

Natural attenuation of nitrogen in groundwater discharging through a sandy beach

Alicia M. Loveless · Carolyn E. Oldham

Received: 7 February 2008 / Accepted: 11 September 2009 / Published online: 6 October 2009
© Springer Science+Business Media B.V. 2009

Abstract This paper presents an uncomplicated approach to improve estimates of groundwater nutrient load to a marine embayment. A two-dimensional chemical profile of shallow groundwater was analysed in a sandy beach in three seasons (early summer, late summer and mid winter) and an adjusted estimate of groundwater nutrient discharge was derived that accounts for a complex biogeochemical environment and non-conservative behaviour of nutrients in the pre-discharge beach groundwater. The study was conducted at Cockburn Sound, Western Australia, where there has been significant groundwater contamination and associated marine ecological degradation. Losses in nitrogen and increases in phosphorus were observed along the discharge pathway beyond that expected from mixing with marine water, and the changes were attributed to chemically and biologically mediated reactions. A slow groundwater velocity ($0.14\text{--}0.18\text{ m day}^{-1}$), high organic carbon ($\text{TOC} = 0.35\text{--}4.9\text{ mmol l}^{-1}$,

$\text{DOC} = 0.28\text{--}4.6\text{ mmol l}^{-1}$) and low to sub-oxic conditions ($\text{DO} = 0.4\text{--}24\%$ saturation) were deemed suitable for chemically and biologically mediated reactions to occur and subsequently alter regional estimates of groundwater nutrient concentration. Accounting for this environment, groundwater loads were calculated that were 1–2 orders of magnitude less than previous regional-based estimates: $0.4\text{--}13\text{ kg NO}_x^- \text{ day}^{-1}$, $0.2\text{--}24\text{ kg NH}_4^+ \text{ day}^{-1}$ and $0.004\text{--}0.8\text{ kg FRP day}^{-1}$. This paper applies knowledge of recent research and presents scope to marine managers or modellers to account for groundwater inputs to the marine environment.

Keywords Groundwater nitrogen · Permeable sand · Coastal aquifer · Submarine groundwater discharge

Introduction

Submarine groundwater discharge (SGD) delivers land-derived nutrients and contaminants to the marine environment and has contributed to coastal water quality decline in a number of locations around the world (Johannes 1980; Corbett et al. 1999; Herrera-Silveira et al. 2002; Gobler and Boneillo 2003; Slomp and Van Cappellen 2004). To respond to the impacts of SGD on marine health, coastal managers require an estimate of the quantity and sources of nutrients that are discharged to the surface waters. The greatest challenge was to be

A. M. Loveless (✉)
Centre for Water Research, University of Western
Australia, Melbourne, VIC, Australia
e-mail: alicia.loveless@gmail.com

C. E. Oldham
School of Environmental Systems Engineering,
University of Western Australia, Crawley, WA, Australia
e-mail: carolyn.oldham@uwa.edu.au

quantification of SGD volume flux (Giblin and Gaines 1990; Moore 1996; Charette et al. 2001), and the body of work in SGD estimation began with proliferation of methods for estimating discharge across the range of physical conditions that determine SGD (e.g. Corbett et al. 1999; Taniguchi et al. 2002; Burnett and Dulaiova 2003; Chanton et al. 2003; Charette et al. 2003; Destouni and Prieto 2003; Moore 2003; Loveless et al. 2008). The need to understand the biological and chemical reactions in the subterranean estuary that affect load estimates has since followed.

Estimates of SGD nutrient load were traditionally based on measured nutrient concentrations from upland monitoring wells, with the assumption that the upland groundwater concentrations are representative of the chemistry of the groundwater that discharges beyond the shoreline. This assumption may hold where nitrogen is transported conservatively, such as in shallow aerobic sandy aquifers of low labile organic content (Giblin and Gaines 1990), however, groundwater nitrogen concentrations have been demonstrated to significantly change over small spatial scales through biologically and chemically mediated reactions in suitable redox conditions (Ullman et al. 2003; Slomp and Van Cappellen 2004; Andersen et al. 2007; Charette and Sholkovitz 2006; Hays and Ullman 2007; Kroeger and Charette 2008; Santos et al. 2008; Spiteri et al. 2008a), thus limiting the ability to make confident mass flux estimates at a regional scale using a two-endmember approach. To account for such non-conservative behaviour in an aquifer, groundwater load estimates can be based upon porewater nutrient concentrations at the seepage zone (Charette et al. 2001; Michael et al. 2003), from a detailed description of the discharge chemical environment through highly resolved field sampling (Kroeger and Charette 2008; Santos et al. 2008) and transport and reaction modeling (Michael et al. 2005; Spiteri et al. 2008b).

We sampled the vertical and horizontal profile of groundwater discharging through a sandy beach in Western Australia to provide snapshots of nutrient concentrations (nitrate + nitrite, NO_x^- , ammonium, NH_4^+ , total nitrogen, TN, and filterable reactive phosphorus, FRP) at different times of the year and determine whether changing concentrations in the discharge zone alter upland estimates of groundwater nutrient discharge.

