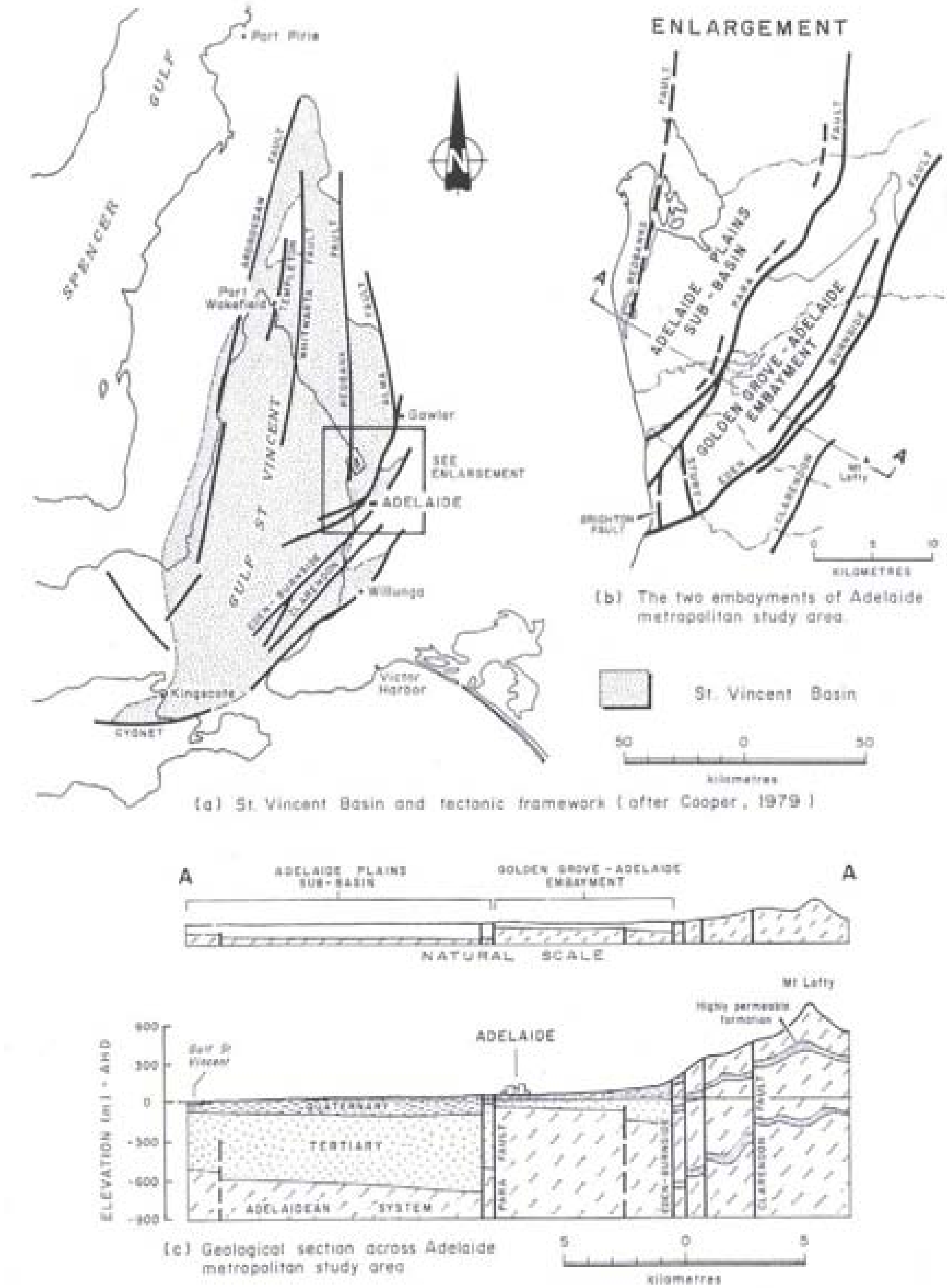

Fig. 1.5. Hydrogeological cross-section of the Adelaide Metropolitan Area.

1.2.1.4 The Northern Adelaide Plains

The Northern Adelaide Plains (NAP) groundwater management area occupies approximately 750 km^2 of the Adelaide coastal plain. It is hydraulically connected to the Adelaide Metropolitan Area and also forms part of the Adelaide Plains sub-basin (Gerges 2001). Generally, two main aquifer systems, Quaternary and Tertiary, are recognised in the NAP area. The Quaternary contains mainly four aquifers, in some areas up to six, and the Tertiary has up to four aquifers (Fig. 1.6; Zulfic 2002). The lithology of the Quaternary sediments is mottled clay and silt with inter-bedded sand, gravel and thin sandstone. The aquifers are designated Q1 to Q6 in order of increasing depth with individual aquifer thicknesses varying between 1-60 m. Salinities in the Q1 and Q2 vary between 2000 and 18,000 mg L^{-1} (Zulfic 2002), with the higher salinities occurring closer to the coast, indicating here again seawater intrusions (Gerges 1999). Hydrographs of the Quaternary aquifers in the Northern Adelaide Plains show an almost continuous decline in water levels in recent times.

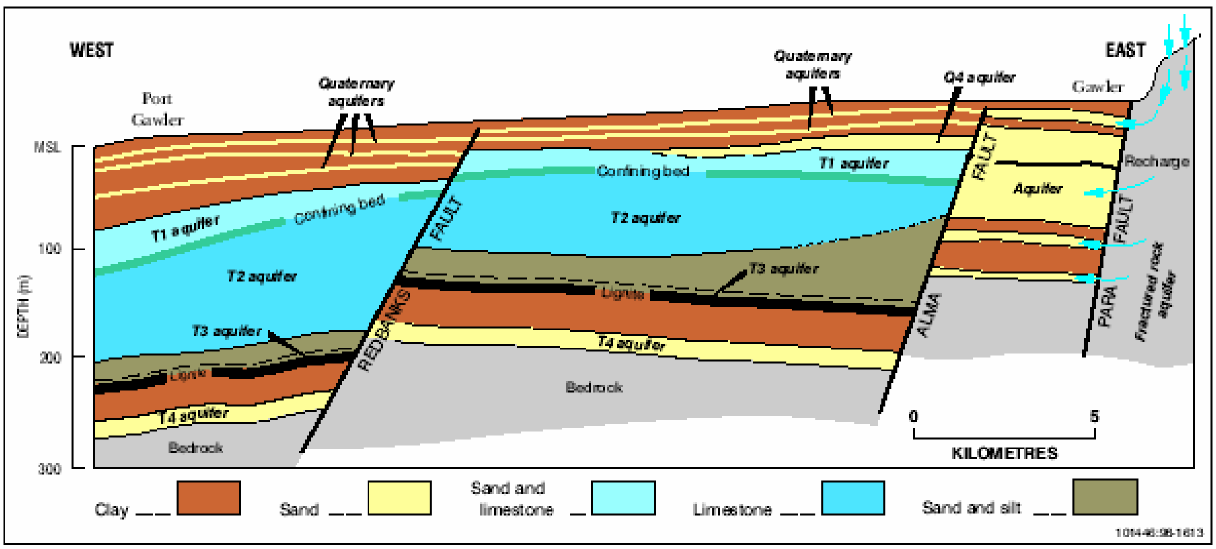

Fig. 1.6. Cross-section of the Northern Adelaide Plains.

1.3 *Estimates of groundwater discharge to Gulf St Vincent*

Groundwater discharge to the coastal zone can be estimated using water balances or with Darcy's law. Using water balances, groundwater discharge is estimated as the residual between the different inputs and outputs from the system (precipitation, surface runoff, etc). This approach is less successful when groundwater discharge is only a small component of the water balance. The use of Darcy's law (or groundwater hydraulics) involves knowing the gradient in the water table (for unconfined aquifer) or in the potentiometric surface (for confined aquifers) and the hydraulic properties of the geological medium (its hydraulic conductivity). Darcy's law can estimate small fluxes of groundwater accurately if both the hydraulic gradients and the variability in the hydraulic conductivity in the system are well characterised. For the three hydrogeological systems contiguous to the ACWS area, a mixture of both approaches has been used in the past to estimate groundwater discharge to the gulf. These will be reviewed here, in combination with a re-evaluation of groundwater discharge from the Willunga using Darcy's Law.

1.3.1 Methodology

A flow net analysis is a graphical method to estimate groundwater discharge from Darcy's Law. The method assumes an isotropic medium and the watertable contours or potentiometric surfaces are discretised graphically into equally spaced flowtubes (Freeze and Cherry 1979). The equipotential contours indicate the change in head is evenly distributed between adjacent flowtubes. The quantity of water or discharge flowing through the flowtube can be determined by rearranging Darcy's Law:

$$q = \frac{Kph}{f} \tag{1.1}$$

Where

q is the total volume discharge per unit width of aquifer [$L^3\ T^{-1}\ L^{-1}$],

K is the hydraulic conductivity [$L\ T^{-1}$],

p is the number of flow paths bounded by adjacent pairs of streamlines,

h is the total head loss over the length of the streamlines [L],

f is the number of squares bounded by any two adjacent streamlines and covering the entire length of flow.

For the Willunga Basin, Martin (1998) also used the Ghyben-Herzberg concept (as described in Hazel [1975]) to describe groundwater flow from the Port Willunga Formation and Maslin Sands. This approach can be better suited in a coastal environment as it takes into account the dynamics of groundwater flow in areas where fresh groundwater flows over denser salt water, which result in "wedges" of seawater intruding under fresher groundwater at the zone of discharge. In more detail:

$$qL = \frac{\left(Kz_0{}^2\right)}{2} \times \frac{\left(\rho_s - \rho_f\right)^2}{\rho_f} \times 1 + \left(\frac{\rho_f}{\rho_s - \rho_f}\right) \tag{1.2}$$

Where

q = discharge [$L^3\ T^{-1}\ L^{-1}$]

L = length of wedge [L]

K = hydraulic conductivity [$L\ T^{-1}$]

z_o = depth of base below datum [L]

ρ_f = density of fresh water [$M\ L^{-3}$]

ρ_s = density of salt water [$M\ L^{-3}$]

1.3.2 Results

1.3.2.1 Willunga Basin

Analysis of the potentiometric surfaces for the Maslin Sands aquifer for April 2002 (Fig. 1.7) showed that discharge to the sea only occurs north of Blanche Point, for approximately 3 km to the extent boundary. South of this point, the zero potentiometric surface for April 2002 is up to 6 km inland suggesting seawater intrusion occurs south of Blanche Point. For the PWF, also based on April 2002 potentiometric contours, discharge only occurs south of Blanche Point for approximately 1 km (Fig. 1.8). South of this discharge zone is a cone of depression approximately 2 km inland, also indicating seawater intrusion. Based on limited bore log records, the thickness of both aquifers at the discharge location is approximately 8.5 m for the MS and 66 m for the PWF.

Martin (1998) suggested seawater intrusion occurs some 5 km inland from Aldinga Beach which is consistent with the potentiometric contours constructed for April 2002. Due to the lack of observation wells in the Port Willunga Formation at the time of Martin's analysis, he could only estimate the wedge intrusion to be 750 m based on rising salinities in observation well WLG88. From water levels of more recent wells, it is evident from the zero potentiometric surface for April 2002 that seawater has intruded.

Broad scale transmissivity for the Port Willunga Formation ranges between 150 and 200 m d^{-1} and 35-50 m d^{-1} for the Maslin Sands (Martin 1998). Due to the lack of spatial data on hydraulic conductivity, it was not possible to either discretise the study area into regions of similar hydraulic conductivity or to determine a representative value for each aquifer. Thus, maximum estimates of groundwater discharge were obtained by using the upper range in hydraulic conductivity for both the PWF (200 m d^{-1}) and MS (50 m d^{-1}). Using the potentiometric contours adjacent to the discharge zones, these upper transmissivity values and the approximated thicknesses of the aquifers in observation wells closest to the discharge zone, the discharge flux is estimated to be 670 ML $year^{-1}$ for the PWF and 120 ML $year^{-1}$ for the Maslin Sands.

For his analysis using the Ghyben-Herzberg principle, Martin (1998) assumed as stated before that the length of the intruded wedge for the Maslin Sands aquifer was 5 km inland from Aldinga Beach based on salinity data from an observation well. Martin calculated the discharge to sea from the Maslin Sands aquifer to be 1060 ML $year^{-1}$. Due to the lack of wells completed in the PWF near the coast, Martin (1998) estimated that the wedge intruded 750 m inland and estimated a discharge to sea of 1820 ML $year^{-1}$ (Table 1.1). It should be noted that the discharge from the flow net analysis is based only on the area 1 km and 3 km respectively adjacent to Blanche Point, whereas the estimates presented in Martin (1998) assumes some discharge to sea along the entire coast. Because groundwater discharge is most likely restricted to only a fraction of the coastline, the lower estimates derived here are probably more accurate.

Table 1.1. Estimates of groundwater discharge to Gulf St Vincent from the Port Willunga Formation and Maslin Sands.

Aquifer	Ghyben-Herzberg (ML year^{-1})	Flow Net (ML year^{-1})
PWF	1820	670
Maslin Sands	1060	120

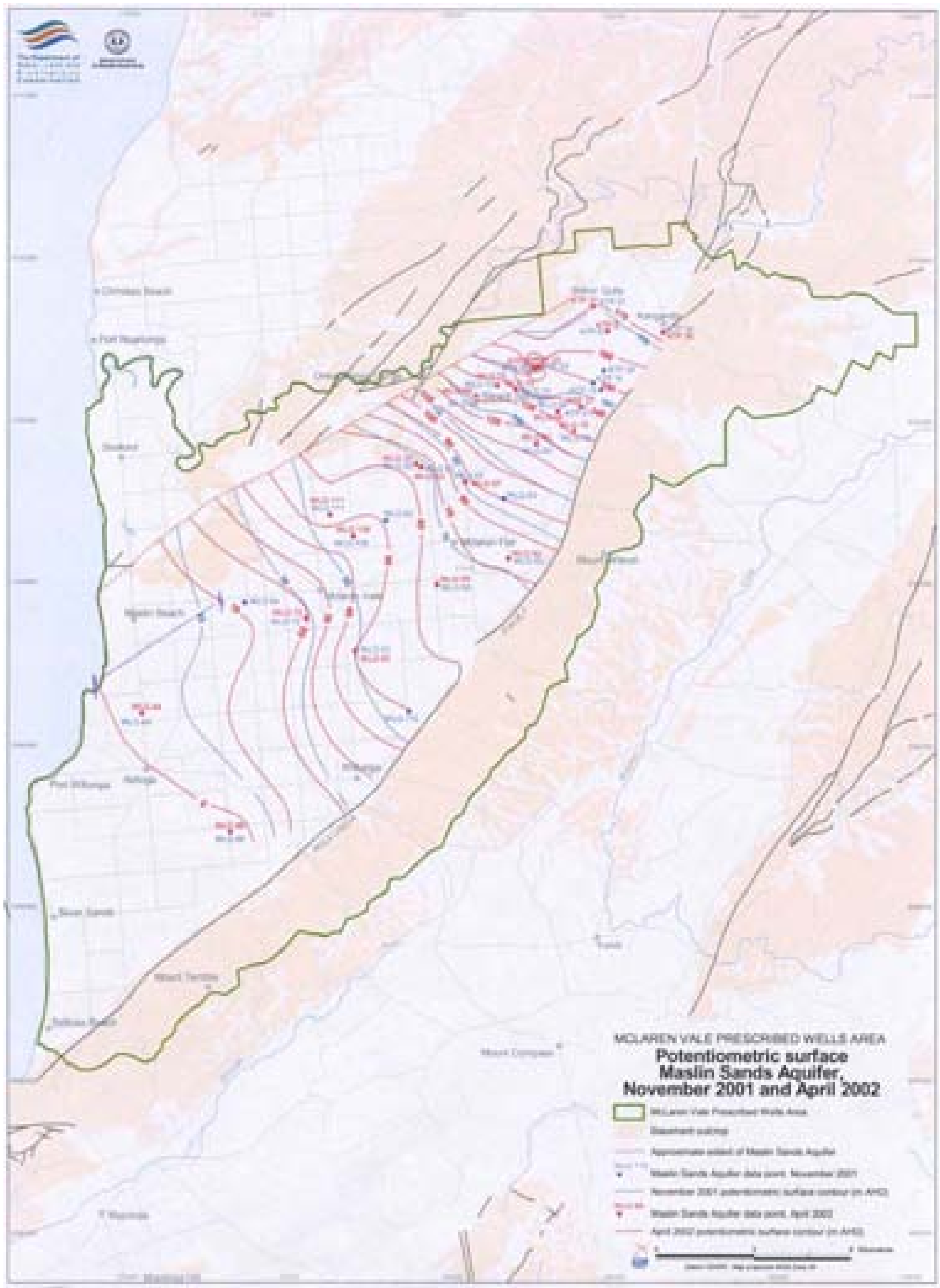

Fig. 1.7. Potentiometric surface for the Maslin Sands aquifer (Clarke 2002).

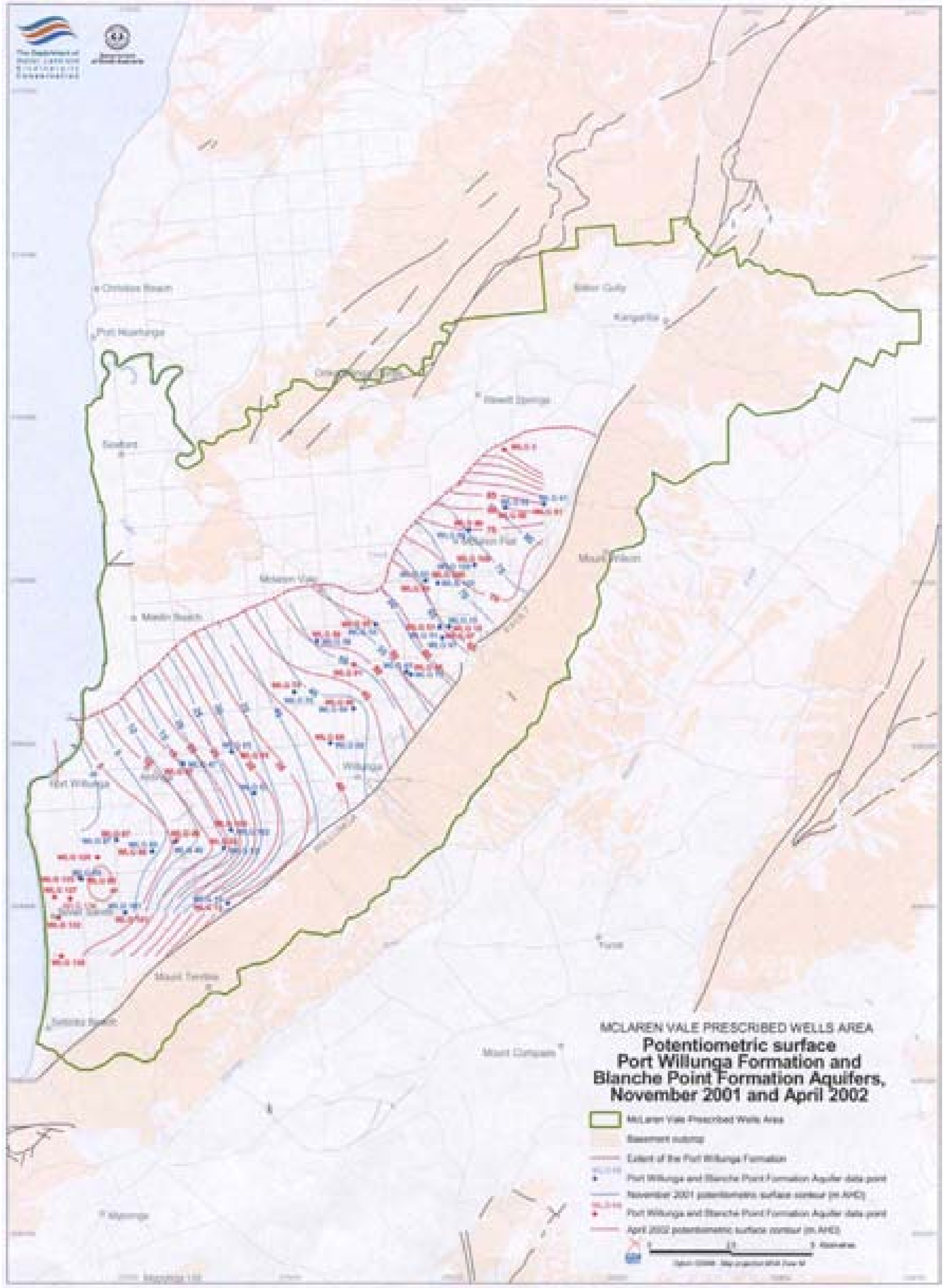

Fig. 1.8. Potentiometric surface of the Port Willunga Formation (Clarke 2002).