Materials and methods

Study site

The study was conducted at Cockburn Sound, Western Australia (Fig. 1a) where the climate is “Mediterranean” with a distinct wet-winter (June–September) and dry-summer (November–April). The Cockburn region receives 0.87 m rainfall annually, of which 30–40% recharges the superficial aquifer (Water Authority of Western Australia, 1993). Superficial groundwater flows westerly from recharge zones to discharge into Cockburn Sound (Fig. 1a). The superficial aquifer consists of an unconfined 5–10 m surface layer of sand of marine origin, called the Safety Bay Sand unit (SBS), underlain by a ~10 m layer of Tamala Limestone (TL; Fig. 1b). Exchange between the SBS and TL is restricted by a clay and shell-sand semi-confining layer of 0.5–1 m thickness and discharge from the sandy aquifer occurs at the beach on the eastern shoreline, through a narrow (~5 m wide) discharge zone (Smith et al. 2003).

Western Australian ocean waters are nitrogen limited, with some elevation of nutrient concentrations occurring at the coast (D’Adamo and Mills 1995; Lourey et al. 2006). Natural regional groundwater nitrogen (N) and phosphorus (P) concentrations ($0.2 \mu\text{mol l}^{-1}$ TN and $0.06 \mu\text{mol l}^{-1}$ FRP) are near analytical detection limits, however, up to $11,000 \mu\text{mol l}^{-1}$ of NO_x^- and $27,000 \mu\text{mol l}^{-1}$ of NH_4^+ have been measured in contaminated groundwater in the Cockburn Sound industrial strip (Smith et al. 2003). Past practices of waste-water injection, chemical spills, the application of domestic fertilizers and leaking septic tanks have contaminated the regional groundwater, and it is proposed that between 420 and 1,106 kg N day^{-1} has been delivered to Cockburn Sound from contaminated groundwater since 1978 (Simpson 1996; Appleyard 1994; Smith and Nield 2003). Annual load estimates of TN have ranged from 490 to 1,240 kg day^{-1} , however, the modern estimate is believed to be $<600 \text{ kg day}^{-1}$ due to groundwater remediation efforts that took effect in the year 2000 (from local studies as cited in Smith and Nield 2003). Regional phosphorus load estimates are significantly less, at 6 kg day^{-1} (Smith and Nield 2003). Nitrogen contamination from point and non-point sources to Cockburn Sound have caused significant water quality decline and seagrass mortality in the marine waters.

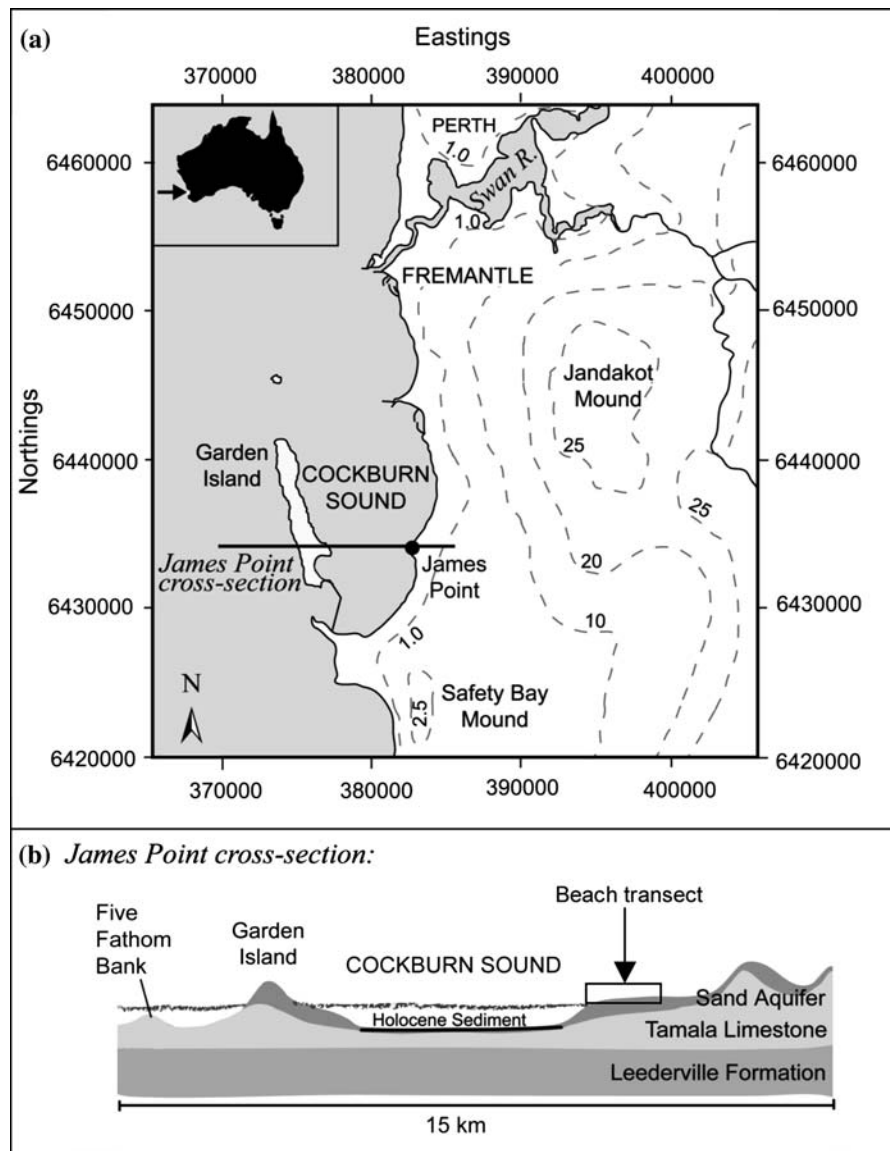


Fig. 1 **a** Study location and regional water table height contours and **b** profile of sampling transect and local hydrogeology