1.3.2.2 Adelaide Metropolitan Area

Gerges (1997) analysis of historic Quaternary aquifer water levels shows a general flow towards the northwest with ultimate discharge under Gulf St Vincent. Gerges (1997) indicates the deepest point in the Gulf is 25 m, hence only the Q1 and Q2 aquifers may naturally outflow into the Gulf. Thick, low permeability sediments overlie deeper Quaternary aquifers with their discharge opportunities limited to structures (faults) under the Gulf and/or through upward diffuse leakage through aquitards. Provided that these structures possess sufficient permeability, they may form discharge boundaries (Gerges 1997).

A network of Q1 observation wells was established in 1980-81 to examine the potentiometric surface of the area (Gerges 1999). The contours (Fig. 1.9) indicate uniform groundwater flow towards the northwest. The potentiometric surface gradient is steep in the east adjacent to the Mount Lofty Ranges. Near the coast and west of the Para Fault the gradient is almost flat. This flat gradient of 1m km^{-1} may be a result of higher transmissivity and/or the effect of gentle topography. Heavy pumping from the underlying Tertiary aquifer has induced downward leakage, which has led to the development of a cone of depression in Q1 in the northern part of the area and may induce seawater intrusion into the Q1 aquifer in this area.

Gerges (1999) analysed and characterised a number of hydrogeological zones (see insert in Fig. 1. 9) based on contrasting characteristics. Given that Quaternary sediments in zones 3 and 2 abut the coast, these will be discussed further.

Using the potentiometric surfaces from Gerges (1999; Fig. 1.9), and focusing on the area west of the Para fault which Gerges characterises as zone 3, it is evident that the hydraulic gradient is almost flat (~1 m km^{-1}), except where the Torrens River crosses the Para fault line. Heavy pumping from the underlying Tertiary aquifer has induced downward leakage, which has resulted in a cone of depression in Q1 in the north (Gerges 1999), which in turn may have induced seawater intrusion. Gerges (1999) concludes that the outflow from the Q1 aquifer to the Gulf St Vincent will be negligible as the gradient at the coast is flat and the transmissivity is low.

Zone 2 and 2A (Fig. 1.9) exhibits a moderate hydraulic gradient of 10 m km^{-1} between the eastern boundary of zone 2 and the Sturt River (Gerges 1999). West of the Sturt River, the hydraulic gradient is 2.5m km^{-1} which reflects the relatively high hydraulic conductivity of the aquifer in this area (Gerges 1999). Based on Gerges' (1999) analysis of the two zones, groundwater discharge to the sea may be more pronounced in the zone 2 area compared with zone 3.

In another study, Pavelic *et al.* (1992) utilised some 1080 bores to characterise depth to water table and the potentiometric surface contours. It should be noted that Pavelic *et al.* (1992) concentrated on the 'Upper Quaternary' aquifer to a depth of 25 m and used historical data to derive the composite contours (Fig. 1.10) in order to give a much generalised picture of flow direction. In contrast, Gerges' (1999) Q1 potentiometric surfaces were constructed from wells with depth ranging from 3 to 10 m. Pavelic *et al*. (1992) combined more than one Quaternary aquifer in the potentiometric surface construction. It should also be noted that topographic elevation was estimated from 1:2500 topographic maps and the inferred elevation has an accuracy of about plus or minus one metre (Pavelic *et al*. 1992). Considering that the potentiometric contours up to 5 km inland from the coast have a 2 ± 1 m AHD accuracy and that they represent a composite aquifer system, it is not possible to determine discharge to the sea.

Overall, while the Quaternary aquifers in the Adelaide Metropolitan area have been studied in some detail, it is not currently possible to estimate groundwater discharge to the sea because of the lack of operational bores and accurate potentiometric levels within 5 km of the coast.

Localised unconfined groundwater systems exist in the beach dunes prevalent along the coastline of the Metropolitan Adelaide area, especially along the LeFevre Peninsula (Martin

1996). The dunes have a high recharge rate and some of the lowest salinity groundwater in the Quaternary in Metropolitan Adelaide. Martin (1996) estimated that groundwater discharge from the LeFevre Peninsula to the Gulf and to the Port River was 630 ML year^{-1}. Some discharge from beach dunes along the coastline is also expected below the Peninsula (see Section 3). Using the gradient measured at West Beach (Section 2), estimates of K_H for sands (1 to 10 m d^{-1}) and about 10 km of coastal dunes below the LeFevre Peninsula, this discharge has been estimated at ranging between 30 – 300 ML year^{-1}, with a value of 100 ML year^{-1} used here as a conservative estimate.

Pending further analysis of regional groundwater systems, groundwater discharge for the Metropolitan Adelaide area is estimated here at 730 ML year^{-1}, principally from the coastal sand dune aquifers. However, some regional groundwater discharge from Zone 2 probably occurs and needs to be further assessed. It is likely that a substantial fraction of groundwater discharge in Metropolitan Adelaide now occurs through interception by the sewerage system. This is supported by the higher than expected salinity and flow volumes collected at the Bolivar wastewater treatment plant (P. Dillon, CSIRO Land and Water, *pers. comm.*)

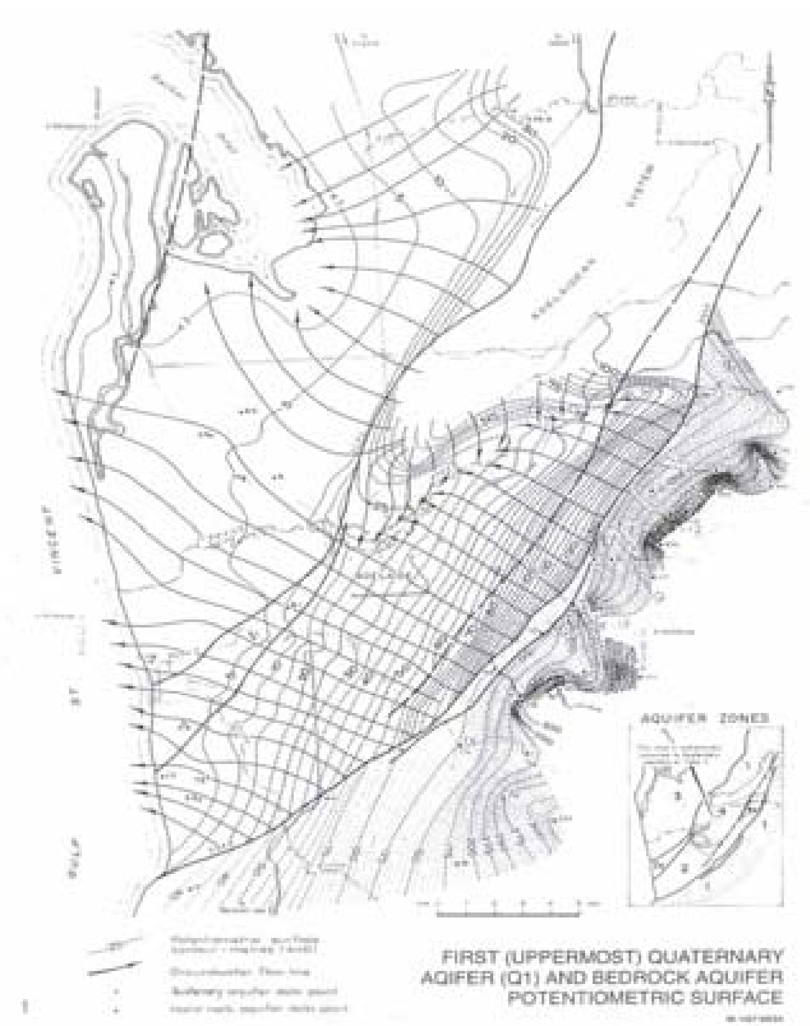

Fig. 1.9. 1980-81 potentiometric surfaces for the Quaternary aquifer in Metropolitan Adelaide (Gerges 1999).

Fig. 1.10. Generalised potentiometric surfaces for the shallow Quaternary system in Metropolitan Adelaide (Pavelic *et al*. 1992).

1.3.2.3 Northern Adelaide Plains

The Quaternary groundwater flow system of the NAP has been substantially modified by groundwater extraction from the underlying Tertiary aquifer (Fig. 1.11; Gerges 2001). Extraction of groundwater from Penrice (ICI)-SAMCOR began in 1957 and most of the groundwater in this area is used for industrial purposes. This pumping centre – the largest and most permanent in the area – contains 12 production wells pumping 2700-3000 ML year^{-1}. The present rate of pumping has created a steep cone of depression over the whole year, which expands to its maximum level during summer (Fig. 1.11). The levels are approximately –20 m AHD in the central area contracting slightly during winter to –16 m AHD. During summer, the large withdrawals from the aquifer produce seasonal variations in the regional flow pattern, creating a groundwater divide between the Penrice (ICI)- SAMCOR permanent cone and the Metropolitan area (West Lakes) seasonal one.

During winter, the location of the permanent cone of depression corresponds to the location of recently developed pumping centres. At present, the cone of depression decreases to its minimum size at the end of winter but the potentiometric surface never recovers to its pre-pumping levels for the following reasons:

- There is continuous industrial pumping during winter with no recovery period.
- The effect of the cumulative drawdown over years of pumping.
- Extensive and continuous pumping from this area has created a regional cone of depression that has changed local flow patterns to a radial flow from all directions toward the centre of the cone. This includes seawater intrusion from Gulf St Vincent.

Given the lack of operational bores in the Quaternary aquifers in the NAP within 5 km of the coast, it is impossible to construct a representative present day potentiometric surface and hence coastal discharge estimation using flow net analysis for this area. Shepherd (1975) surmised that minor groundwater outflow probably occurs through all Quaternary aquifers and has estimated this to be 500 ML year^{-1} by water balance methodology.

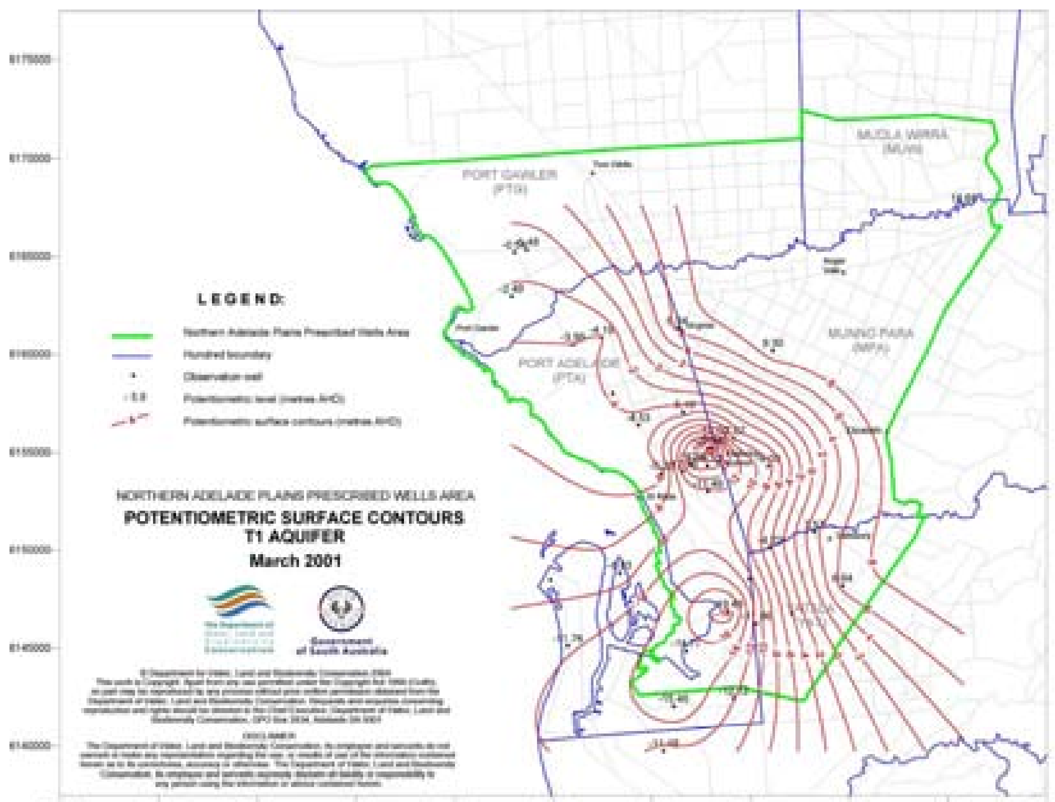

Fig. 1.11. Potentiometric surfaces in the T1 aquifer, Northern Adelaide Plains.

1.4 *Conclusions*

From the limited information available, potentiometric surfaces in the NAP and Metropolitan Adelaide area suggest that there is limited discharge from the Q1 aquifer to the sea. Moreover, potentiometric surfaces indicate that many sections of the coastline adjacent to the Quaternary aquifers are undergoing seawater intrusion. In the absence of an adequate spatial distribution of monitoring wells in the Quaternary aquifers for the NAP and Metropolitan Adelaide area, a more detailed analysis of the extent of the groundwater discharge or seawater intrusion could not be made.

In the Willunga Basin, the potentiometric surface for the Port Willunga Formation suggests there is only a small zone adjacent to Point Blanche where water is discharged to the sea. Using a flow net methodology, the discharge from this zone to the sea is estimated at 670 ML $year^{-1}$. South of this assumed discharge zone, the potentiometric surface indicates salt-water intrusion. Similarly for the Maslin Sands aquifer, the potentiometric surfaces show that discharge to the sea only occurs in a small zone north of Point Blanche. Flow net analysis indicates the discharge from this zone is approximately 120 ML $year^{-1}$. The best estimate of groundwater discharge to the ACWS area based on the flow net and water balance reviews is 2020 ML $year^{-1}$ (or $2.0 \cdot 10^6$ m^3 $year^{-1}$) but is highly uncertain (Table 1.2).

Accurate estimates of groundwater discharge to Gulf St Vincent cannot be made due to the limited groundwater monitoring along the coastline. This is compounded by the low hydraulic gradients near the coastline and the added complexity of sharp density gradients at the land-sea interface.

Table 1.2. Summary of groundwater discharge estimates for the AWCS area based on flow nets and water balance analyses.

Hydrogeological system	Groundwater Discharge	
	(ML $year^{-1}$)	(m^3 $year^{-1}$)
North Adelaide Plains	500	$5 \cdot 10^5$
Metropolitan Adelaide	730	$7.3 \cdot 10^5$
Willunga Basin		
Port Willunga Formation	670	$6.7\ 10^5$
Maslin Sands	120	$1.2 \cdot 10^5$
Total for ACWS area	**2020**	$\mathbf{2.0 \cdot 10^6}$

2 Determination of N concentration in groundwater and recirculated seawater

2.1 *Introduction*

A number of studies have shown that submarine groundwater discharge can be a significant source of nutrients to the coastal environment (Kohout and Kolipinski 1967; Burnett *et al*. 2001; Smith *et al*. 2003; Ullman *et al*. 2003). In addition, nutrients can also be added to coastal zones by seawater recirculation, the movement of seawater in-and-out of beachfaces by tidal pumping (Ataie-Ashtiani *et al*. 2001). Seawater recirculation complicates the assessment of nutrient input from regional groundwater discharge because it will induce a mixing of seawater and fresh groundwater before groundwater discharges to the coastal zone (Slomp and van Cappellan 2004). It is suspected that active biogeochemical cycling occurs during this mixing process (Uchiyama *et al*. 2000; Ueda *et al*. 2003; Ullman *et al*. 2003). In other words, the quantity and form of the nutrients discharged by groundwater to the coastal zone could be different than what is expected from measurements made in groundwater some distance from the ocean.

In this section, a survey of the concentration of nitrogen and other nutrients in regional groundwater and a seawater recycling field study at West Beach are presented. The aim of the regional groundwater survey was to define the expected nutrient concentrations in regional groundwater discharging to the ACWS area. The aim of the beachface field study was to evaluate the quantity of nutrients that could be returned to the Gulf by seawater recycling and whether biogeochemical transformations of N and other nutrients occur at the interface between fresh groundwater and seawater.

2.2 *Methods*

2.2.1 Regional survey

Groundwater samples from 21 wells were collected along two transects (one in the metropolitan area and the other in the Willunga Basin; Fig. 2.1). In the metropolitan area, nine wells were sampled north and south of the Torrens River but never within 500 m of the river (to avoid sampling areas affected by river recharge). North of the river, wells were sampled from the Findon to Klemzig suburbs and, south of the river, from Millswood to Burnside. Samples were taken from the Quaternary aquifers (especially the Q1). Twelve wells were sampled in the Willunga Basin, including nine in the Port Willunga Formation and three in the Maslin Sands. In each area (Metropolitan and Willunga Basin), wells were pre-selected to cover the range in salinity found in the aquifers for the environmental tracers investigation (see section 3).

2.2.2 Seawater recirculation

A coastal dune and beach system at West Beach was selected for the seawater recycling field study because it was found during a preliminary assessment that it was a zone of mixing between fresh groundwater and seawater. The origin of the fresh groundwater is unclear but it is probably derived locally from recharge in the nearby sand dunes. The beachface was instrumented from the base of a sand dune to the low tide level with three wells and a series of drive point piezometres (Fig. 2.2).

Fig. 2.1. Location of groundwater bores sampled during the study.

The wells were used to measure the change in water table elevation during the day (i.e. from high to low tide on 18 November 2003), to collect large volume samples to characterise the environmental tracers signature of recirculated seawater and to provide an integrated estimate of beachface groundwater nutrient concentrations. The drive point sampler was used to collect more detailed vertical profiles of nutrient concentrations. The wells and the drive points were installed along parallel transects 10 m from one another to minimise interference. The wells were made of 5 cm ID PVC and the drive point of 12 mm OD stainless steel. Details about well and drive point construction and installation can be found in Lamontagne *et al*. (2003).

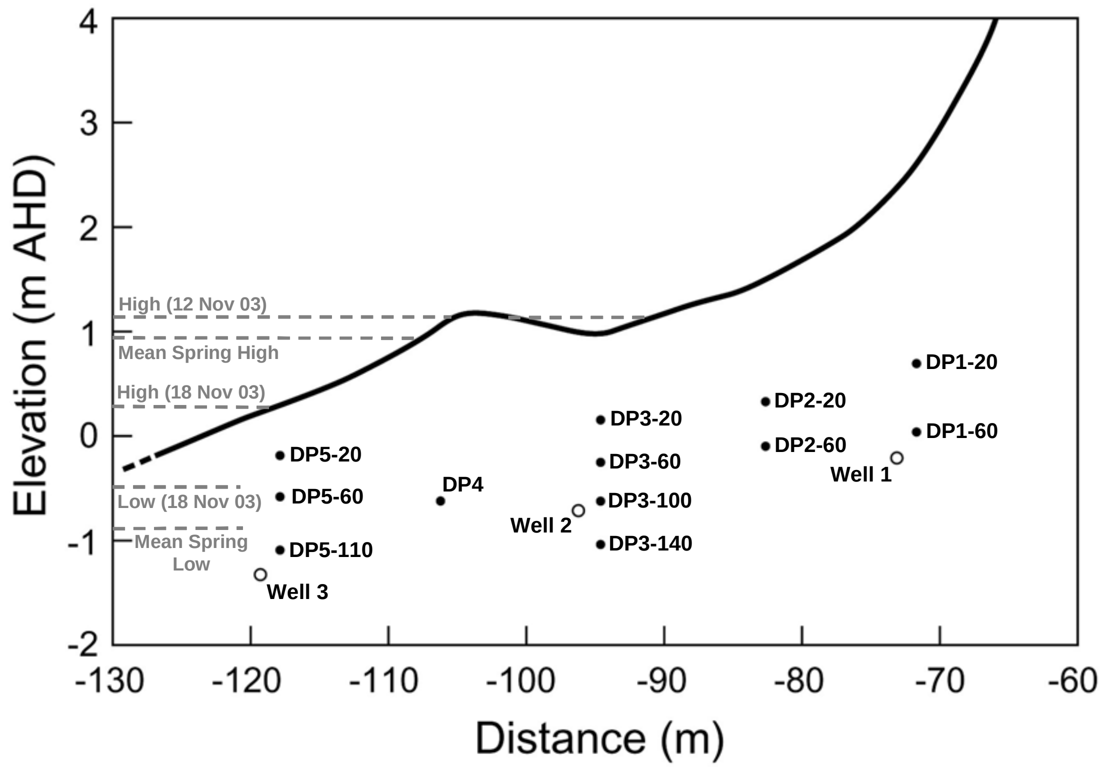

Fig. 2.2. Cross-section of the West Beach beachface transect sampled on 18 November 2003. Open circles are for the wells and closed circles represent drive points (with the number following the drive points the approximate distance from the water table in cm). Distances are in metres along a SW – NE transect perpendicular to the shoreline, with the SA Department of Lands Survey Mark 6528 2036 as the origin. Also indicated are representative tide heights (Port Adelaide Outer Harbour).

2.2.3 Groundwater sampling

Wells and drive points were flushed for three volumes prior to sample collection. For the beachface samples, electrical conductivity and pH were measured in the field using a WTW multimeter. For the regional groundwater samples, pH, Eh, temperature, EC and dissolved oxygen were measured using a flow through cell (FL90). The pH, temperature and EC were also double-checked with a portable meter. For Fe^{2+} analysis, a small subsample (~20 mL) was collected in a syringe with minimal exposure to the atmosphere and filtered on-line (with 0.45 μm Gelman Supor membranes) into a vial containing pre-prepared reagents (modified phenanthroline method from Hislop and Grace, Monash University, *pers. comm.*). The remaining samples were also filtered in the field and split into two subsamples. The subsample for NH_4^+ and total dissolved phosphorus (TDP) were acidified to pH < 2 with sulfuric acid and the subsample for dissolved organic carbon (DOC), NO_3^-, NO_2^-, total dissolved nitrogen (TDN) and filterable reactive phosphorus (FRP) analysis remained unacidified. All samples were stored in an ice chest and were later frozen until analysis. Alkalinity was measured in the field on filtered samples using a Hach field titrator. Samples for stable isotope of water were collected in gas-tight glass bottles with screw caps (McCartney bottles). Electrical conductivity was converted to total dissolved solids (TDS) using a relationship derived specifically for the meter and probe. Samples for radium isotope analysis (10 – 20 L) were collected in well-rinsed 20 L carboys. Samples for ^{222}Rn analyses were collected as described in Herczeg *et al*. (1994) for regional groundwater samples and Cook *et al*. (2003, 2004) for beachface groundwater and surf zone samples.

2.2.4 Analytical techniques

Nitrogen species, NO_3^-, NO_2^-, NH_4^+, total dissolved phosphorus and filterable reactive phosphorus were measured at the Environmental Health Laboratory, Flinders University, following American Public Health Association (1998). To account for the wide range of salinity encountered in the samples, standard lines were constructed for fresh water, sea water and a mix of fresh water and sea water in equal proportions. Indicative values for the slope of the standard lines are given in the table below (Table 2.1). The small differences observed between both the sea water and fresh water standards were taken into account when converting the absorbance to concentrations. Low detection limits (±25 μg L^{-1}) were achieved across the range of analyses. For each element, the analyses were done in triplicates on a single sample.

Table 2.1. Details of the analytical techniques used at the Environmental Health Laboratory, Flinders University for the analyses of the nitrogen species, total phosphorus and reactive filterable phosphorus.

Analyses	US Standard Methods	Variations from the methods	Standard line slope		Detection limit* (μg L^{-1})	Average Standard Deviation (at 25 μg L^{-1})
			Fresh Water	Sea Water		
NO_3^-	4500-NO3 UV Spectrometric screening method	1/10 of the recommended amount	1/3957	1/4123	25	6.5%
NO_2^-	4500-NO2 B Colorimetric Method	Colour reagent formulae and amounts of reagent added	1/339	1/402	25	1.4%
NH_4^+	4500-NH3 D Phenate Method	Amount of sample and reagent were halved	1/4785	1/3115	25	6.4%
TDP	4500-P B for sample preparation, and 4500-P D for PO4 determination	Ammonium persulphate 40% solution used not 0.04g powder	1/1822	1.2858	25	27%
FRP	4500-P D Stannous Chloride Method	None	1/1142	1/1424	25	11.1%

DOC and TDN were measured by combustion methods and infra red measurement of CO_2 (for DOC) or chemiluminescent measurement of NO (for TDN) at the CSIRO Analytical Laboratory, Waite Campus (Lamontagne *et al*. 2003). Dissolved organic nitrogen was calculated by difference between TDN and the inorganic N species. Stable isotope ratios in water samples (^2H:^1H and ^{18}O:^{16}O) were measured by mass spectrometry at CSIRO's Environmental Isotope Laboratory. Results are expressed in parts per thousand (‰) relative to the V-SMOW standard using the delta (δ) notation ($\delta_{sample} = [Ratio_{sample}/Ratio_{standard} - 1]\cdot 1000$).

2.3 *Results*

2.3.1 Regional groundwater

2.3.1.1 Metropolitan area

Salinity in the Q1 aquifer was generally fresh to brackish, ranging from 0.5 to 2.3 g L^{-1} (Table 2.2a). However, one sample from each of the Q1, Q2 and Q4 aquifers had salinities greater than 3.5 g L^{-1}. Isotopic signatures were relatively depleted ($\delta^{18}O$ = –5.1 to –3.5 ‰), suggesting that groundwater originated mainly from winter rainfall. A large range in DOC concentration was found, from 4 to 40 mg C L^{-1} (mean = 14 mg C L^{-1}). It is possible that the presence of methane in anoxic samples may have contributed to some of the high DOC values (A. Beech, CSIRO Land and Water, *pers. comm.*) The main form of N in groundwater was NO_3^-, ranging from 0.01 to 39 mg N L^{-1} (average = 6.8 mg N L^{-1}). The second most important form was DON, ranging from 0.1 to 1.5 mg N L^{-1}. The overall mean TDN concentration was 7.4 mg N L^{-1}. The predominance of oxidised N forms was consistent with the primarily oxic state of the aquifers (as inferred by low Fe^{2+} concentrations).

2.3.1.2 Willunga Basin

Salinity in the PWF ranged from fresh to saline (0.8 to 13 g L^{-1}) and from fresh to brackish (0.5 to 1.3 g L^{-1}) in the MS (Table 2.2b). Isotopic signatures were similar to the ones in the Quaternary aquifers in the Metropolitan Area. The range in DOC concentration was very large (range = 7 – 71 mg C L^{-1}; mean = 18 mg C L^{-1}) and may also indicate the presence of methane in some wells. However, nitrogen concentrations were lower than in the Quaternary aquifers (TDN = 1.6 mg N L^{-1}; range = <0.05 to 12 mg N L^{-1} for the PWF) with NO_3^- still as the predominant form present. In general, the PWF and the MS appeared in a more reduced state (i.e. richer in Fe^{2+}) than the Quaternary aquifers.

Table 2.2a. Water chemistry in the regional wells sampled during the ACWS study – Metropolitan area. Data in mg L^{-1} (of C, N or P) unless otherwise shown. * = detectable H_2S smell during sample collection

Sample Number	Forma-tion	Easting	Northing	Total Depth (m)	T (ºC)	TDS (g L^{-1})	pH	Alk (meq L^{-1})	$\delta^{18}O$ (‰ vs SMOW)	$\delta^{2}H$ (‰ vs SMOW)	DOC	TDN	DON	NO_3^- (µg L^{-1})	NO_2^- (µg L^{-1})	NH_4^+ (µg L^{-1})	TDP (µg L^{-1})	FRP (µg L^{-1})	Fe^{2+}
ACW 03 40	Q4	278155	6139441	52.50	22.0	3.6	7.2	6.06	-4.5	-24	5	<0.5	<0.3	161	0	0	9	3	0.3
ACW 03 43	Q1	278954	6137049	9.56	20.1	1.9	7.3	16.4	-3.8	-18	40	7.8	0.6	6990	2	230	61	41	<0.1*
ACW 03 44	Q2	283492	6138122	26.48	20.4	3.8	7.0	10.26	-4.1	-20	10	14	1.6	12810	24	1	104	63	<0.1
ACW 03 45	Q1	280055	6140046	7.00	20.9	6.7	7.2	18.48	-3.7	-20	21	<0.5	<0.1	425	2	94	73	72	1.1*
ACW 03 46	Q1	274578	6136025	9.00	19.6	2.3	7.1	6.70	-4.0	-19	7	11	1.3	9730	37	49	164	156	<0.1
ACW 03 47	Q1	273422	6134657	8.70	19.2	2.2	7.3	10.6	-3.5	-18	13	38	<0.1	39430	2	60	23	31	<0.1
ACW 03 48	Q1	285847	6131529	10.95	17.3	0.82	7.0	8.90	-4.7	-19	16	1.0	0.9	96	2	14	50	25	2.6*
ACW 03 49	Q1	283120	6127871	17.33	20.4	0.53	7.1	5.70	-5.1	-23	10	2.1	1.5	531	33	0	198	109	0.7*
ACW 03 50	Q1	279716	6129065	14.59	19.8	1.2	6.8	10.1	-3.9	-17	15	5.1	0.7	4380	0	0	5	15	<0.1

Table 2.2b. Water chemistry in regional groundwater collected during the ACWS study – Willunga Basin. Data in mg L^{-1} (in C, N or P) unless otherwise shown. * = H_2S smell during sample collection.

Sample Number	Formation	Easting	Northing	Total Depth	T	TDS	pH	Eh	Alk	$\delta^{18}O$	$\delta^{2}H$	DOC	TDN	DON	NO_3^-	NO_2^-	NH_4^+	TDP	FRP	Fe^{2+}
				(m)	(ºC)	(g L^{-1})		(mV)	(meq L^{-1})	(‰ vs SMOW)					(µg L^{-1})	(µg L^{-1})	(µg L^{-1})	(µg L^{-1})	(µg L^{-1})	
ACW 03 25	PWF	275801	6093894	139.00	21.8	0.81	6.8		6.46	-5.0	-24	10	<0.5	<0.4	102	3	32	20	15	<0.1
ACW 03 26	MS	275953	6099037	102.40	24.0	0.70	8.3		6.6	-4.8	-24	13	<0.5	<0.4	59	0	33	45	27	<0.1*
ACW 03 30	MS	283393	6096481	309.00	22.1	1.3	7.2	-119	7.66	-4.8	-23	13	<0.5	<0.3	178	2	0	13	12	1.3*
ACW 03 31	PWF	270377	6089956	53.30	22.3	1.9	8.9	-89	4.46	-4.8	-25	9	1.2	0.7	268	0	162	8	4	<0.1
ACW 03 32	PWF	268342	6089792	13.60	18.6	3.0	7.4		8.40	-4.7	-24	9	1.0	0.3	701	2	0	45	13	<0.1
ACW 03 33	PWF	268422	6088615	25.50	19.9	1.1	7.2		7.12	-4.9	-23	9	<0.5	<0.4	67	0	0	10	7	<0.1
ACW 03 34	PWF	280048	6098727	49.30	20.4	1.0	6.7	101	6.00	-5.0	-25	8	1.6	0.4	1139	9	75	33	17	<0.1
ACW 03 35	PWF	274669	6164137	23.43	19.0	2.0	7.1		8.08	-4.8	-24	7	<0.5	<0.4	52	0	0	10	14	<0.1
ACW 03 36	MS	283717	6105458	114.00	23.5	0.53	7.7	-121	4.86	-4.8	-24	35	<0.5	<0.2	2892	0	15	65	17	0.8
ACW 03 37	PWF	269531	6091665	17.11	20.9	4.2	7.5		13.1	-4.1	-19	71?	12	1.3	10574	18	236	55	42	<0.1
ACW 03 38	PWF	268979	6091009	17.18	20.1	10.1	7.0		19.7	-4.6	-21	41	0.7	0.2	364	3	148	17	43	0.1
ACW 03 39	PWF	268206	6090421	15.21	19.4	13.3	7.2		6.46	-4.4	-24	24	1.2	0.5	709	5	0	20	24	0.5

Table 2.3. Results of the chemical analyses on beachface groundwater samples (West Beach, 18 November 2003).

Sample Number			Sample Description	Depth	TDS	pH	Alk	$\delta^{18}O$	$\delta^{2}H$	DOC	TDN	DON	NO_3^-	NO_2^-	NH_4^+	TDP	FRP	Fe^{2+}
				(m below surface)	(g L^{-1})		(meq L^{-1})	(‰ V-SMOW)		(mg L^{-1})	(mg N L^{-1})	(mg N L^{-1})	(μg N L^{-1})	(μg N L^{-1})	(μg N L^{-1})	(μg L^{-1})	(μg L^{-1})	(mg L^{-1})
ACW	03	12	DP1-20	1.93	2.2	8.26	5.2			28	3.1	0.7	2298	0	24	102	104	<0.1
ACW	03	14	DP1-60	2.53	4.7	8.03	4.6			8	2.8	2.2	447	0	156	184	29	<0.1
ACW	03	4	DP2-20	1.17	14.3	8.03	3.3	-1.9	-10	13	4.9	1.2	3682	3	0	145	114	<0.1
ACW	03	9	DP2-60	1.57	15.9	8.05	3.7	-1.4	-7	16	4.3	1.3	2949	6	43	161	103	<0.1
ACW	03	2	DP3-20	0.80	39.2	7.92	2.0			26	0.8	<0.1	795	1	19	174	119	<0.1
ACW	03	3	DP3-60	1.20	31	8.16	2.5			9	2.0	0.3	1639	1	30	71	60	<0.1
ACW	03	5	DP3-100	1.60	26.9	7.9	2.9	-0.5	0	9	2.2	0.4	1782	0	1	199	96	<0.1
ACW	03	10	DP3-140	2.00	30	8.08	3.1	0.1	2	13	1.8	0.2	1567	1	104	224	90	<0.1
ACW	03	18	DP4-100	1.65	39.6	7.96	2.9			8	<0.5	<0.1	485	6	95	126	77	<0.1
ACW	03	11	DP5-20	0.45	39.3	7.9	2.0	1.2	9	12	0.5	<0.1	590	3	14	127	72	<0.1
ACW	03	13	DP5-60	0.85	37.9	7.95	2.4	1.3	8	11	0.6	<0.1	484	0	63	187	87	<0.1
ACW	03	19	DP5-110	1.35	39.2	7.99	2.4			8	0.6	<0.1	488	0	191	139	76	<0.1
ACW	03	8	Well 1	2.79	0.87	7.91	4.7	-3.3	-35	9	8.7	1.1	7249	366	0	96	96	<0.1
ACW	03	7	Well 2	1.67	36.5	7.83	2.3	0.6	11	6	1.4	0.1	1272	3	19	320	163	<0.1
ACW	03	6	Well 3	1.49	38.5	7.67	2.2	1.1	16	10	<0.5	<0.1	485	0	63	153	116	0.2
ACW	03	1	Seawater		38.3	8.31	2.3			6	<0.5	<0.1	393	3	14	26	18	<0.1

2.3.2 Beachface transect

Total dissolved solids at the beachface transect ranged from 0.87 to 39.5 g L^{-1} showing mixing between relatively fresh groundwater and seawater (38 g L^{-1}). The transition between seawater and fresh groundwater appears in the vicinity of drive point DP3 (Fig. 2.3), near the level of a recent large high tide mark (Fig. 2.2). Similarly, the stable isotopes of water ranged from a relatively depleted signature (–3.3 and –35‰ in ^{18}O and ^{2}H respectively) to a signature slightly more enriched than the SMOW (+1.3 and +16‰ in ^{18}O and ^{2}H respectively) consistent with partially evaporated seawater. A graph of oxygen-18 versus TDS shows a straight mixing line between the dune end-member (Well 1) and seawater, suggesting mixing between these two sources of water (Fig. 2.4). The signature of the coastal aquifer groundwater being slightly more depleted in stable isotope (–3.5 to –4‰ in oxygen-18) with a similar TDS suggests little influence from the inland groundwater on the beach groundwater system.

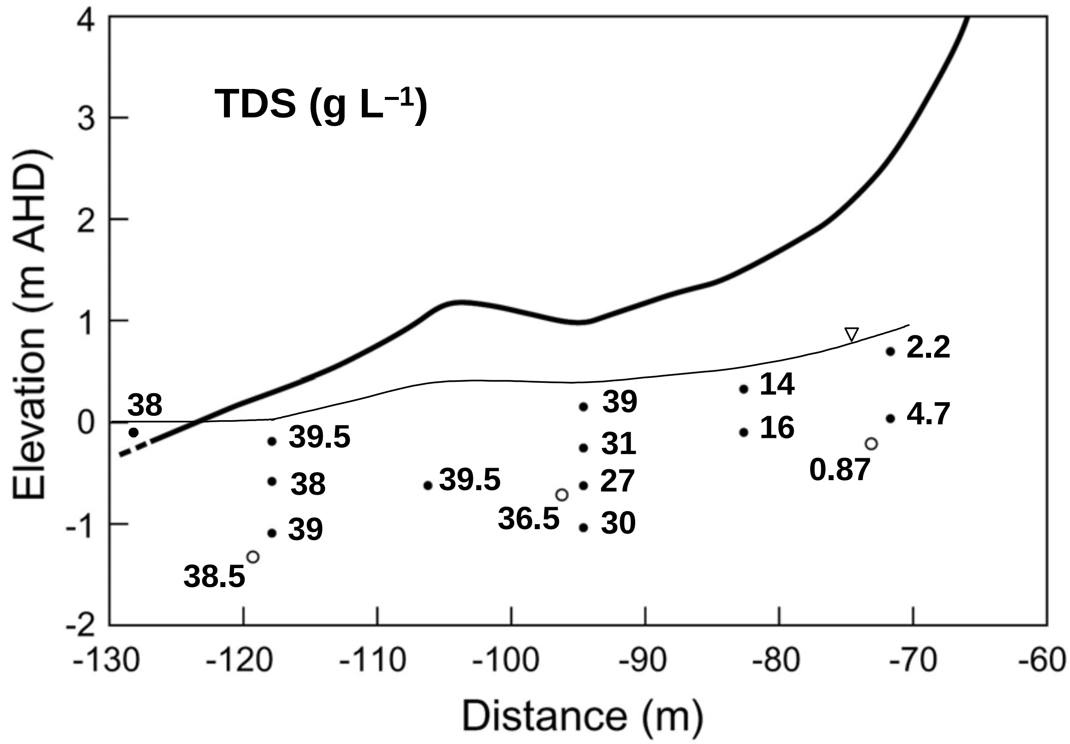

Fig. 2.3. Salinity (as TDS) along the West Beach beachface cross-section. The inverted triangle shows the position of the water table.