Despite removal of point-sources (primarily, a sewage treatment outfall) and the re-establishment of low surface water nitrogen concentrations, chlorophyll-*a* concentrations remained elevated and there has been no recovery of seagrasses (Pearce et al. 2000; Kendrick et al. 2002).

The lack of estuarine response to land remediation efforts is a global issue that exposes a continued need to better understand links between loads and the discharge environment (Duarte 2002). Possible reasons for a lack in seagrass recovery despite removal of point source nutrient loads may be deterioration of

sediments, siltation or continued eutrophic effects from an unknown or underestimated groundwater N source. To obtain a better understanding of groundwater N delivery to these marine waters, we investigated the spatial and temporal variation in the NO_x^- , NH_4^+ , TN and FRP concentrations that are discharged to the coastal waters by shallow groundwater.

Sample collection

Groundwater and marine water at Cockburn Sound have been severely impacted by industrial discharges

Table 1 Locations of groundwater wells A–E, surface-water F sampling station and screened depth of wells bwt

Nest name	Location eastings	Location northings	Well name	Depth bwt m
A	383004	6434629.8	A1	f10
			A2	f12–20
B	383014.5	6434629.8	B1	0
			B2	8
			B3	12
			B4	16
C	383014.5	6434629.8	C1	1
			C2	3
			C3	5
D	383022	6434629.8	D1	1
			D2	3
			D3	5
E	383040	6434629.8	E1	1
			E2	3
			E3	5
F	383058	6434629.8	SW	0

bwt Screened depth below the water table during installation, *f* fully slotted from the water table to bottom of aquifer

of nitrogen. At the study site location, James Point, groundwater has been contaminated with ammonium sulphate from an ammonia, ammonium nitrate, chlor-alkali and sodium cyanide plant operations. A comprehensive history of contamination sources in the region is given in Smith et al. (2003). We installed a 53 m transect of monitoring wells and nested beach piezometers perpendicular to the shoreline and parallel to the groundwater flow (Fig. 1b). The transect (Table 1) facilitated a two-dimensional study of the pre-discharge environment where groundwater could be sampled from 2 and 3 depths beneath the water table at 5 distances from the shoreline (labelled A–E) and one surface marine water location (F). Wells A1 and A2 were pre-existing monitoring bores that were screened fully through the SBS aquifer and TL aquifer, respectively, and wells B1 and B2 were pre-existing wells that were screened at the top and bottom of the SBS unit, and wells B3 and B4 were screened at the top and bottom of the TL unit. At the time of installation, the beach wells were screened at 1, 3 and 5 m below the water table (bwt) in the unconfined SBS aquifer (Fig. 1b) and were left in the beach for the duration of the project.

Groundwater samples were collected at low tide on November 15 2004, April 8 2005 and August 15 2005. These months corresponded to an early summer, late summer and mid winter seasonal sampling regime. Wells B3 and B4 were sampled using a peristaltic hammerhead pump and all other wells were sampled using a hand bailer. The bailer was rinsed with at least two times its volume before samples were collected. Water samples for N and P analysis were collected in 100 ml high density polyethylene containers, and samples for carbon (C) analysis were collected in 100 ml amber glass bottles. All containers were previously acid soaked in 10% hydrochloric acid, rinsed twice with deionised water (MilliQ Ultrapure) water and air dried then rinsed three times with sample water during collection. The water samples were stored in darkness and on ice and were filtered on the same day at the laboratory. Samples were filtered through 0.45 µm Sarstedt disposable filters and frozen for analysis (within 10 days) of NO_x^- , NH_4^+ , and FRP. Samples for total organic carbon (TOC), dissolved organic carbon (DOC) and total inorganic carbon (TIC) were stored at 4°C and were analysed within 2 days by combustion non-dispersive infrared method (NDIR; Shimadzu Corporation TOC 5000A). Filterable reactive phosphorus was analysed by the ascorbic acid method (Johnson 1982). Total nitrogen and total phosphorus were determined from autoclave digests with potassium persulphate (Valderrama 1981). Water samples were analysed for NO_x^- by copper-cadmium reduction (Johnson 1983), NH_4^+ by the alkaline phenate method (Switala 1993) and FRP by the ascorbic acid method (Johnson 1982). All analyses were carried out on a Lachat Quick-Chem 8000 Automated Flow Injection Analyser. Salinity, temperature, dissolved oxygen (DO) and pH were measured in the field immediately upon sample collection using a hand-held TPS WP-81 pH-Cond-Salinity meter with a conductivity probe (part number 122201) and a TPS Aqua-D DO meter with a TPS ED1 sensor. In the April 2005 sampling event a Yeo-Kal 611 multi-parameter water quality meter was used.