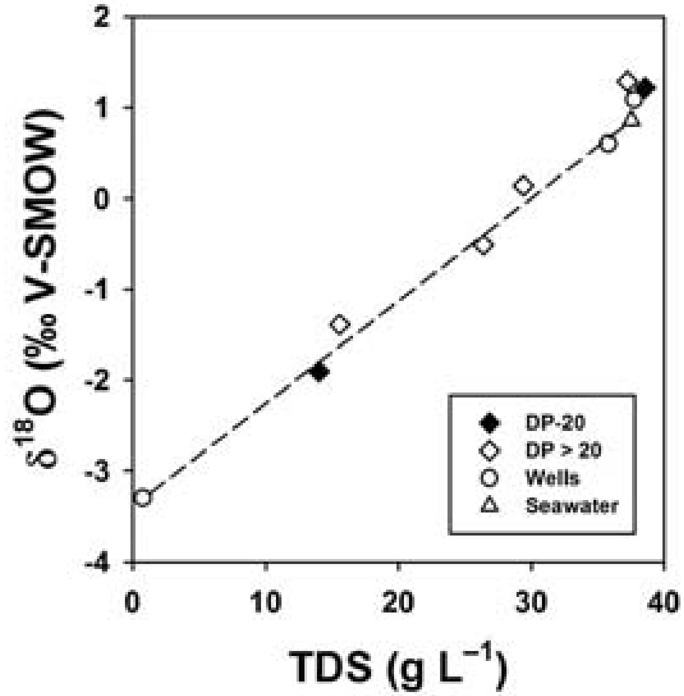

Fig. 2.4. $\delta^{18}O$ versus salinity (as TDS) for beachface groundwater samples. The dashed line represents a mixing line between the freshwater end-member (as represented by Well 1) and seawater.

Dissolved Organic Carbon shows high concentrations just below the water table, ranging from 28 mg C L^{-1} near the dune to 12 mg C L^{-1} next to the sea. Lower concentrations were observed further at depth, ranging between 6 to 13 mg C L^{-1} (Fig. 2.5). While seawater DOC is 6 mg C L^{-1}, DOC concentrations in beachface groundwater near the sea are slightly higher, ranging from 8 to 12 mg C L^{-1} in DP5 and Well 3.

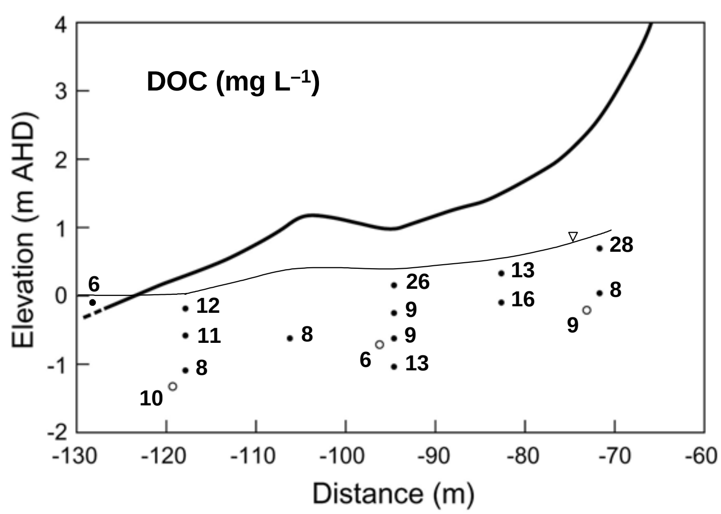

Fig. 2.5. DOC concentration along the beachface cross-section.

Total dissolved N ranged between 0.5 to 9 mg N L^{-1} in most of the beach groundwater samples but was below detection limit in seawater, Well 3 and DP4 (Table 2.3). The highest TDN concentrations (between 2 and 9 mg N L^{-1}) were found in the freshwater samples. The high TDN concentrations were mostly due to elevated concentrations of NO_3^- (Fig. 2.6). Measurable concentrations of NO_2^- were also found in several wells (Fig. 2.6) but Fe^{2+} was undetectable in all but in Well 3 (Table 2.2), indicating that the redox environment in the aquifer was oxic to sub-oxic. DON concentration was 0.7 – 2.2 mg N L^{-1} in the freshwater samples but was generally below detection limit in saline groundwater (Fig. 2.7). NH_4^+ concentrations ranged from <1 to 191 μg N L^{-1} and tended to increase with depth (Fig 2.8).

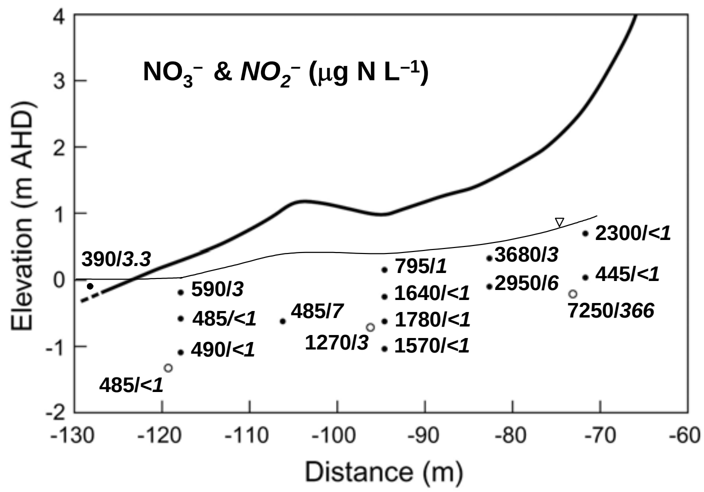

Fig 2.6. NO_3^- and NO_2^- concentrations in beachface groundwater.

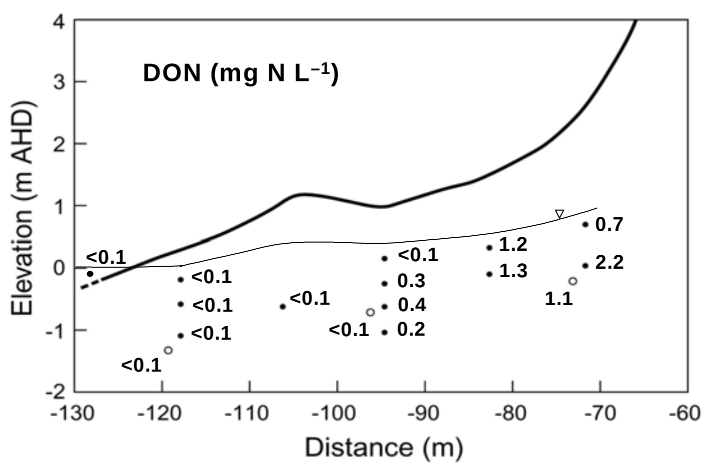

Fig. 2.7. DON concentration in beachface groundwater.

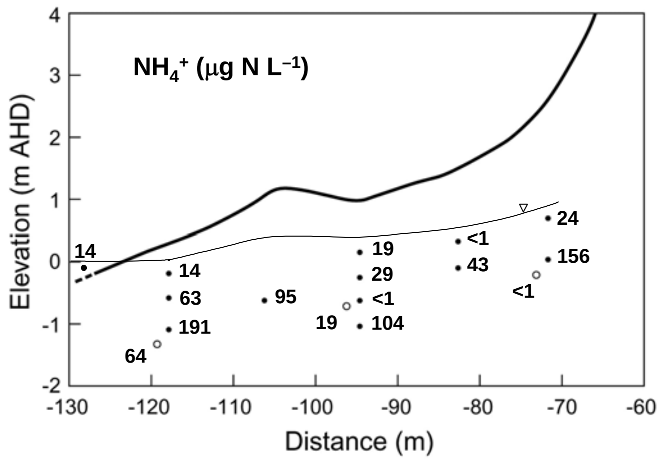

Fig. 2.8. NH_4^+ concentration in beachface groundwater.

Total Dissolved P (TDP) and Filterable Reactive P (FRP) were elevated in all groundwater samples relative to seawater (Fig. 2.9 and Fig. 2.10), with the FRP fraction usually representing more than 50% of the TDP pool. There was no obvious pattern in the distribution of FRP and TDN as a function of depth or salinity.

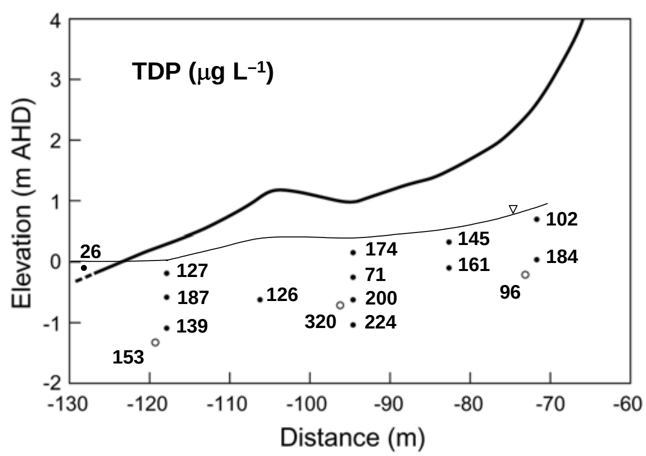

Fig. 2.9. TDP concentration in beachface groundwater.

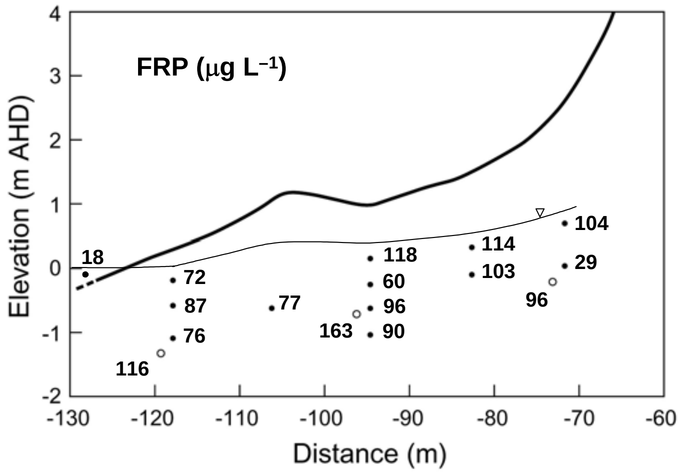

Fig. 2.10. FRP concentration in beachface groundwater.

2.3.3 Recirculated seawater discharge rate

The volume of recirculated seawater discharged from the beachface was approximated by using the volume of beachface sand dewatered during the 18 November 2003 falling tide along the transect (Fig. 2.11). The volume dewatered over the half tide cycle was ~4.4 m^3 per metre of beachface. Assuming complete dewatering and a porosity of 0.3, this would represent a volume of 1.3 m^3 m^{-1}. This is probably an underestimate for an average tide because the tide amplitude was only 0.75 m on 18 November 2003, relative to ~1.5 m on average during spring in this area. Assuming a linear relationship between tide amplitude and the volume of seawater recirculation (that is 1.7 m^3 (m tide)$^{-1}$ (m beach)$^{-1}$), the average recirculation rate would be: 1.5 m tide^{-1} * 2 tides d^{-1} * 1.7 m^3 (m tide)$^{-1}$ (m beach)$^{-1}$ = ~5 m^3 m^{-1} d^{-1}.

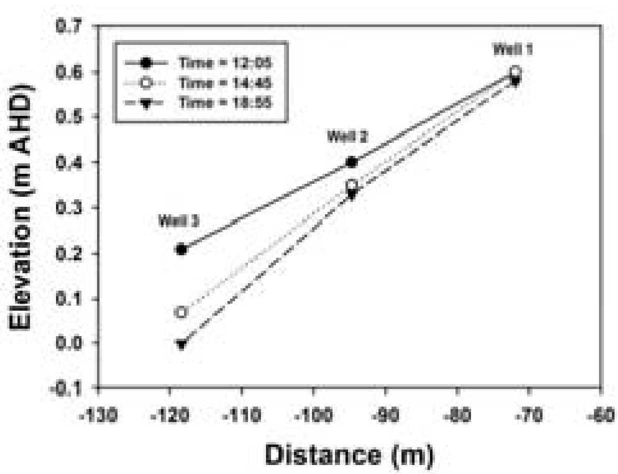

Fig. 2.11. Change in water table elevation during the 18 November 2003 falling tide at West Beach.

2.4 *Discussion*

2.4.1 Groundwater nitrogen concentrations

Nitrogen concentrations in groundwater and recirculated seawater were more elevated than in seawater. Groundwater from the Quaternary aquifers had the highest NO_3^- concentrations (average NO_3^- = 6.8 mg N L^{-1}). However, a larger bore survey by Dillon *et al*. (1995) found that the average NO_3^- concentrations in the upper Quaternary aquifers was 11.8 mg N L^{-1} in the metropolitan Adelaide area. The discrepancies between the two studies are not unexpected due to the large variability in NO_3^- concentrations across the aquifers. The NO_3^- concentration found in beach dune groundwater at West Beach (7.2 mg N L^{-1}) is also within the range found in similar dune systems on the LeFevre Peninsula (i.e., near Semaphore) by Dillon *et al*. (1995).

It is unclear why groundwater nitrogen concentrations were lower in the Willunga Basin relative to the metropolitan Adelaide area. While population density is lower in the Willunga Basin, the N loading rate in recharge could still be high due to the high proportion of agricultural land-use in the area (vineyards, orchards, etc). However, it should be stressed here that N concentration in groundwater is not static but tends to adjust slowly (often at the scale of decades and centuries) to changes in land-use (Lamontagne 2002). Because of longer water residence times, NO_3^- concentration in larger aquifers tends to adjust more slowly to changes in land-use. Thus, lower N concentrations in the Willunga Basin could represent some combination of lower historical NO_3^- loading rates relative to the metropolitan Quaternary aquifers and a longer water residence time (a longer time required to adjust to the modern land-use).

The potential to attenuate NO_3^- is likely to vary between aquifers. The "attenuation" of NO_3^- occurs when plants or microorganisms consume or transform NO_3^- into other N forms. Potential mechanisms of NO_3^- attenuation in regional aquifers include assimilatory reduction by microorganisms, dissimilatory reduction to NH_4^+ and denitrification. Denitrification is often considered the "favoured" form of attenuation because N is converted to essentially non-available forms of N (N_2O and N_2 gases), whereas N is converted into other biologically available N forms with the other processes. Denitrification is promoted when sufficient quantities of reductants are present in the aquifer to generate sub-oxic conditions (i.e. oxygen concentrations <1 mg L^{-1}). Such reductants include: 1) high concentrations of labile DOC in groundwater (Starr and Gillham 1993), 2) buried organic matter deposits (Hill *et al*. 2000) and 3) reduced minerals such as pyrite (Böhlke *et al*. 2002). Measurable concentrations of Fe^{2+} (representative of sub-oxic to anoxic conditions; Lamontagne *et al*. 2005) in some bores indicate that at least parts of the Quaternary, PWF and MS aquifers have a potential for denitrification. However, rates of denitrification in the Quaternary or the Willunga Basin aquifers are currently not known.

2.4.2 Beachface biogeochemical cycling

It is possible to infer whether nutrients are gained or lost through biogeochemical processes in beachface groundwater by comparing the changes in concentrations relative to the ones expected from mixing alone between different sources (Ullman *et al*. 2003). In the West Beach system, fresh groundwater (as represented by Well 1) and seawater are the most likely sources of water for beachface groundwater. In general, the patterns relative to the mixing line suggest that DOC, TDP and NH_4^+ are gained during the mixing process and that NO_3^- is lost (Fig. 2.12). This is inferred from DOC, TDP and NH_4^+ concentrations generally falling above the mixing lines while NO_3^- concentrations are falling below (Ullman *et al.* 2003). Such patterns in nutrient concentration would be expected from the decomposition of organic matter in a sub-oxic aquifer. Under low O_2 conditions, N mineralisation stops at the NH_4^+ stage, NO_3^- can be lost through denitrification and PO_4^{3-} tends to be released from the weathering of iron oxides (Baldwin and Mitchell 2000). Similarly, both Hill *et al*. (2000) and Ueda *et al*. (2003) found that active zones of NO_3^- removal in shallow aquifers were associated with the presence of buried organic matter depsoits. In the ACWS area, seagrass and macroalgae litter is common on beaches and can occasionally be found as buried deposits within beach sands. However, the exact nature of the burried organic matter in ACWS beaches is still to be determined.

A closer inspection of the vertical concentration profiles also suggests that a third source of water may contribute to the beachface groundwater pool. Most shallow drive point samples (i.e., 20 cm below the water table) had high DOC concentrations relative to samples at greater depths (Fig. 2.12). This suggests that vertical recharge (induced by large tides or rainfall) also contributes DOC and possibly nutrients to the groundwater pool. While DOC usually does not travel far in the unsaturated zone (Kalbitz *et al*. 2000), high rate of DOC recharge have been observed in sandy aquifers with shallow (<3 m) water tables (Starr and Gillham 1993; Pabich *et al*. 2001). Alternatively, the movement of the water table during tide cycles could also flush the unsaturated zone of DOC-rich porewaters. The source for the DOC is not clear. However, the decomposition of seagrass and macroalgal litter could be one potential source. By maintaining well oxygenated and wet conditions, a fluctuating water table would provide an ideal environment to promote organic matter decomposition and DOC generation (Belyea 1996). Alternatively, exudates from intertidal benthic diatoms (Daborn *et al*. 1993 and terrestrial litter (Ueda *et al*. 2003) could also contribute to the groundwater DOC pool.

Overall, the presence of high DOC concentrations in beachface groundwater indicates that a potential exists to fuel biogeochemical processes during the discharge of groundwater to the sea from the unconfined aquifer. In the oceanic environment, this potential will be magnified by the presence of strong density gradients, which will tend to force fresh groundwater to discharge close to the shoreline across the beachface (Slomp and van Cappellan 2004). On one hand, the mixing of DOC-rich beach groundwater with fresh groundwater may promote N removal through denitrification. On the other hand, organic N tends to be recycled as NH_4^+ by decomposition and P (another potentially limiting nutrient for algal growth) tends to be found at higher concentrations in more anoxic groundwater. Although not measured here, silica (a limiting nutrient for diatom growth) would also be expected to increase in concentration during transit through the beachface zone.

The recirculated seawater discharge rate estimated here (~5 $m^3\ m^{-1}\ d^{-1}$) is consistent with values found elsewhere. For example, Ullman *et al*. (2003) measured recirculation rates by tidal pumping ranging between 4.8 to 6.1 $m^3\ m^{-1}\ d^{-1}$ for a sandy beachface in Delaware and Webster *et al*. (1994) found 4.3 $m^3\ m^{-1}$ per side of the Bega Estuary in SE Australia. A better estimate of the seawater recirculation rate at West Beach could be obtained by measurements of the variability in the water table for the range in tide amplitudes at this site, by measurements of the beach sand porosity and by measurements of the residual water content following dewatering. When combined with a representative estimate of TDN concentration in recirculated seawater (~1 mg N L^{-1}), the annual recycling of N through tidal pumping (220,000 kg N $year^{-1}$) appears to be a significant source of N to the ACWS area (see Section 3).

2.4.3 Implications for nutrient input estimates to the ACWS area

Nitrogen concentration in regional groundwater is elevated relative to seawater, which can make this source a significant load of N, even if a small source of water, to the coastal zone. The beachface study has also demonstrated a significant potential for the transformation of nutrients during transit between groundwater and the sea. The net result for N loading is unclear because while some forms may be lost during the transit (especially NO_3^-) other N forms may be gained. The maximum reduction in N loading will occur if the principal attenuation process for NO_3^- is denitrification, but this still needs to be demonstrated.

The beachface study has also hinted that the input of organic matter through seagrass and macroalgal litter may indirectly foster N attenuation at the beachface. Presumably, the greater the accumulation of seagrass litter in beach sands, the more likely that the geochemical environment will be made suitable for NO_3^- attenuation. This hypothesis should be tested with repeated sampling of a beachface profile over a year, especially before and after periods when seagrasses accumulate along the shoreline following storms.

While stormwater runoff (a potentially important source of N) occurs in winter, algal blooms in the ACWS area tend to occur in summer. Some of the nutrients added to the coastal zone as particulate organic matter in stormwater in winter could be stored in beach sands and recycled during summer, when temperatures are warmer. Even if groundwater discharge is small or absent, seawater recirculation would provide the mechanism to return regenerated nutrients in beachface groundwater to the coastal zone. This hypothesis could be tested by comparing nutrient concentration and the geochemical environment in beachface groundwater in beach sections near and further from stormwater discharge points.

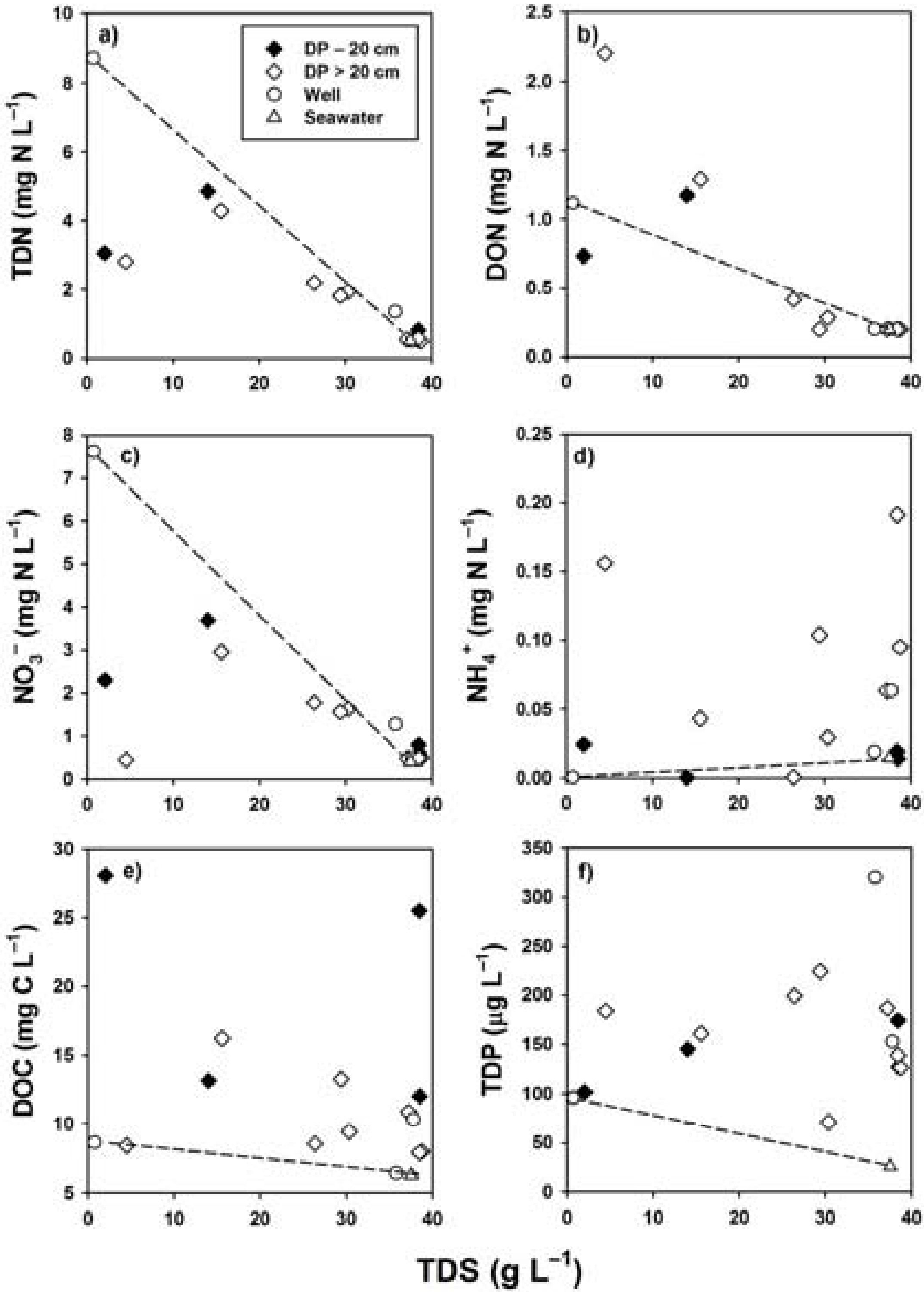

Fig. 2.12. Changes in nutrient concentration in beachface groundwater as a function of groundwater salinity. The dashed line represents the expected concentration for mixing between fresh groundwater (as represented by Well 1) and seawater.

3 Groundwater flux estimates using environmental tracers

Environmental tracers are increasingly used to estimate groundwater discharge to coastal areas (Bugna *et al*. 1996; Cable *et al*. 1996a,b; Moore 1996; Rama and Moore 1996; Osmond and Cowart 2000). While a variety of tracers have been used, the four radioisotope of radium (the "radium quartet") and ^{222}Rn (a naturally occurring radioactive gas) currently appear the most versatile. Both the radium quartet and ^{222}Rn originate from the decay of uranium and thorium radioisotopes that are present in most rocks. Due to a greater contact time with geologic material, groundwater tends to be enriched in these tracers relative to surface water. Environmental tracers have a number of advantages over flow net analysis to estimate groundwater discharge to the ocean. Flow net estimates of groundwater discharge require precise knowledge of the hydraulic gradient and the hydraulic conductivity of geological materials at the land-sea interface. The presence of strong density gradients between fresh and salt waters also complicates the application of flow net analyses. The main advantage of environmental tracers is that they integrate groundwater discharge over large areas and they provide an independent estimate of groundwater discharge against which flow net estimates can be compared.

The use of the radium quartet offers another advantage in that it can be used to estimate both the groundwater and the recirculated seawater input rate to coastal areas (Boehm *et al*. 2004). "Recirculated seawater" is ocean water that moves in and out of sediments and beachfaces by waves, currents and tidal action. Because of active biogeochemical cycling at the interface between sediments and seawater (Ullman *et al*. 2003), recirculated seawater can be a significant source of nutrients to coastal areas (Section 2). It is possible to distinguish between groundwater and recirculated seawater input rates to coastal areas by comparing the trends in the short- and long-lived radioisotopes of Ra in seawater. Because the exposure of recirculated seawater to geologic material is much shorter (hours to days), it tends to be more enriched in the short-lived ^{223}Ra (half-life = 11.4 days) and ^{224}Ra (half-life = 3.6 days) relative to the long-lived ^{226}Ra (half life = 1600 years) and ^{228}Ra (half-life = 5.7 years). In contrast, the longer exposure of regional groundwater to aquifer material (years to millenia) makes this source more enriched in longer-lived isotopes.

One confounding factor in the use of the radium quartet is the effect of salinity changes on the activity of the radioisotopes in groundwater. Radium is a cation with similar properties to calcium. As for cations in most geologic material, much of the "pool" of radium isotopes will be located on exchange sites rather than freely dissolved in water. However, because of competition with Na^+ and other ions for the exchange sites, a greater proportion of the radium isotopes will tend to be in pore water at higher salinities. In practical terms, this means that when salinity is increasing in an aquifer (from pollution, seawater intrusions, etc) the Ra isotope activity in groundwater will increase as well.

To complement the flow net component of Subprogram 3, a study was undertaken to evaluate 1) which environmental tracers appear most useful to measure groundwater discharge in this environment and 2) if possible, estimate the input of groundwater and recirculated seawater to the study area. To characterise the signature of the radium quartet and of ^{222}Rn in groundwater and recirculated seawater, a survey was first made of the activity of these tracers in regional groundwater and beachface groundwater (see also Section 2). This was combined with measurements of temperature, salinity, the radium quartet and ^{222}Rn in seawater at two onshore – offshore transects in the study area.

3.1 *Methods*

3.1.1 Bore sampling

Sampling for environmental tracers in groundwater was made in a subset of the bores sampled for N concentration in the regional survey. Five bores were sampled from the Quaternary aquifers (four in the Q1 and one in the Q4) in the Metropolitan Adelaide area, and six from the Port Willunga Formation and three from the Maslin Sands Formation in the Willunga Basin. The bores were selected to cover the range in salinities found in each aquifer. Details about bore location and sampling methods are found in Section 2.

3.1.2 Beachface study

The environmental tracer signature in recirculated seawater was measured by sampling beachface groundwater at two sites located in the vicinity of the offshore transects. Groundwater was sampled at each site along a transect spanning the edge of the beach at low tide to the base of a dune above high tide level (West Beach - Northern transect; see also Section 2) or the base of a cliff (Port Willunga - Southern transect; Fig. 3.1). Groundwater was sampled by installing three wells at equidistant locations along each transect with the aim to capture the whole gradient in salinity present at each site. At the Southern Transect, groundwater had seawater-like salinities throughout the beachface, with the exception of one small spring discharge with a lower salinity at the base of a cliff (15.6 mS cm^{-1}) The wells (5 cm ID PVC) had a 30 cm screened interval installed 0.5 to 1 m below the water table. The wells were flushed for a minimum of three well volumes before they were sampled for EC, pH, major ions, nutrients, Fe^{2+} and environmental tracers (see more details in Section 2).

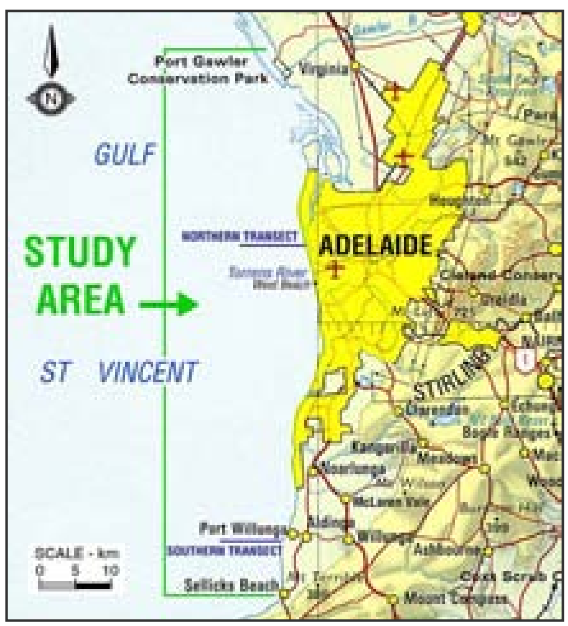

Fig 3.1. Location of the Northern and Southern offshore transects sampled for environmental tracers in seawater. Also shown is the location of the two beach sites (West Beach and Port Willunga) used to characterise the tracer signature of recirculated seawater. The Northern Transect is off Henley Beach Jetty and the Southern Transect is off Blanche Point.

3.1.3 Offshore transects

Seawater samples were collected during two cruises on the Flinders University Research Launch “Hero”. On the first cruise (4 November 03), 11 samples were taken along an offshore transect in the northern section of the ACWS area, near Henley Beach Jetty (“Northern Transect”; Lat = –34°55’; Fig. 3.1). On the second cruise (26 November 03), 12 samples were collected along a transect in the southern end of the study area (“Southern Transect”; Lat = –35°16’) near Port Willunga. The timing of the sampling (end of spring) should have coincided with the period of greatest groundwater discharge to the ACWS area (i.e. water tables tend to be highest in the region during that period). Along each transect, samples were taken following a “logarithmic” design with samples taken more frequently closer to the shoreline (every 100 to 200 metres) than offshore (every 1 to 2 km). At each sampling station, vertical profiles for salinity, turbidity and temperature were taken at every metre (Northern Transect) or two metres (Southern Transect). Samples for environmental tracers were collected 1 m below the surface using a bilge pump fitted with a filter to remove large particles (>1 mm). For radium isotopes, 40 L was collected for “inshore” samples (≤5 km) and 80 L for “offshore” samples (>5 km) and stored in 20-L carboys. Radon-222 was concentrated in a mineral oil cocktail from 1-L samples immediately following collection using the method outlined in Cook *et al*. (2003).

3.1.4 Radium quartet and radon analyses

Rn-222 samples were analysed by liquid scintillation in a LKB Quantullus counter using the pulse shape program to discriminate between alpha and beta decay (Herczeg *et al*. 1994). Radium isotopes were quantitatively extracted from water samples using MnO coated acrylic fibres (“MnO fibres”). Samples were gravity-fed through columns containing a glassfiber wool plug to remove small particles (which was periodically replaced) and between 2.0 to 3.5 g of MnO fibres (Moore 1976) depending on sample volume (more for the larger volume samples). Filtration rates ranged between 2 to 6 L h^{-1}. Once samples were filtered, they were backflushed with distilled water to remove the remaining seawater, tightly packed, and sent to CSIRO’s laboratories in Canberra to measure Ra activity. Removal efficiency (assessed by reprocessing filtered samples) ranged between 95 and 99%. The maximum time span between sample collection and the beginning of counting for ^{223}Ra, ^{224}Ra and ^{222}Rn activities was less than 3 days.

Measurements of the activity of short-lived Ra isotopes (^{223}Ra and ^{224}Ra) were made by partially drying the MnO fibres and placing them in an air circulation system described by Moore and Arnold (1996). Gaseous ^{219}Rn and ^{220}Rn, formed by the decay of ^{223}Ra and ^{224}Ra, was flushed from the MnO fibres into a scintillation cell where alpha particles from the decay of Rn and its daughters were detected by a photomultiplier tube, and identified using a delayed coincidence system. The counting efficiency of the system was determined using MnO fibres containing known activities of ^{223}Ra and ^{224}Ra in secular equilibrium with their parents ^{232}Th and ^{227}Ac.

The long-lived isotopes, ^{226}Ra and ^{228}Ra, were determined by alpha spectrometry following radiochemical separation (Hancock and Martin 1991). After the addition of a yield tracer (^{225}Ra in equilibrium with its parent ^{229}Th) the fibres were leached with hot 5 M HCl to remove Ra. The solution was then purified by co-precipitation and ion-exchange techniques. The purified solution was electroplated onto a stainless steel disc and ^{226}Ra determined by high-resolution alpha-particle spectrometry. The disc was recounted about 6 months later, and ^{228}Ra was determined via ingrowth of its alpha-emitting daughter, ^{228}Th.

3.1.5 Estimation of groundwater discharge

The magnitude of groundwater discharge along the coastline (including both groundwater and recirculated seawater) can be measured using the patterns in radium isotope activity with distance offshore. The pattern in radium activity (A) over time (t) and distance offshore (x) may be expressed as a balance between advection and diffusion (Moore 2000). Assuming that net advection offshore can be neglected, the offshore transport of radium will be primarily through diffusive processes:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = K_{\mathrm{H}} \frac{\partial^2 A}{\partial x^2} - \lambda A \tag{3.1}$$

where K_{H} is the eddy diffusion coefficient and λ the decay constant for a given radium isotope (at the timescales of coastal transport processes, the last term can be neglected for the longer-lived ^{228}Ra and ^{226}Ra; Moore 2000). For the boundary conditions:

$A = A_i$ at $x = 0$,

$A \rightarrow 0$ at $x \rightarrow \infty$

If K_{H} is constant and the system is at steady state the activity of Ra isotopes with distance offshore is approximated by:

$$A_x = A_0 \exp\left[-x\sqrt{\frac{\lambda}{K_{\mathrm{H}}}}\right], \tag{3.2}$$

where A_x the activity at distance x offshore and A_0 the activity at distance 0 from the coast. A plot of ln ^{223}Ra or ln ^{224}Ra as a function of the distance from the coast can be used to estimate K_{H}. In this case, the slope,

$$m = \sqrt{\frac{\lambda}{K_{\mathrm{H}}}}. \tag{3.3}$$

The estimates of K_{H} obtained with the short-lived isotopes can be used to calculate the total offshore flux (J_{total}) of the longer-lived isotopes using:

$$J_{total} = -K_{\mathrm{H}} i z, \tag{3.4}$$

where J_{total} is the flux of ^{226}Ra or ^{228}Ra (in Bq d^{-1} per m of shoreline), i the slope of ^{226}Ra or ^{228}Ra activity over distance from the shoreline, and z the depth of the transect.

This flux of radium would represent the sum of all inputs along the shoreline, including regional groundwater (J_{gw}) and recirculated seawater (J_{rsw}). Recirculated seawater itself will be the combination of exchanges along beachfaces (J_{beach}) and exchange with the seafloor (J_{sf}). Thus,

$$J_{\mathrm{total}} = J_{\mathrm{gw}} + J_{\mathrm{rsw}} \quad (3.5)$$

and

$$J_{\mathrm{rsw}} = J_{\mathrm{beach}} + J_{\mathrm{sf}} \quad (3.6)$$

The volumetric fluxes from a particular source can be estimated by dividing the Ra flux due to that source by the Ra activity in the source. For example, in the case of regional groundwater:

$$Q_{\mathrm{gw}} = J_{\mathrm{gw}} / A_{\mathrm{gw}} \quad (3.7).$$

3.2 *Results*

3.2.1 Regional groundwater and beachface groundwater signatures

A wide range in Ra isotope and ^{222}Rn activity was found in beachface groundwater and in regional groundwater samples taken in the vicinity of the ACWS area (Table 3.1). In general, the range in ^{223}Ra and ^{224}Ra activities overlapped between geological formations. However, ^{226}Ra and ^{222}Rn activities tended to be lower in beachface groundwater (0.32 – 5.3 mBq L^{-1} and 0.59 – 2.1 Bq L^{-1}, respectively) relative to regional groundwater (3.0 – 207 mBq L^{-1} and 2.1 – 59 Bq L^{-1}, respectively). The Port Willunga Formation had the highest and widest range in activities for all isotopes.

Within geological formations, a part of the variability in Ra activity was related to salinity (Figs. 3.2 and 3.3). The activity of the short-lived Ra isotopes was positively related to TDS in beachface porewater and in the Quaternary aquifers but not in the Port Willunga Formation or the Maslin Sands. For example, in beachface porewater, ^{223}Ra activity varied from 0.42 mBq L^{-1} at TDS = 0.87 g L^{-1} to 6.6 mBq L^{-1} at TDS = 38.5 g L^{-1}. Similarly, ^{226}Ra activities also increased from 0.32 to 5.3 mBq L^{-1} along the same salinity gradient. Rn-222 activity was unrelated to salinity (Fig. 3.2c-d).

Overall, there were notable differences in the signature for several potential tracers between regional groundwater and recirculated seawater (as inferred from beachface porewater samples with TDS > 20 g L^{-1}; Table 3.2). Recirculated seawater was more saline and more depleted in ^{226}Ra, ^{228}Ra and ^{222}Rn relative to regional groundwater but had relatively high ^{223}Ra and ^{224}Ra activities. However, due to a large natural variability in radium and radon activity in some of the aquifers (such as the PWF), a larger number of wells will be required to precisely define the signature for some of the regional aquifers.

Table 3.1. Activities of the radium quartet and of ^{222}Rn in regional groundwater and beachface groundwater in the vicinity of the ACWS area. Mean ± SE.