Beach sediment characterisation

Soil samples were collected at well location C at 1 m depth intervals for composition analysis. Grain size distribution was determined by Settling-Tube Analysis (2.22 m, 14°C) and the Gibbs equation (Gibbs

et al. 1971). Carbonate content of each sample was determined by acid decomposition, and organic carbon content was determined by sediment combustion at 540°C for 72 h.

Results

Beach sediment profile

Grain size was medium sized (70% of sediment = 0.5–2 ϕ size class) and was composed of carbonate, silicate and organic material (24–47% CO₃²⁻, 2.4–3.6% organic carbon). The organic carbon content of dried sediment was low at all depths except for 4 m from the surface (1.5 m bwt), where the combustion analysis returned high organic carbon (22%). The saturated sediments were highly fluidized and had a sulfurous odour. The sand colour was orange–white above the water table and became increasingly grey with depth, which suggested a progressively reducing environment.

Sea water

Salinity (Fig. 2) of the shoreline ocean water was measured at 34.9 in the early summer, 31.9 in the late summer and 30.6 during mid winter, the temperature ranged from 23.8, 21.9 and 16.8°C, respectively. We attribute the unexpectedly low salinity and temperature at the end of summer to freshwater flows delivered by rain and a cold front on the days prior to sampling. The dissolved oxygen (DO) content of the ocean water was at 50, 56 and 101% saturation (indicating high saturation due to wave activity) and dissolved nutrient concentrations were low (NO_x⁻ = 0.8–3.1 $\mu\text{mol l}^{-1}$, NH₄⁺ =

1–2.7 $\mu\text{mol l}^{-1}$, FRP = 4–16 $\mu\text{mol l}^{-1}$) reflecting the oligotrophic nature of the coastal waters.

Integrated and deep groundwater

The water temperature in the SBS and TL wells of locations A and B were similar (22.1°C), except for at the bottom of the TL aquifer at location B (23.7°C), which was similar to marine surface water temperatures (23.8°C) at the time of sampling and suggests recent seawater infiltration.

Samples of groundwater at locations A and B demonstrated high TN concentrations in the local groundwater (between 48.9 \pm 5 and 449 \pm 14 $\mu\text{mol l}^{-1}$ TN) and the majority of the N was present in the form of NH₄⁺ (between 29 and 332 $\mu\text{mol l}^{-1}$ TN). NO_x⁻ concentrations were similar to background levels (below detection limits, bdl, and 0.86 $\mu\text{mol l}^{-1}$ TN). Total organic carbon (TOC) were 1–2 orders of magnitude higher than TN concentrations, and greater TOC concentrations were measured in the SBS (3,372 \pm 83 mmol l⁻¹) than in the TL (137 \pm 41 mmol l⁻¹ at the top and 1,624 \pm 0.0 mmol l⁻¹ at the bottom of the TL aquifer). Filterable reactive phosphorus and TP concentrations were low in both aquifers (FRP was always below 2.0 $\mu\text{mol l}^{-1}$ and TP below 4.5 $\mu\text{mol l}^{-1}$). Evidence of seawater intrusion was observed in the TL at location B ($S = 7.4$ – 34.2 salinity in TL) but was not observed in the SBS or TL at location A ($S = 0.3$ – 0.8). It appears that both the TL and SBS aquifers contained elevated concentrations of NH₄⁺ at location A, with greater contamination in the upper sand aquifer. The source of high concentrations were likely to be associated with a chemical plant and/or an oil refinery that is located immediately adjacent to the beach site.

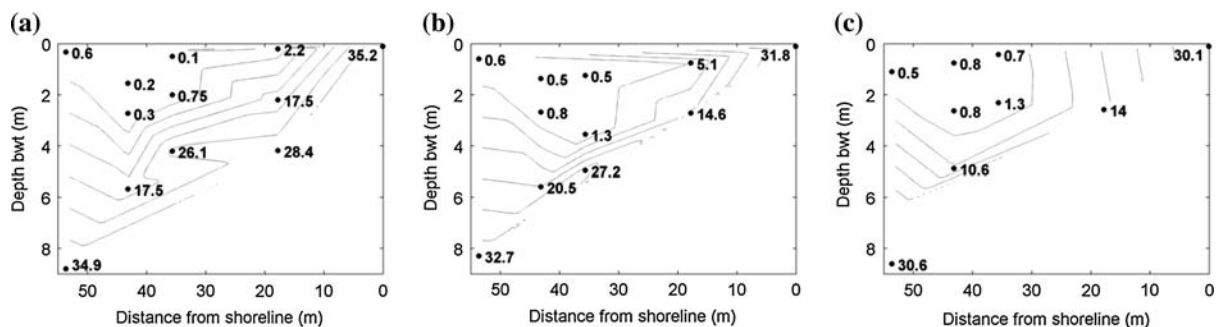


Fig. 2 Salinity profiles in the beach groundwater with inferred contour lines at intervals of five

The purpose of bores at location A aimed to provide an upland endmember estimate of natural or regional nitrogen concentrations but as location A contained a high source of nitrogen and was located a long distance from the rest of the transect, the data from these bores are not described further. Only beach processes will be focussed upon in this paper.