	^{223}Ra (mBq L^{-1})	^{224}Ra (mBq L^{-1})	^{226}Ra (mBq L^{-1})	^{228}Ra (mBq L^{-1})	^{222}Rn (Bq L^{-1})
Beachface					
North 1	0.42 ± 0.04	5.3 ± 0.2	0.32 ± 0.02	3.3 ± 0.25	0.59 ± 0.010
North 2	5.4 ± 0.33	74 ± 1.4	2.8 ± 0.17	24 ± 1.5	0.69 ± 0.012
North 3	6.6 ± 0.44	106 ± 1.9	3.3 ± 0.08	33 ± 1.4	1.02 ± 0.017
South 1	4.9 ± 0.32	89 ± 1.8	5.3 ± 0.28	21 ± 1.1	1.17 ± 0.020
South 2	5.2 ± 0.29	72 ± 1.3	4.1 ± 0.15	15 ± 0.6	1.09 ± 0.018
South 3	1.1 ± 0.11	18 ± 0.6	2.4 ± 0.14	4.3 ± 0.45	2.14 ± 0.036
Quaternary (Q1)					
ACW0340*	3.4 ± 0.27	106 ± 1.6	23 ± 0.8	99 ± 3.5	12.3 ± 0.28
ACW0345	2.0 ± 0.19	62 ± 1.3	22 ± 0.8	54 ± 2.5	26.2 ± 0.60
ACW0347	1.3 ± 0.18	30 ± 1.1	9 ± 0.5	25 ± 1.3	7.0 ± 0.16
ACW0349	0.39 ± 0.044	7.3 ± 0.23	3.6 ± 0.35	7.8 ± 0.77	25.8 ± 0.59
ACW0350	0.93 ± 0.14	23 ± 0.9	12 ± 0.6	39 ± 3.4	19.8 ± 0.45
Port Willunga Formation					
ACW0325	5.2 ± 0.36	22 ± 0.9	56 ± 2.5	14 ± 0.9	37.5 ± 0.54
ACW0339	5.6 ± 0.58	326 ± 6	71 ± 2.8	359 ± 12	17.5 ± 0.40
ACW0331	0.32 ± 0.060	8.4 ± 0.45	5.7 ± 0.26	6.0 ± 0.37	2.1 ± 0.09
ACW0333	0.44 ± 0.059	19 ± 0.7	5.5 ± 0.28	11 ± 0.9	5.7 ± 0.14
ACW0334	18 ± 1.3	342 ± 6	207 ± 20	137 ± 17	23.8 ± 0.55
ACW0335	5.9 ± 0.45	74 ± 1.8	28 ± 1.2	53 ± 2.1	58.9 ± 1.3
Maslin Sands					
ACW0326	0.59 ± 0.059	9.2 ± 0.32	3.0 ± 0.13	3.2 ± 0.26	4.4 ± 0.13
ACW0330	0.93 ± 0.13	20 ± 0.9	10 ± 0.5	10 ± 0.9	9.5 ± 0.17
ACW0336	2.0 ± 0.25	43 ± 1.5	35 ± 2.3	70 ± 3.6	3.7 ± 0.17

*Q4 aquifer

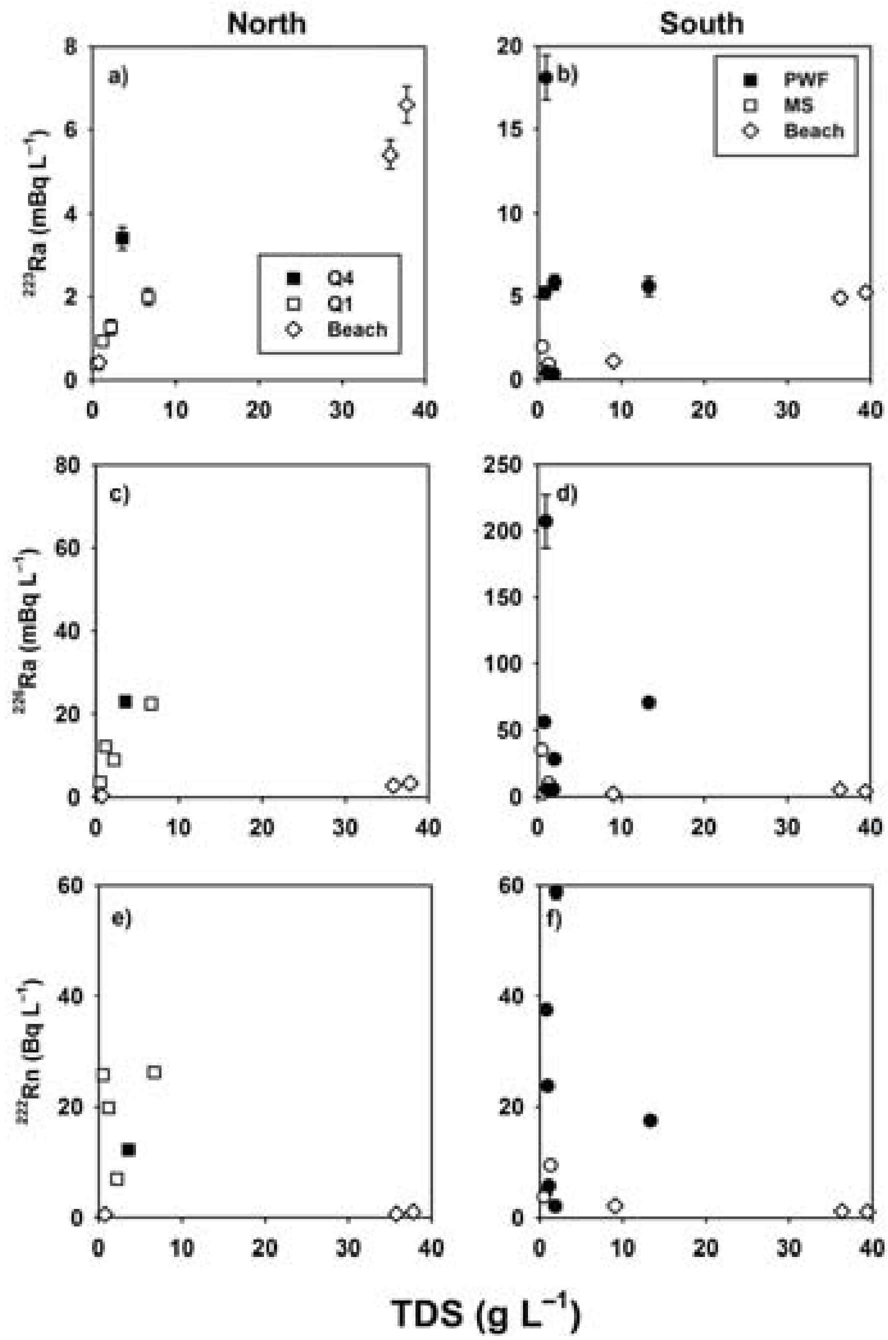

Fig. 3.2. Activities of ^{223}Ra, ^{226}Ra and ^{222}Rn in regional groundwater and beachface groundwater as a function of salinity.

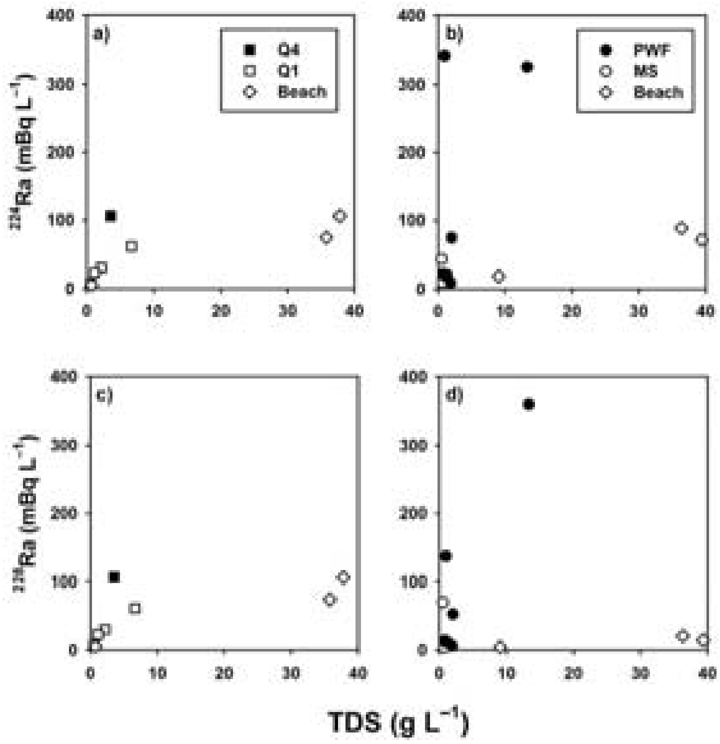

Fig. 3.3. ^{224}Ra and ^{228}Ra activities in regional groundwater and beachface groundwater as a function of salinity.

Table 3.2. Signature for potential tracers of groundwater discharge to coastal waters (mean ± SD). Both the Q1 and Q4 formations included for the Quaternary aquifer signature.

	Recirculated seawater (n = 4)	Quaternary (n = 5)	Port Willunga Formation (n = 6)	Maslin Sands (n = 3)	Open Ocean
Temp. (°C)	23 ± 2.2	20 ± 1.1	20 ± 1.3	23 ± 1.0	
TDS (g L^{-1})	38 ± 1.6	2.8 ± 2.4	3.4 ± 4.9	0.85 ± 0.41	36[b]
^{222}Rn (Bq L^{-1})	0.99 ± 0.21	18 ± 8.4	24 ± 21	5.9 ± 3.1	<0.004
^{223}Ra (mBq L^{-1})	5.5 ± 0.73	1.6 ± 1.2	46 ± 39	14 ± 8.5	<0.1
^{224}Ra (mBq L^{-1})	85 ± 16	46 ± 39	132 ± 158	24 ± 17	<1
^{226}Ra (mBq L^{-1})	3.9 ± 1.1	14 ± 8.5	62 ± 76	16 ± 17	1.1[b]
^{228}Ra (mBq L^{-1})	23 ± 7.8	45 ± 35	97 ± 138	28 ± 37	0.38[b]
^{228}Ra/^{226}Ra	5.8 ± 3.6[a]	2.7 ± 0.51	1.5 ± 0.7	1.4 ± 0.5	0.35[b]

[a]North Transect = 9.3; South Transect = 3.8.

[b]Veeh *et al*. (1995)

3.2.2 Offshore transects

There were horizontal and small vertical temperature and salinity gradients at the two transects at the time of sampling (Figs 3.4 and 3.5). The range in seawater temperature was small (15.4 – 17.3°C and 16.4 – 18.5°C for the Northern and Southern transects, respectively) with the highest temperatures nearer to the shore and in the first few metres of the water column. Salinities ranged from 36.60 to 37.09 g L^{-1} at the Northern Transect and from 36.37 to 37.26 g L^{-1} at the Southern Transect. With the exception of a small decrease in salinity at the shoreline of the Northern Transect, salinities were higher inshore than offshore.

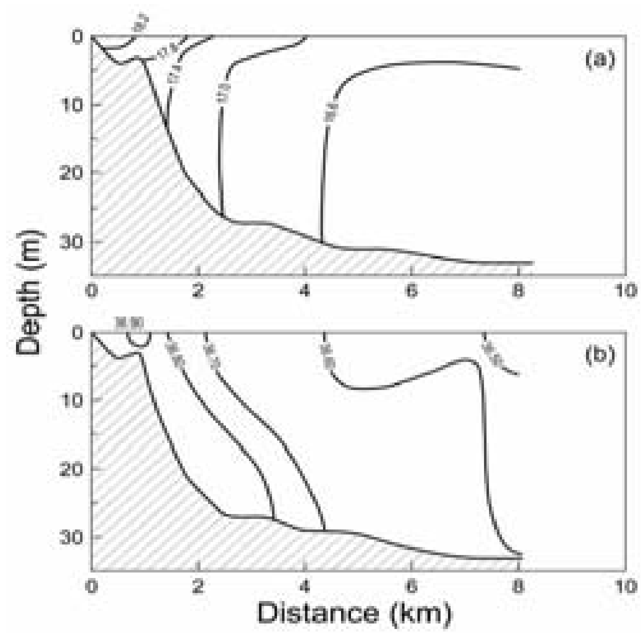

Fig. 3.4. *a)* Temperature (°C) and *b)* salinity profiles (as TDS, g L^{-1}) at the Northern Transect, 4 November 2003.

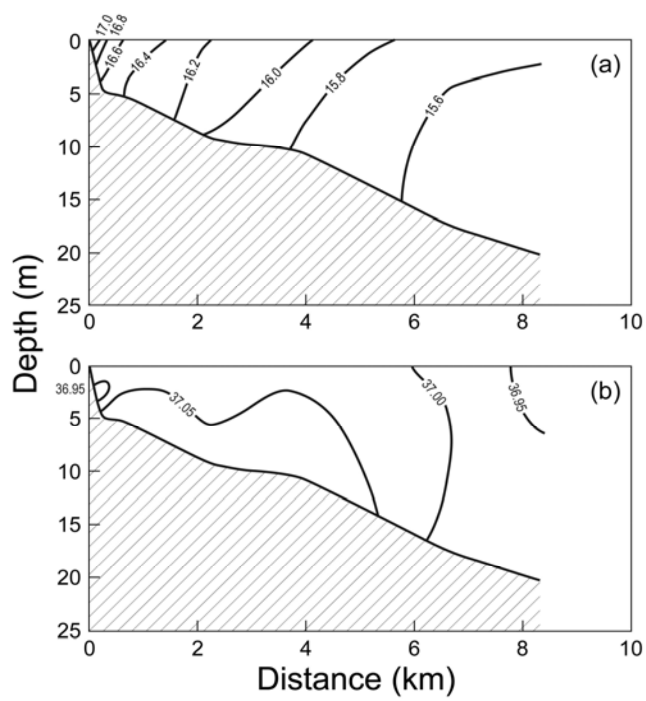

Fig. 3.5. *a*) Temperature (°C) and *b*) salinity profiles (as TDS, g L^{-1}) at the Southern Transect, 26 November 2003.

3.2.3 Radium quartet and ^{222}Rn

Most seawater samples had ^{222}Rn activities at or below background levels (<4 mBq L^{-1}; data not shown), with the exception of a few near shore and surf zone samples with low activities (5 – 9 mBq L^{-1}). In general, Ra isotope activities were also low (Table 3.3) but negative offshore gradients in Ra isotope activity were notable, especially for the shorter-lived ^{223}Ra and ^{224}Ra (Fig. 3.6). At the Northern Transect, ^{223}Ra and ^{224}Ra activities were 0.6 and 8 mBq L^{-1}, respectively, in the surf zone and declined exponentially to <0.1 and <1 mBq L^{-1}, respectively, at offshore locations (Fig. 3.6a). In contrast, ^{226}Ra activities were ~2 mBq L^{-1} at all locations. Radium isotope activities tended to be lower at the Southern Transect. Ra-223 and ^{224}Ra activities were 0.2 mBq L^{-1} and 2.5 mBq L^{-1}, respectively, in the surf zone and decreased to <0.1 mBq L^{-1} and <0.5 mBq L^{-1}, respectively, offshore (Fig. 3.6b). Ra-226 activities were usually $\leq$2 mBq L^{-1} but were slightly more elevated near the shore. There was also an offshore negative gradient in the ratio of ^{228}Ra:^{226}Ra at both transects (Fig. 3.7).

Table 3.3. Radium isotope activity at the Northern and Southern transects in November 2003. All activities in mBq L^{-1} (mean ± SE).

Distance (km)	^{223}Ra	^{224}Ra	^{228}Ra	^{226}Ra
		Northern Transect		
0 (surf zone)	0.598 ± 0.053	7.89 ± 0.23	4.06 ± 0.21	1.95 ± 0.06
0.07	0.272 ± 0.023	4.17 ± 0.13	3.63 ± 0.21	2.09 ± 0.09
0.27	0.228 ± 0.030	2.92 ± 0.14	3.40 ± 0.18	2.05 ± 0.09
0.65	0.142 ± 0.016	2.01 ± 0.08	3.21 ± 0.21	2.08 ± 0.09
1.41	0.156 ± 0.016	1.81 ± 0.08	2.98 ± 0.17	1.89 ± 0.07
2.18	0.168 ± 0.017	1.48 ± 0.07	4.08 ± 0.21	2.63 ± 0.1
2.93	0.120 ± 0.015	1.20 ± 0.06	3.38 ± 0.18	1.93 ± 0.07
3.71	0.130 ± 0.014	1.13 ± 0.05	2.81 ± 0.16	1.88 ± 0.07
5.22	0.106 ± 0.016	1.13 ± 0.06	2.87 ± 0.18	1.99 ± 0.08
6.73	0.072 ± 0.008	0.62 ± 0.04	2.38 ± 0.11	1.98 ± 0.07
8.34	0.063 ± 0.007	0.54 ± 0.03	2.26 ± 0.13	1.75 ± 0.09
		Southern Transect		
0 (surf zone)	0.205 ± 0.020	2.46 ± 0.09	2.55 ± 0.19	1.99 ± 0.09
0.53	0.105 ± 0.013	0.92 ± 0.05	1.90 ± 0.18	1.62 ± 0.09
0.95	0.101 ± 0.022	1.41 ± 0.10	2.43 ± 0.21	1.88 ± 0.08
1.79	0.069 ± 0.019	0.50 ± 0.05	2.00 ± 0.15	1.89 ± 0.07
1.82	0.078 ± 0.017	0.49 ± 0.05	1.91 ± 0.11	1.66 ± 0.09
2.53	0.070 ± 0.009	0.45 ± 0.03	1.77 ± 0.10	1.81 ± 0.07
3.28	0.062 ± 0.012	0.41 ± 0.04	1.73 ± 0.09	1.76 ± 0.06
4.03	0.059 ± 0.008	0.37 ± 0.02	2.11 ± 0.17	1.88 ± 0.10
4.78	0.043 ± 0.010	0.27 ± 0.03	1.69 ± 0.10	1.74 ± 0.09
5.54	0.046 ± 0.008	0.23 ± 0.02	1.35 ± 0.08	1.48 ± 0.06
7.05	0.045 ± 0.009	0.29 ± 0.03	1.49 ± 0.09	1.66 ± 0.06
7.81	0.060 ± 0.009	0.34 ± 0.02	1.84 ± 0.14	1.71 ± 0.06

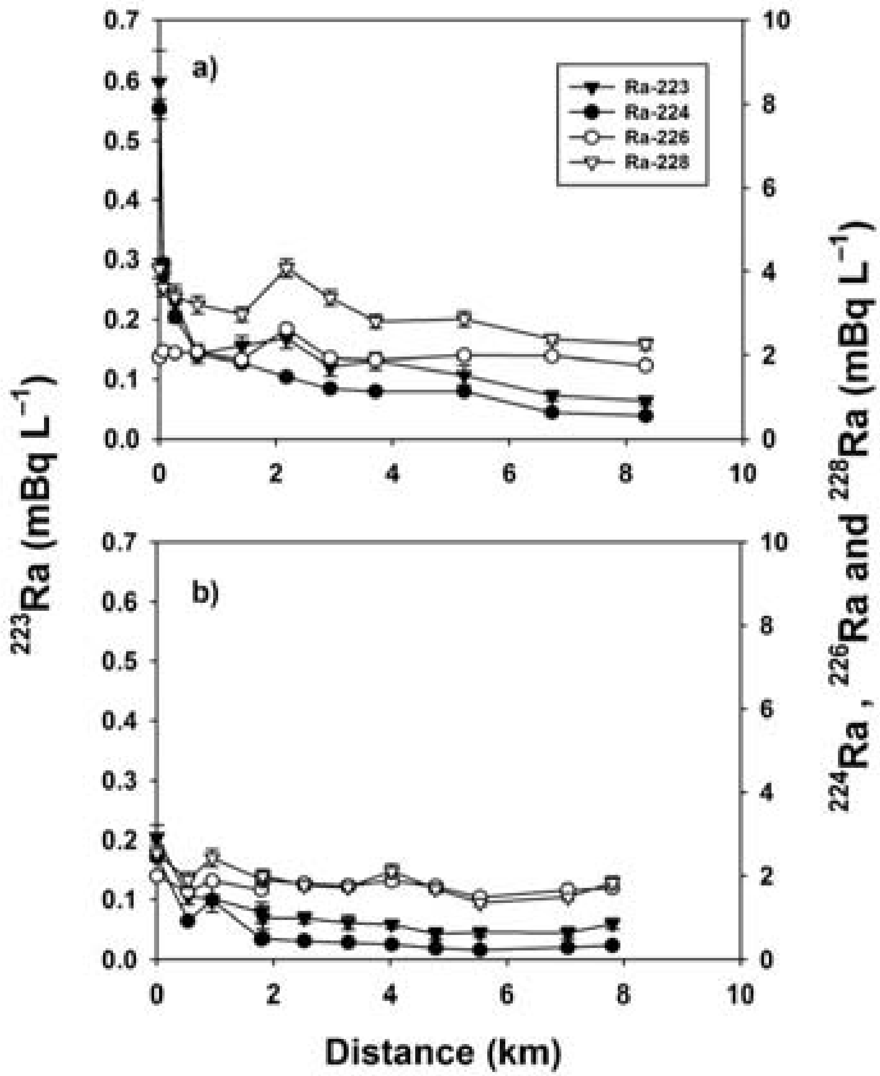

Fig. 3.6. Radium isotope activities in seawater along *a*) the Northern Transect and *b*) the Southern Transect.