Shallow groundwater

Two-dimensional (2D) profiles of beach chemistry are presented in Figs. 2, 3, 4 and 5. In these figures the sample depths are relative to the water table height. Contour lines were inferred by linear interpolation of the data points and have been drawn at a higher resolution than the data points as an aid for discussion of the data. During the course of the study three wells were damaged by storms and they were not replaced, and so some data points are missing from the profiles of the late summer and winter studies.

The 2D salinity profiles (Fig. 2a–c) revealed the typical saline characteristics of a subterranean estuary, where a lens of fresh groundwater (0.1 salinity) tapered narrowly toward the seaward discharge region over an intruding salt wedge of sea water (with a salinity of up to 35 in the salt wedge), and where a vertical salinity gradient indicated that there was some mixing between the two layers. The highest salinities for each well was observed at the end of summer, after a long dry period of little rain, and the lowest salinity for each well was observed during winter, indicating an increased flow of fresh groundwater with the seasonal rainfall. The salinity in the deeper beach wells decreased by as much as 7 in mid-winter. Porewater surveys of Smith et al. (2003) demonstrated that the freshwater layer discharged up

to 5 m beyond the shoreline in this region. In this study, samples were not collected beyond the shoreline, and it is possible that freshwater was discharging beyond the water-line at the time of sample collection.

Temperature differences between the fresh and marine groundwater also demonstrated the Ghyben-Herzberg gradient (not shown) and reflected the summer and winter air temperatures. The temperature of the freshwater lens was up to 3°C cooler than the seawater at the surface. In late summer, the groundwater temperature profile was uniform ($\pm 0.5^\circ\text{C}$) regardless of salinity, reflecting the long period of consistent temperature conditions in surface and ground waters.

Groundwater was anoxic or suboxic at all times, however, the oxygen gradients were different across sampling events (Fig. 3a–c). The fresh water lens in the shallow wells displayed similar low oxygen concentrations across the seasons (7–13% saturation, and an incident of a higher 24% oxygen saturation) in the deeper wells we recorded the lowest oxygen conditions (0.4% saturation).

Two-dimensional profiles of NO_x^- , NH_4^+ and TN concentrations for the three sampling events are presented in Fig. 4. At the upland end of the groundwater transect, N concentrations (up to $407 \mu\text{mol TN l}^{-1}$, $143 \mu\text{mol l}^{-1} \text{NO}_x^-$ and $371 \mu\text{mol l}^{-1} \text{NH}_4^+$) were an order of magnitude greater than reported regional groundwater background levels ($0.2 \mu\text{mol l}^{-1} \text{TN}$, from Appleyard 1994; Smith et al. 2003) and in surface water samples collected in this study ($0.2\text{--}39 \mu\text{mol l}^{-1}$, Fig. 4). The NO_x^- and NH_4^+ concentrations tended to decrease toward discharge, however, the distribution was more temporally patchy with some hotspots, for example there was an end-of-summer pool of NO_x^- in the mid-region of the transect at

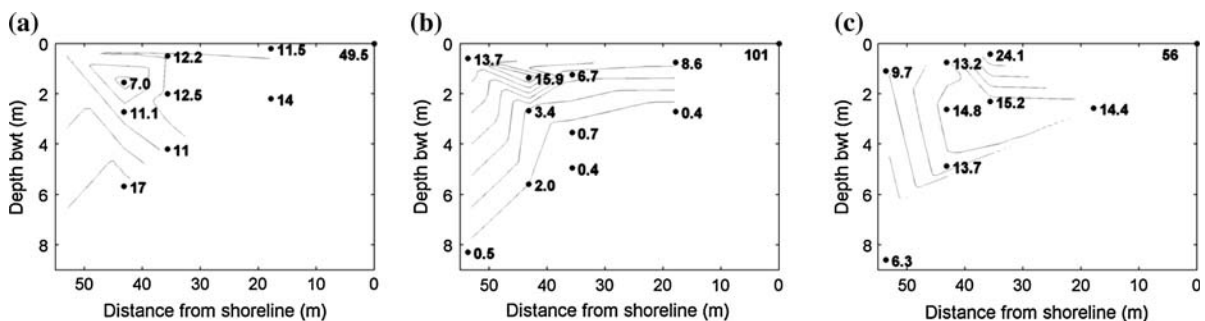


Fig. 3 Seasonal dissolved oxygen (% saturation) in beach groundwater with inferred contour intervals of 2%

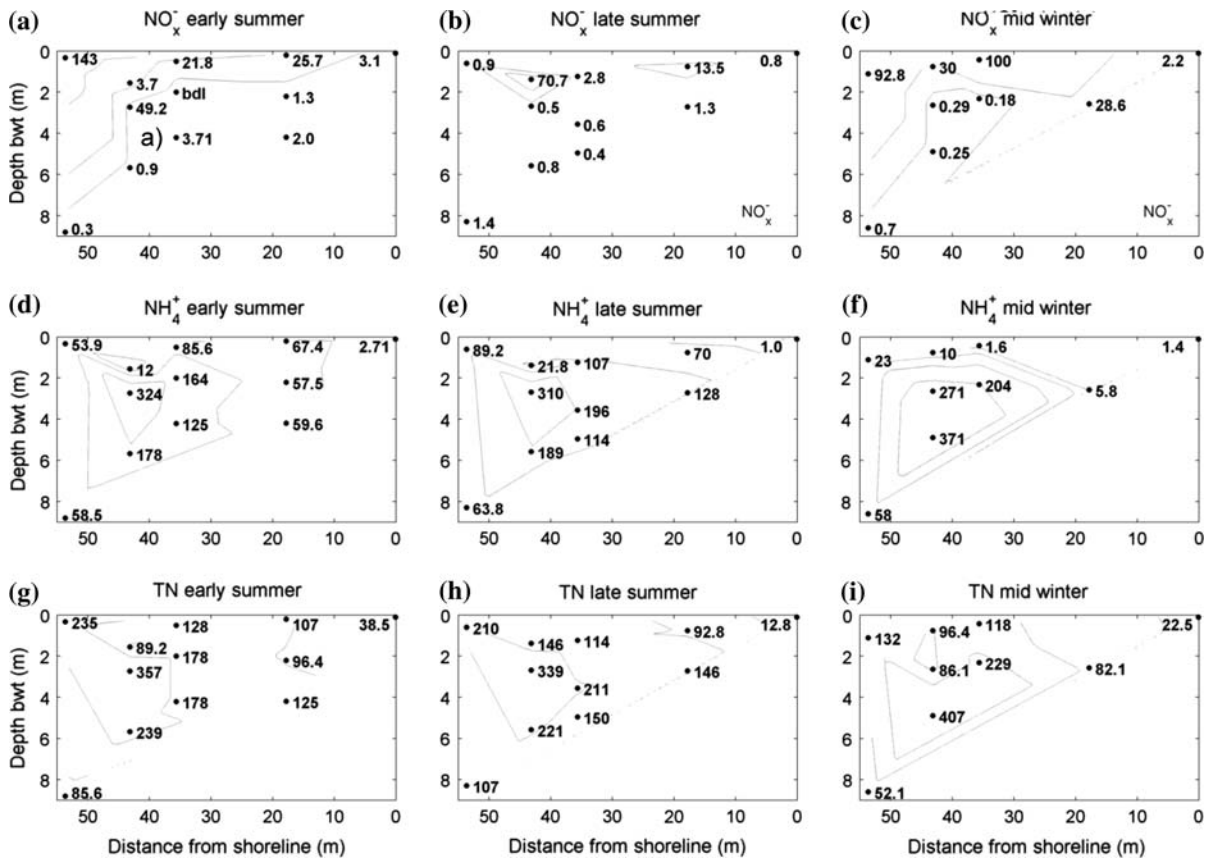
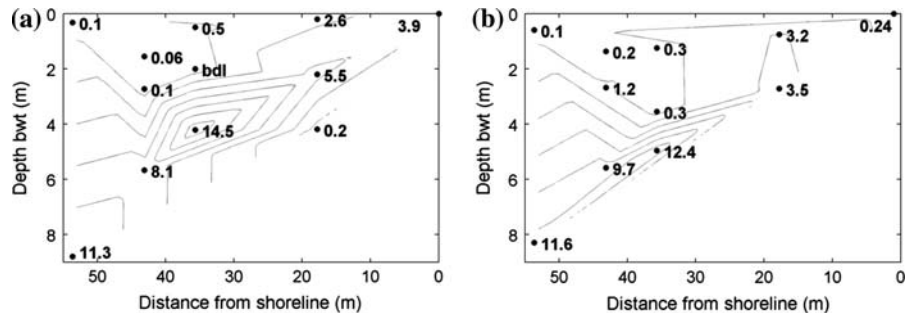


Fig. 4 Seasonal groundwater pre-discharge nitrogen concentrations. **a** NO_x^- $\mu\text{mol l}^{-1}$ at the end of winter, **b** end of summer and **c** mid-winter; **d** NH_4^+ $\mu\text{mol l}^{-1}$ at the end of winter, **e** end

of summer and **f** mid winter; **g** TN $\mu\text{mol l}^{-1}$ at the end of winter, **h** end of summer and **i** mid winter with adjusted logscale contour lines to highlight hotspots of variable concentration

Fig. 5 Elevated filterable reactive phosphorus, FRP $\mu\text{mol l}^{-1}$ at the freshwater–marine water interface with inferred contour lines of 2 μM **a** at the end of winter, and **b** end of summer



Well C1, Fig. 4b). Ammonium peak concentrations (Fig. 4d–f) were located at the bottom of the freshwater lens. At the end of summer, higher NH_4^+ concentrations were detected closer to the watertable that at other sampling times.

The TN concentration in Well C2 in mid winter was questionable ($86.1 \pm 50 \mu\text{mol l}^{-1}$, Fig. 4i) as it

is less than the sum of NO_x^- and NH_4^+ ($271 \pm 7.1 \mu\text{mol l}^{-1}$). This may be due to a handling error of this sample. There was agreement between duplicate samples in all other samples.