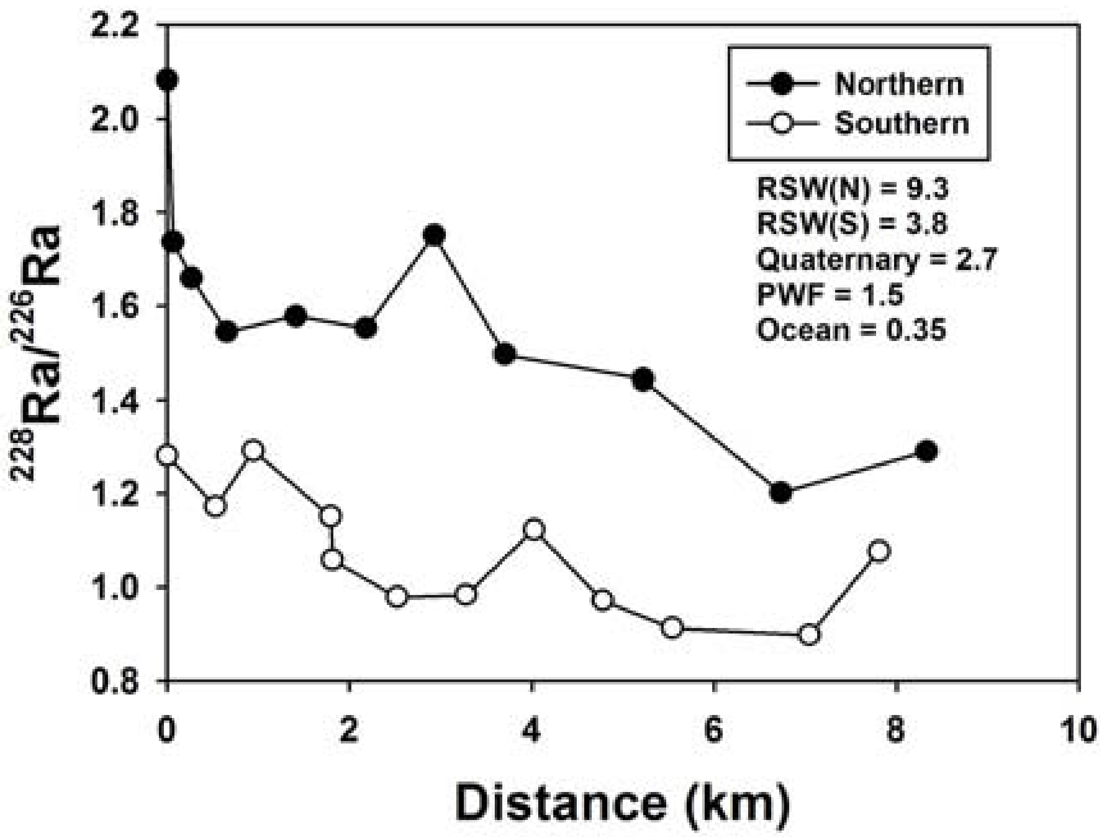

Fig. 3.7. Ratio of $^{228}Ra/^{226}Ra$ activity relative to distance offshore at the two transects. Ratio in different sources of water also indicated. RSW(N) – Recirculated seawater, Northern Transect; RSW(S) – Recirculated seawater, Southern Transect.

3.2.4 Ra activity gradients

To determine K_H and J_{total}, linear gradients in activity (or ln activity for the short-lived isotopes) must be present. The pattern in the decline in ^{223}Ra and ^{224}Ra activities with distance offshore was non-linear at both transects, even when activities were expressed on a logarithmic scale (Fig. 3.8). In general, there was apparently two distinct gradients along the transects, with a steeper one closer to the shoreline (<2 km). One possibility for this non-linear pattern in ln(activity) is that water depth increased with distance offshore (unlike the constant depth assumed in Equations 3.1–3.4). Alternatively, the two gradients may represent different types of mixing processes in the Gulf. The presence of distinct inshore and offshore gradients in Ra activity has also been noted in other studies (Moore 2000, 2003). Which set of gradients to use to calculate the radium fluxes is somewhat arbitrary – however, inshore K_H values must be used with inshore ^{226}Ra and ^{228}Ra activity gradients to calculate J_{total}, and vice-versa. Inshore and offshore gradients (and associated K_H values) were measured using linear regressions by arbitrarily selecting a “hinge point” for each transect (Fig. 3.8 and Table 3.4).

There were notable differences between K_H values derived from inshore and offshore gradients, but values were similar between transects (Table 3.4). Inshore K_H values ranged between 0.55 – 1.5 $m^2\ s^{-1}$ at the Northern Transect and 2.9 – 3.5 $m^2\ s^{-1}$ at the Southern Transect, while offshore K_H ranged between 45.1 – 77.2 $m^2\ s^{-1}$ and 148 – 258 $m^2\ s^{-1}$ for the same transects, respectively. These K_H values are within the range measured for similar inshore and offshore activity gradients in the Gulf of Mexico (Moore 2003).

It is more difficult to reliably estimate J_{total} using the Ra activity data. Unlike the short-lived isotopes, ^{226}Ra and ^{228}Ra activities were only slightly above oceanic background and both inshore and offshore gradients were either small or non-existant (Table 3.4). In addition, part of the "gradients" in long-lived isotopes are due to the gradient in salinity (that is, evaporative enrichment). Regressions using Ra activities corrected for salinity showed that this was especially important for the ^{226}Ra but not for the ^{228}Ra activity gradients (data not shown). However, most of the ^{226}Ra and ^{228}Ra activity gradients were not statistically significant. Thus, either no gradients are present or they were too small to be measured accurately using our sampling design.

Table 3.4. Summary of regression statistics (see Fig. 3.8 for definition of the inshore and offshore gradients). N – Northern transect, S – Southern transect; *in* – inshore gradient; *of* – offshore gradient

Regression	*m*	SE of *m*	*n*	*P*	Adj. r^2	K_H ($m^2\ s^{-1}$)
1 (N_{of}, ^{224}Ra)	–0.170	0.0164	8	<0.001	0.94	77.2
2 (N_{of}, ^{223}Ra)	–0.125	0.0184	8	<0.001	0.87	45.1
3 (N_{in}, ^{224}Ra)	–1.21	0.220	3	0.10	0.95	1.5
4 (N_{in}, ^{223}Ra)	–1.13	0.090	3	0.05	0.99	0.55
5 (S_{of}, ^{224}Ra)	–0.093	0.031	9	0.02	0.51	258
6 (S_{of}, ^{223}Ra)	–0.069	0.027	9	0.038	0.41	148
7 (S_{in}, ^{224}Ra)	–0.798	0.204	5	0.030	0.78	3.5
8 (S_{in}, ^{223}Ra)	–0.490	0.115	5	0.024	0.81	2.9
9 (N_{of}, ^{228}Ra)	–0.160	0.059	8	0.035	0.48	–
10 (N_{of}, ^{226}Ra)	–0.043	0.037	8	0.28	0.05	–
11 (N_{in}, ^{228}Ra)	–0.688	0.160	3	0.15	0.89	–
12 (N_{in}, ^{226}Ra)	–0.004	0.007	3	0.96	~0.01	–
13 (S_{of}, ^{228}Ra)	–0.054	0.036	9	0.18	0.13	–
14 (S_{of}, ^{226}Ra)	–0.026	0.020	9	0.22	0.09	–
15 (S_{in}, ^{228}Ra)	–0.244	0.175	5	0.26	0.19	–
16 (S_{in}, ^{226}Ra)	–0.061	0.111	5	0.62	0.09	–
17 (N, TDS)	–0.037	0.012	9	0.021	0.50	–
18 (S, TDS)	–0.064	0.024	11	0.025	0.38	–

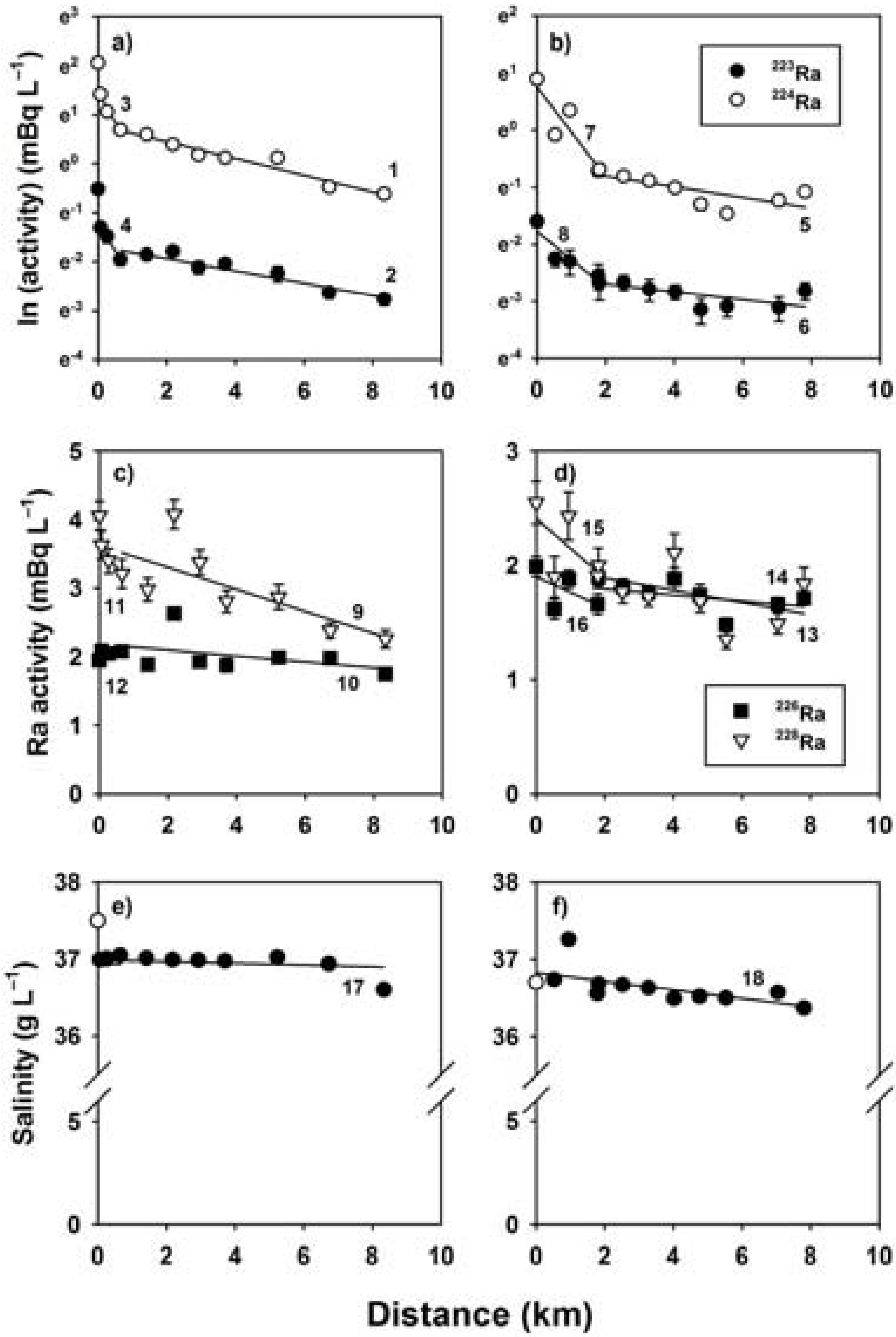

Fig. 3.8. Estimation of the gradients in Ra activity and in salinity with distance offshore. Short-lived Ra isotopes for the *a*) Northern and *b*) Southern transect, long-lived Ra isotopes for the *c*) Northern and *d*) Southern transect and surface salinity for the *e*) Northern and *f*) Southern transect. See Table 3.4 for the summary of the regression statistics. Open circles on *e*) and *f*) represent data collected with a less accurate hand held meter.

3.2.5 Estimation of groundwater discharge from ^{228}Ra gradients

While not always statistically significant, the inshore ^{228}Ra activity gradients and K_H values were used to gain a potential range in J_{total} at both transects. The inshore gradients were used to estimate J_{total} as it was hypothesised that this would be more representative of groundwater discharge from unconfined aquifers in the ACWS area (the main ones targeted by the environmental tracer study). In other studies with similar patterns in Ra activities, the inshore gradients were also used (Moore 2003).

Because the gradients in ^{226}Ra activity were similar to or smaller than the salinity gradients (Table 4), only the inshore ^{228}Ra activity gradients were used to estimate J_{total}. The ^{228}Ra gradients themselves are 4 to 19-fold larger than the salinity gradients and are not significantly affected when ^{228}Ra activities are standardised for salinity (*data not shown*). Using the range in K_H values found with the short-lived isotopes, J_{total} was estimated at 163 – 446 Bq m^{-1} d^{-1} at the Northern Transect and 245 – 295 Bq m^{-1} d^{-1} at the Southern Transect (Table 3.5).

Table 3.5. Estimation of the total ^{228}Ra, beachface ^{228}Ra, regional groundwater and recirculated seawater fluxes to the ACWS area. K_H values derived from the inshore ^{224}Ra and ^{223}Ra activity gradients. Q_{rsw_max} is the seawater recirculation flux assuming that regional groundwater discharge does not contribute any Ra to the ACWS area (and vice versa for Q_{gw_max}).

		Northern Transect	Southern Transect
		J_{total}	
K_H	($m^2\ s^{-1}$)	0.55 – 1.5	2.9 – 3.5
i	($mBq\ L^{-1}\ km^{-1}$)	–0.688	–0.244
z	(m)	5	4
J_{total}	($Bq\ m^{-1}\ d^{-1}$)	163 – 446	245 – 295
		J_{beach}	
Q_{beach}	($m^3\ m^{-1}\ d^{-1}$)	5[A]	5[A]
A_{beach}	($mBq\ L^{-1}$)	29	18
J_{beach}	($Bq\ m^{-1}\ d^{-1}$)	145	90
		Q_{gw}	
$J_{gw} = J_{total} - J_{rsw}$		0 – 156[B]	65 – 115[B]
A_{gw}	($mBq\ L^{-1}$)	45	97
Q_{gw}	($m^3\ m^{-1}\ d^{-1}$)	<0.1 – 3.5	0.7 – 1.2
		Q_{rsw_max}	
$J_{rsw} = J_{total}$		163 – 446	245 – 295
A_{rsw}	($mBq\ L^{-1}$)	29[C]	18[C]
Q_{rsw_max}	($m^3\ m^{-1}\ d^{-1}$)	5.6 – 15	14 – 16
		Q_{gw_max}	
$J_{gw} = J_{total}$		163 – 446	245 – 295
A_{gw}	($mBq\ L^{-1}$)	45	97
Q_{gw_max}	($m^3\ m^{-1}\ d^{-1}$)	3.6 – 9.9	2.5 – 3.0

[A]from Section 2

[B]assumes that $J_{beach} \sim J_{sf}$

[C]assumes that $A_{beach} \sim A_{sf}$

3.3 *Discussion*

3.3.1 Regional groundwater and seawater recirculation fluxes

Several lines of evidence indicate that seawater recirculation was the principal source of groundwater to the ACWS area in November 2003. Firstly, salinity was highest in nearshore areas whereas fresh groundwater discharge from unconfined aquifers would be expected to reduce salinity. Secondly, a high ^{228}Ra:^{226}Ra ratio, a relatively higher activity of the short-lived relative to the long-lived Ra isotopes and the lack of ^{222}Rn in nearshore seawater are also indicative that the volume of regional groundwater discharge was small relative to one of seawater recirculation. The low ^{226}Ra and ^{222}Rn activities in seawater are good indicators that regional groundwater discharge is low in the ACWS area.

Further analysis of the potential regional groundwater and seawater recirculation ^{228}Ra fluxes is also consistent with the latter process being the main source of Ra isotopes to the ACWS area. Recirculation of seawater along beachfaces by tidal action (Q_{beach}) has been estimated at ~5 $m^3\ m^{-1}\ d^{-1}$ in the ACWS area (Lamontagne *et al*. 2005), similar to values found elsewhere (Ullman *et al*. 2003). When combined with ^{228}Ra activities measured in recirculated seawater, this yields a beachface ^{228}Ra flux (J_{beach}) of ~145 Bq $m^{-1}\ d^{-1}$ at the Northern Transect and ~90 Bq $m^{-1}\ d^{-1}$ at the Southern Transect (Table 3.5). Thus, J_{beach} alone can account for 33% – 89% of J_{total} at the Northern Transect and 31 – 37% of J_{total} at the Southern Transect. No estimates are currently available for the seawater recirculation flux from the seafloor (J_{sf}) in the surf zone. This flux would include all the exchanges with shallow sediments promoted by currents, wave action, etc. Veeh *et al*. (1995) estimated that the areal Ra flux from offshore sediments (F_{sf}) in nearby Spencer Gulf ranged between 0.033 – 0.13 Bq $m^{-2}\ d^{-1}$. However, F_{sf} from surf zone sediments is probably larger than in offshore sediments because of the greater exchange of porewater promoted by wave action. Assuming that surf zone F_{sf} ranges between 0.2 – 2.0 Bq $m^{-2}\ d^{-1}$, J_{sf} for a ~100 m surf zone would range between 20 – 200 Bq $m^{-1}\ d^{-1}$. Thus, the magnitude of surf zone J_{sf} is probably similar to J_{beach}. Assuming that $J_{sf} \sim J_{beach}$, the proportion of J_{total} accounted for by seawater recirculation, would range between 66 – 100% at the Northern Transect and 62 – 74% at the Southern Transect (Table 3.5). However, the lack of excess ^{226}Ra and ^{222}Rn activity in nearshore waters suggests that the seawater recirculation flux is underestimated by assuming $J_{sf} \sim J_{beach}$.

In terms of volume of water discharged, seawater recirculation (Q_{rsw}) also appears to be a larger flux than regional groundwater discharge (Q_{gw}). An upper boundary for regional groundwater discharge (Q_{gw_max}) can be set by assuming that all the ^{228}Ra flux is derived from regional groundwater. In this case, Q_{gw} would range between 3.6 – 9.9 $m^3\ m^{-1}\ d^{-1}$ at the Northern Transect and 2.5 – 3.0 $m^3\ m^{-1}\ d^{-1}$ at the Southern Transect (Table 5). Conversely, a similar upper boundary for the seawater recirculation discharge in absence of any regional groundwater discharge (Q_{rsw_max}) would range between 5.6 – 15 and 14 – 16 $m^3\ m^{-1}\ d^{-1}$ for the Northern and Southern Transects, respectively. The best estimates for Q_{gw} (that is when $J_{gw} = J_{total} – J_{rsw}$, with $J_{beach} \sim J_{sf}$) ranges between <0.1 – 3.5 and 0.7 – 1.2 $m^3\ m^{-1}\ d^{-1}$ for the Northern and Southern Transects, respectively. Thus, Q_{gw} is most likely smaller than Q_{beach} (~5 $m^3\ m^{-1}\ d^{-1}$). Also, when we assume that Q_{gw} is negligeable, Q_{sf} must be approximately twice Q_{beach}.

3.3.2 Comparison with other Australian studies

Few studies have been made on the use of environmental tracers to quantify submarine groundwater discharge in Australia. In Spencer Gulf (also in South Australia), Veeh *et al*. (1995) reported a similar pattern in ^{228}Ra and ^{226}Ra activities as observed in Gulf St Vincent, with activities increasing along a salinity gradient. Veeh *et al*. (1995) postulated that input from the seafloor could account for the excess ^{228}Ra but could not account for all the excess ^{226}Ra. They suggested that the excess ^{226}Ra input could originate from periodic surface runoff from sabkhas at the northern end of the gulf or from regional groundwater discharge from the granitic basement rock. Even if small, groundwater discharge from regional basement rock could be a significant source for ^{226}Ra in either gulfs because older groundwaters tend to be enriched in this isotope. Because of its long half-life, long residence times (>2000 years) in aquifers are required for ^{226}Ra to reach secular equilibrium with its parent ^{230}Th. In the Bega Estuary (New South Wales), Hancock *et al*. (2000) estimated that groundwater discharge had an upper limit of 0.3 cm d^{-1} using porewater profiles for ^{226}Ra. By combining offshore transects for Ra and Rn activities with a numerical model, Cook *et al*. (2004) estimated that both regional groundwater and recirculated seawater fluxes were significiant in Bowling Green Bay (Burdekin Delta, Queensland). On an annual basis, groundwater discharge was estimated to range between 50 – 400 10^{3} ML year^{-1} (5.0 – 40·10^{7} m^{3} year^{-1}) Unlike in the ACWS area, ^{222}Rn activity was significant in Bowling Green Bay, ranging from 2 – 13 mBq L^{-1} in February 2004 to 5 – 26 mBq L^{-1} in April 2004 along transects parralel to the shoreline. The temporal variability in ^{222}Rn activity in Bowling Green Bay indicates that the rates of submarine groundwater discharge could vary significantly during the year (Cook *et al*. 2004).