Total organic carbon and DOC concentrations in groundwater (TOC = 0.35–4.9 mmol l^{-1} , DOC = 0.28–4.6 mmol l^{-1}) were elevated relative to the

surface marine water (TOC = 0.14–0.2 mmol l⁻¹, DOC = 0.1–0.19 mmol l⁻¹), with lowest concentrations observed in the shallow wells C1–E1 (0.61–2.6 mmol l⁻¹) during early and late summer, and highest concentrations (up to 4.9 mmol l⁻¹) were observed in B1 and the mid-depth wells (C2 and E2). In mid-winter we observed much lower concentrations of TOC across the transect, between 0.4 and 0.9 mmol l⁻¹ in all wells except C2, where a high value of 3.0 ± 0 mmol l⁻¹ was recorded. This corresponds to a region of high POC concentration in the sediment grain analysis and may represent an in situ source of organic matter. In all sampling events, carbon concentration decreased with distance towards discharge and was in excess to the quantity of nitrogen (TOC/TN ranged from 6.8 to 10 in early summer, 7.2 to 15 in late summer, and 4.1 to 30 in midwinter, and the highest ratios always observed in Well C2). The measured pH of the groundwater was neutral (6.8–7.5) in all studies.

Filterable reactive phosphorus and TP concentrations were measured during early summer (Fig. 5a) and the end of summer (Fig. 5b). Analysis for FRP was unintentionally omitted for mid winter. At the sampled times, FRP was very low in the shallow wells and in the surface ocean water (0.24–4.0 $\mu\text{mol l}^{-1}$), with a similar trend for TP, but with elevation in the beach ground waters.

Discussion

Controls on beach groundwater quality

Water level

Coastal groundwater seepage is driven by the groundwater table elevation, mean sea level and tidal amplitude (Turner et al. 1997; Robinson et al. 2007a, b). We collected groundwater samples during the spring low tide to capture maximum outflow from the beach, which includes saline and fresh groundwater. However, because the south-western Australian ocean is microtidal with a maximum spring tide of approximately 0.75 m, the effect of tide on discharge would be expected to be minor compared to other oceanographic effects.

The seasonal fluctuation of regional groundwater levels is 1–1.5 m, with the maximum water level at the end of spring (October), and minimum at the end

of autumn (May; data from Western Australian Department of Environment 2004). We did observe a seasonal change in water table height between the early summer (November 1.775 Australian Height Datum, mAHD) and end of summer (April 1.765 mAHD), and elevation of the water table in mid-winter (August 2.205 mAHD). The low water table level observed in the early summer in 2004 coincided with the end of a relatively dry winter in which 198.6 mm of rainfall was recorded in the region from January to June 2004, compared 504.2 mm of rain from January to June 2005 (Bureau of Meteorology 2005).

Salinity

Salinity was higher at the end of summer than early summer, indicating weakening of the freshwater hydraulic gradient and landward progression of the marine interface in the beach groundwater. Refreshing was observed in mid winter as freshwater flow in the aquifer was re-established.

Temperature

No seasonal increase or decrease of overall beach groundwater temperature was observed for the three sampling events. From temperature profiles, it appeared that wells at the seaward end were influenced by ocean temperatures. In early summer, the groundwater temperature gradient showed a cooler (21.4–21.7°C) freshwater lens that reflected the outgoing winter water, and an underlying warmer salt-wedge (23.1–24.6°C) that reflected warmer marine water. After the passage of a cold-front in late summer, the nearshore wells showed lower temperatures, demonstrating infiltration of cooler water through the beach, while the upland and deep wells showed warmer saline conditions that were typical of the summer season. In mid winter the groundwater temperature profile was more uniform due to the similarity of land and marine water temperature at this time.

Chemistry

We observed a hotspot in the top of the water table at Well C1, where the NO_x^- concentration was

18–68 $\mu\text{mol l}^{-1}$ greater than up-gradient and down-gradient wells and the NH_4^+ concentration was 11–87 $\mu\text{mol l}^{-1}$ less than the up-gradient and down-gradient wells (Fig. 5). An assessment of the beach TOC and DOC concentrations (normalised to salinity to account for dilution by seawater, data not shown here) indicated that the groundwater at Well C1 and E1 were depleted in organic carbon relative to the other wells, and so it is possible that carbon was being consumed in this hotspot of biogeochemical activity. The hotspot may have been the result of a localised injection of organic matter or nutrients, however, our sampling resolution was not sufficient to identify a point-source of NO_x^- within the flow field. As there was no visible above-ground source of disturbance to Well C that might have contributed to changed nutrient concentrations we attribute the variable nutrient concentrations to redox-driven biogeochemical reactions.