3.3.3 N load estimates to the ACWS area

The potential significance of regional groundwater and recirculated seawater as sources of N to the ACWS area can be estimated using the flow net and ^{228}Ra-derived water fluxes with representative values for total dissolved N (TDN) concentration in different aquifers. The N loads from seawater recirculation are estimated to be similar between the Northern and Southern sections of the study area (110 – 330·10^{3} kg N year^{-1}; Table 3.6). In contrast, both flow net-derived and ^{228}Ra-derived regional groundwater N discharge were different between areas. For the flow net-derived estimates, the N flux was 8.8·10^{3} and 1.3·10^{3} kg N year^{-1} for the Northern and Southern area, respectively. For the ^{228}Ra-derived estimates, the N flux was 15 – 570·10^{3} and 24 – 42·10^{3} kg N year^{-1}, for the Northern and Southern area, respectively. These differences were primarily driven by the higher average groundwater TDN concentrations in the Northern (7.4 mg N L^{-1}) relative to the Southern area (1.6 mg N L^{-1}). However, due to a small number of bores sampled along the coastal fringe (i.e., <1 km inland), it is unclear whether these TDN values are representative of values expected in groundwater discharge zones. Also, it is probable that the Q_{gw} derived using ^{228}Ra overestimates the true groundwater discharge rates because J_{sf} could only be conservatively estimated. Likewise, because regional groundwater discharge should be higher in spring, the annual Q_{gw} extrapolated from the spring radium transects may overestimate the true annual groundwater discharge rate. Despite these shortcomings, this analysis indicates that N discharge from groundwater could be more significant for the Northern section relative to the Southern section of the study area because of elevated N concentrations in the Quaternary aquifers (Dillon *et al*. 1995). Overall, regional groundwater discharge from unconfined aquifers contributes probably less than 50·10^{3} kg N year^{-1} to the ACWS area (<50 ton N year^{-1}). It is unlikely that discharge from confined aquifers would increase this substantially, but this needs to be verified.

At the scale of the ACWS area, the contribution of groundwater to the annual N budget is probably small relative to other sources. For example, assuming a bulk deposition rate of 1 – 2 kg N ha^{-1} year^{-1} (Blackburn and McLeod 1983), the atmospheric N load to the ACWS area (120 km by 20 km) would be approximately 240 – 480·10^{3} kg N year^{-1}. Similarly, N discharge rates to the ACWS area are estimated at ~680·10^{3} N year^{-1} from waste water treatment plants, ~1460·10^{3} kg N year^{-1} from the Penrice salt production operations and 250·10^{3} kg N year^{-1} from stormwater. Thus, the input of N from regional groundwater is a negligible source for the ACWS area on a regional scale, but could still be significant locally.

Table 6. Estimated annual nitrogen loads to the ACWS area from recirculated seawater and regional groundwater discharge. Each half of the study area is 60 km in width. For recirculated seawater, the range in Q represents values expected from Q_{beach} only (lower boundary) to Q_{rsw_max} (upper boundary). For regional groundwater, an estimate obtained from a review of flow net studies (Section 1) and the range in ^{228}Ra-derived Q_{gw} are used (see Table 3.5). ^{228}Ra-derived Q_{gw} values represent upper boundaries because they are likely to overestimate the true Q_{gw}.

Source	Q (10^8·m^3 year^{-1})	TDN (mg N L^{-1})	Loading rate (10^3·kg N year^{-1})
	Northern area		
Recirculated SW	1.1 – 3.3	1.0	110 – 330
GW – *Flow net*	0.012	7.4	8.8
GW – *^{228}Ra*	<0.02 – 0.77	7.4	15 – 570
	Southern area		
Recirculated SW	1.1 – 3.3	1.0	110 – 330
GW – *Flow net*	0.008	1.0	1.3
GW – *^{228}Ra*	0.15 – 0.26	1.6	24 – 42
	Total ACWS area		
Recirculated SW	2.2 – 6.6		220 – 660
GW – *Flow net*	0.02		10
GW – *^{228}Ra*	0.17 – 1.0		39 – 612

3.3.4 Further studies

The results of this study indicate that environmental tracers could be useful tools to quantify nutrient recycling rates at the scale of the ACWS area but less useful to quantify the groundwater discharge rate. This occurs because the input of Ra isotopes from groundwater is similar to or smaller than other sources. The ability to measure nutrient recycling at the large scale would be a useful complement to traditional methods, which are typically made at the scale of cores and incubation chambers. Such small-scale methods are not ideal in a shallow oceanic setting because they cannot account for physical exchange processes driven by tides, waves and currents. A better understanding of seawater recirculation in the ACWS would be helped by:

- Seasonal sampling to investigate the temporal variability in Ra isotope activity;
- Sampling a greater range of beaches;
- The measurement of the concentration of the parent isotopes and a quantification of Ra isotope production rates in inshore and offshore sediments.

To improve on the estimates of groundwater discharge to the ACWS area using environmental tracers would require a significant effort. The Ra isotope signature of groundwater needs to be better defined and it is still not clear what happens to this signature when groundwater undergoes partial mixing with seawater before discharging to the ocean. Many of the aquifers in the ACWS area are undergoing salinisation (from more saline recharge water or seawater intrusions) which further complicates defining the Ra isotope signature of groundwater. In that regard, ^{222}Rn could be more useful to detect discrete groundwater discharge zones than the Ra isotopes because it is not impacted by changes in salinity when fresh and saline water mix in aquifers. Because of complex circulation patterns in Gulf St Vincent, the interpretation of the radium isotope data may require more detailed mass-balance analysis the the one used here.

While accurate measurements of groundwater discharge may be difficult, environmental tracers could be use to map zones of groundwater discharge across the ACWS, including offshore spring discharge from confined aquifers. This could be done relatively inexpensively by continuous measurements of salinity, temperature and ^{222}Rn in bottom waters during transect surveys. Rn-222 can now be measured continuously in real time using shipborne equipment (Cook *et al*. 2004). Such assessment of groundwater discharge zones could be used to verify the zones of groundwater discharge predicted by hydrological models, assess whether groundwater discharge has any links with the distribution of organisms in the Gulf (Rutkowski *et al*. 1999) and help focus efforts to measure the rates of groundwater discharge using tracers or other techniques.

In summary, further studies of groundwater discharge in the ACWS area using environmental tracers would include:

- Mapping surveys to detect localised sources of groundwater discharge;
- More detailed mass-balances for Ra by measuring the contribution of other sources (stormwater, STP discharge, etc), improving the seawater recirculation flux estimates and measuring the advection of Ra in and out of the study area.
- Better characterise the Ra signature of regional groundwater (including in basement rock aquifers);

4 Conclusions and Recommendations

A number of conclusions can be made from this study. These are that:

- At least three hydrogeological systems can potentially discharge groundwater to the ACWS area (the North Adelaide Plains system, the Metropolitan Adelaide system and the Willunga Basin).
- Practically all these groundwater systems appear significantly impacted by human activity (including through extraction, nitrogen contamination and salinisation).
- There is a significant risk of seawater intrusion in many of the aquifers adjacent to the coastal zone across the ACWS area.
- Groundwater is a small source of water and of N to the ACWS area at the regional scale.
- Groundwater may be a significant source of N at specific locations.
- Groundwater is more enriched in N in the Quaternary sedimentary aquifers characteristic of the North Adelaide Plains and Metropolitan systems relative to the aquifers in the Willunga Basin.
- Seawater recirculation by tidal pumping and wave action is probably a significant mechanism to recycle C, N and P stored in beach sands and seafloor sediments, including from particulate inputs from stormwater, decaying seagrasses, etc.
- The discharge of fresh groundwater to the coastal zone has almost certainly decreased substantially in the last decades due to significant extraction rates. In addition, the Adelaide sewerage system probably intercepts a portion of the groundwater that formerly would have discharged to the sea. What effects this could have had on biological communties is unclear.

Recommendations for future studies relevant to the management of groundwater in the ACWS area include:

- To use selected environmental tracers to map zones of localised groundwater discharge;
- To develop and implement a better groundwater monitoring program along the coastal margins of the ACWS area, including a greater coverage of monitoring bores;
- To further investigate the use of Ra isotopes to quantify seawater recirculation and groundwater discharge to the Gulf;
- To investigate the seasonality of nutrient recycling by tidal pumping along beachfaces.

References

Aldam, R. G. 1989. Willunga Basin hydrogeological investigations 1986/88. South Australian Department of Mines and Energy. Report Book 89/22.

American Public Health Association, American Water Works Association and Water Environment Federation. 1998. Standard methods for the examination of water and wastewater, 20th ed., Washington, DC.

Ataie-Ashtiani, B., Volker, A.E. and Lockington, D.A. 2001. Tidal effects on groundwater dynamics in unconfined aquifers. *Hydrological Processes* **15**: 655–669.

Baldwin, D.S. and Mitchell, A.M. 2000. The effects of drying and re-flooding on the sediment and soil nutrient dynamics of lowland river – floodplain systems: A synthesis. *Regulated Rivers: Research and Management* **16**: 457–467.

Blackburn, G. and McLeod, S. 1983. Salinity of atmospheric precipitation in the Murray-Darling Drainage division, Australia. *Australian Journal of Soil Research* **21**: 411–434.

Belyea, L.R. 1996. Separating the effects of litter quality and microenvironment on decomposition rates in a patterned peatland. *Oikos* **77**: 529–539.

Boehm, A.B., Shellenbarger, G.C. and Paytan, A. 2004. Groundwater discharge: Potential association with faecal indicator bacteria in the surf zone. *Environmental Science and Technology* **38**: 3558–3566.

Böhlke, J.K., Wanty, R., Tuttle, M., Delin, G., and Landon, M. 2002. Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer. Water Resources Research **38**(7), Art. No. 1105.

Bugna, G.C., Chanton, J.P., Cable, J.E., Burnett, W.C. and Cable, P.H. 1996. The importance of groundwater discharge to the methane budgets of nearshore and continental shelf waters of the northeastern Gulf of Mexico. *Geochimica et Cosmochimica Acta* **60**: 4735–4746.

Burnett, W.C., Taniguchi, M. and Oberdorfer, J. 2001. Measurement and significance of the direct discharge of groundwater into the coastal zone. *Journal of Sea Research* **46**: 109 – 116.

Cable, J.E., Bugna, G.C., Burnett, W.C., and Chanton, J.P. 1996a. Application of ^{222}Rn and CH4 for assessment of groundwater discharge to the coastal ocean. *Limnology and Oceanography* **41**: 1347–1353.

Cable, J.E., Burnett, W.C., Chanton, J.P., Weatherly, G.L. 1996b. Estimating groundwater discharge into the northeastern Gulf of Mexico using radon-222. *Earth and Planetary Science Letters* **144**: 591–604.

Clarke, D., 2002. McLaren Vale Prescribed Wells Area groundwater monitoring status report 2002. Department of Water, Land and Biodiversity Conservation. Report Book DWLBC 2002/06.

Cook, P.G., Stieglitz, T. and Clark, J. 2004. Groundwater discharge from the Burdekin Floodplain aquifer, North Queensland. CSIRO Land and Water Technical Report No. 26/04.

Cook, P.G., Favreau, J.C., Dighton, J.C. and Tickell, S. 2003. Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers. *Journal of Hydrology* **277**: 74–88.

Cooper, N. J., 1979. Eocene to Miocene Stratigraphic of the Willunga Embayment. Rep. Invest. Surv. S. Aust. 50.

Daborn, G.R., Amos, C.L., Brylinsky, M., Christian, H. and Drapeau, G. 1993. An ecological cascade effect: Migratory birds affect stability of intertidal sediments. *Limnology and Oceanography* **38**: 225–231.

de Silva Samarasinghe, J.R., Bode, L. and Mason, L.B. 2003. Modelled response of Gulf St Vincent (South Australia) to evaporation, heating and winds. *Continental Shelf Research* **23**: 128 –1313.

Dillon, P.J., Pavelic, P., Rattray, K.J., Schultz, M., Winkler, I.G., Ragusa, S.R., Stanger, G., and Armstrong, D. 1995. The quality of water in the Upper Quaternary Aquifer at three selected sites in the Adelaide Metropolitan area – GROUNDWATER WATCH: A study involving South Australian high school students. Centre for Groundwater Studies Report No. 60. 26 pp.

Ellis, D. and D. Fox. 2001. Adelaide Coastal Waters Study: Research requirements report. CSIRO Environmental Projects Office E/BUS/5.

Freeze, R.A. and Cherry, J.A. 1979. Groundwater. Prentice-Hall: Englewood Cliifs, New Jersey. 604 p.

Gerges, N. Z., 1997. Overview of the Hydrogeology of the Adelaide Metropolitan Area. Department of Mines and Energy Geological Survey South Australia. Report Book 97/3.

Gerges, N. Z., 1999. The Geology and Hydrogeology of the Adelaide Metropolitan Area. Thesis. Faculty of Science and Engineering. The Flinders University of South Australia.

Gerges, N.Z., 2001. Northern Adelaide Plains groundwater review. South Australia Department for Water Resources. Report, DWR 2001/013.

Hancock, G.J. and Martin, P. 1991. Determination of radium in environmental samples by alpha-particle spectrometry. *Applied Radiation and Isotopes*, **42**, 63-69.

Hatton, T. and Evans, R. 1998. Dependence of ecosystems on groundwater and its significance to Australia. Land and Water Resources Research and Development Corporation Occasional Paper No. 12/98.

Hazel, C. P. 1975. Groundwater Hydraulics. Lecture Notes. Australian Water Resources Council's Groundwater School, Adelaide.

Herczeg, A.L., Dighton, J.C., Easterbrook, M.L. and Salomons, E. 1994. Radon-222 and Ra-226 measurements in Australian groundwaters using liquid scintillation counting. pp: 53-57 In Proceedings Workshop on Radon and Radon Progeny Measurements in Environmental Samples. February 1994. Canberra.

Hill, A.R., Devito, K.J., Campagnolo, S., Sanmugadas, K. 2000. Subsurface denitrification in a riparian zone : Interactions between hydrology and supplies of NO_3^- and organic carbon. *Biogeochemistry* **51**: 743–755.

Johannes, R.E. 1980. The ecological significance of the submarine discharge of groundwater. *Marine Ecology – Progress Series* **3**: 365–373.

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B. and Matzner, E. 2000. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Science* **165**: 277–304.

Kamermans, P., Hamminga, M.A., Tack, J.F., Mateo, M.A., Marba, N., Mtolera, M., Stapel, J., Verheyden, A., Vandaele, T. 2002. Groundwater effects on diversity and abundance of lagoonal seagrasses in Kenya and on Zanzibar Island (East Africa). *Marine Ecology – Progress Series* **231**: 75–83.

Kohout F.F. and Kolipinski M. C. 1967. Biological zonation related to groundwater discharge along the shore of Biscayne Bay, Miami, Florida. *In* Lauff, G. H. [ed.], Estuaries. AAAS Publ. No **83**: 488–499.

Lamontagne, S. 2002. Groundwater delivery rate of nitrate and predicted change in nitrate concentration in Blue Lake, South Australia. *Marine and Freshwater Research* **53**: 112 –1142.

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

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

Martin, R.R. 1996. Sustainability of supplies from a coastal aquifer and the impact of artificial recharge; LeFevre Peninsula, South Australia. PhD thesis, Flinders University, South Australia. 219 p.

Martin, R. R., 1998. Willunga Basin – Status of Groundwater Resources 1998. South Australia. Primary Industries and Resources SA. Report Book 98/28.

Moore, W.S. 1976. Sampling ^{228}Ra in the deep ocean. *Deep Sea Research* **23**: 647–651.

Moore, W.S. 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature* **380**: 612–614

Moore, W.S. 2000. Determining coastal mixing rates using radium isotopes. *Continental Shelf Research* **20**: 1993–2007.

Moore, W.S. 2003. Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. *Biogeochemistry* **66**: 75–93.

Moore, W.S. and Arnold, R. 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. *Journal of Geophysical Research* **101**: 1321–1329.

Osmond, J.K. and Cowart, J.B. 2000. U-series nuclides as tracers in groundwater hydrology *In* Cook, P.G. and Herczeg, A.L [eds.] 1999. Environmental tracers in subsurface hydrology. Kluwer, pp: 145–173.

Pabich, W.J., Valiela, I. and Henmond, H.F. 2001. Relationship between DOC concentration and vadose zone thickness and depth below water table in groundwater of Cape Cod, USA. *Biogeochemistry* **55**: 247–268.

Pavelic, P., Gerges, N. Z., Dillon, P.J., and Armstrong, D. 1992. The Potential for Storage and Re-Use of Adelaide's Stormwater Runoff Using the Upper Quaternary Groundwater System. Centre for Groundwater Studies Report No. 40.

Rama and Moore, W.S. 1996. Using the radium quartet for evaluating groundwater input and water exchange in salt marshes. *Geochimica et Cosmochimica Acta* **60**: 464–4652.

Rutkowski, C.M., Burnett, W.C., Iverson, R.L. and Chanton, J.P. 1999. The effect of groundwater seepage on nutrient delivery and seagrass distribution in the Northeastern Gulf of Mexico. *Estuaries* **22**: 1033–1040.

Shepard, R. G., 1975. Northern Adelaide Plains groundwater study, stage II 1968-1974. *Department of Mines South Australia*. Report Book 75/38.

Slomp, C.P. and van Cappellen, P. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact. *Journal of Hydrology* **295**: 64–86.

Smith, A.J., Turner, J.V., Herne, D.E. and Hick, W.P. 2003. Quantifying submarine groundwater discharge and nutrient discharge into Cockburn Sound, Western Australia. Centre for Groundwater Studies Report No. 104. 185 p.

Starr, R.C. and Gillham, R.W. 1993. Denitrification and organic carbon availability in two aquifers. *Ground Water* **31**: 934–947.

Stieglitz, T. and Ridd, P. 2000. Submarine groundwater discharge from paleochannels? "Wonky holes" on the inner shelf of the Great Barrier Reef, Australia. Conference Proceedings HYDRO 2000, Perth 20 – 23 November 2000.

Uchiyama, Y., Nadaoka, K., Rölke, P., Adachi, K. and Yagi, H. 2000. Submarine groundwater discharge into the sea and associated nutrient transport in a sandy beach. *Water Resources Research* **36**: 1467–1479.

Ueda, S., Go, C.-S.U., Suzumura, M. and Sumi, E. 2003. Denitrification in a seashore sandy deposit influenced by groundwater discharge. *Biogeochemistry* **63**: 187–205.

Ullman, W.J., Chang, B., Miller, D.C. and Madsen, J.A. 2003. Groundwater mixing, nutrient diagenesis, and discharge across a sandy beachface, Cape Henlopen, Delaware (USA). *Estuarine, Coastal and Shelf Science* **57**: 539–552.

Veeh, H.H., Moore, W.S. and Smith, S.V. 1995. The behaviour of uranium and radium in an inverse estuary. *Continental Shelf Research* **15**: 1569–1583.

Webster, I.T., Hancock, G.J. and Murray, A.S. 1994. Use of radium isotopes to examine pore-water exchange in an estuary. *Limnology and Oceanography* **39**: 1917–1927.

Zulfic, H., 2002. Northern Adelaide Plains Prescribed Wells Area groundwater monitoring status report 2002. *South Australia. Department of Water, Land and Biodiversity Conservation. Report,* DWLBC 2002/14.