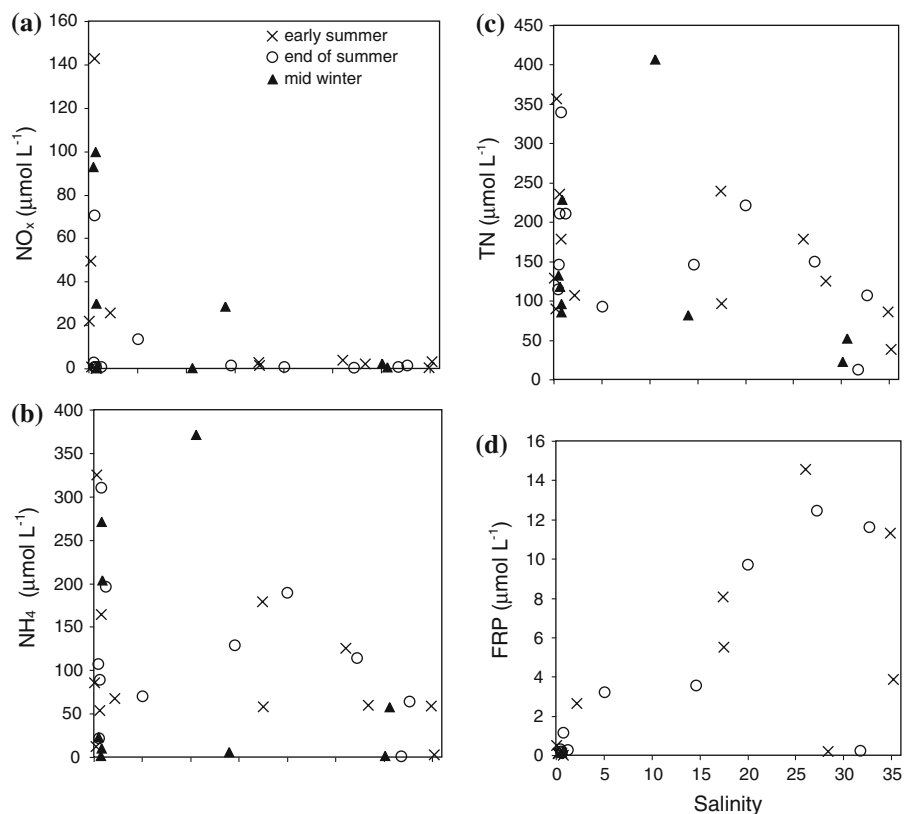
Mixing plots were constructed (Fig. 6) using the concentration of surface seawater at as one endmember, and upland concentrations of Well B1 to represent the other endmember. The measured

concentrations (symbols in Fig. 6) illustrate that declining nitrogen concentrations did not coincide with an increase in salinity.

We measured low concentrations of FRP in surface of the upland wells ($0.1 \mu\text{mol l}^{-1}$) that were consistent with the reported regional concentrations. We also measured an increase in FRP with depth into the aquifer (Fig. 5a, b). These concentrations are closely associated with increasing salinity (Fig. 6d) suggesting reducing conditions in the saline groundwater or the precipitation and dissolution of sediment-bound iron-oxides in the salt wedge (Suzumura et al. 2000; Charette and Sholkovitz 2002; Charette et al. 2005; Spiteri et al. 2008b). Thus, redox conditions in the subterranean discharge environment may produce a local source of P to marine surface waters.

Aquifer material, changing recharge conditions, overlying sources of nutrients, groundwater residence time, inputs of oxygen (mixing or overhead diffusion), subterranean marine water mixing, and the consumption of oxygen and nutrients by bacterially mediated decomposition of organic matter are environmental processes that can influence N speciation

Fig. 6 Mixing plots of groundwater nutrient concentrations relative to groundwater salinity grouped for the early summer, late summer and mid winter sampling events. **a** $\text{NO}_x^- \mu\text{mol l}^{-1}$, **b** $\text{NH}_4^+ \mu\text{mol l}^{-1}$, **c** TN $\mu\text{mol l}^{-1}$ and **d** FRP $\mu\text{mol l}^{-1}$



(Drever 1982). The NO_x^- and NH_4^+ profiles demonstrate that NO_x^- was the dominant form of dissolved N at the top of the shallow groundwater and NH_4^+ dominated in the mid-region (Fig. 4a, b). This suggested that oxic conditions were overlying reducing conditions in the beach groundwater (Corbett et al. 2000; Ullman et al. 2003; Slomp and Van Cappellen 2004; Hays and Ullman 2007; Kroeger and Charette 2008).

We did not expect that nitrogen assimilation by interstitial aerobic organisms was significant in the aquifer due to the largely anaerobic subsurface pre-discharge environment (Korom 1992) and discount it from consideration in this study. Decomposition of particulate organic matter was a possible source of ammonium increase, through ammonification, and this process may be restricted to the surface of the groundwater lens if suitable electron acceptors are more concentrated in the unsaturated zone than the saturated zone. Denitrification from NO_3^- to nitrogen gas (N_2) in anaerobic conditions may lessen NO_x^- concentrations and would be indicated by a corresponding decrease of TN. Dissimilatory nitrate reduction to ammonia (DNRA) could decrease the NO_3^- concentrations, by reducing the nitrogen to NH_4^+ under anaerobic conditions without any net loss of TN.

We believe that vertical stratification of NO_x^- and NH_4^+ within the groundwater was the result of nitrogen oxidation at the top of the watertable where oxygen is intermittently available, and so at the higher measured levels of DO ($\sim 15\%$ saturation) in the aquifer nitrification of the N source produced higher NO_x^- concentrations. At intermediate DO concentrations in the aquifer ($\sim 5\text{--}15\%$ saturation) there was an increase in NO_x^- , a decrease in NH_4^+ , and decrease in TN, and so potentially there is nitrification coupled with denitrification. At the lowest measured DO levels ($<5\%$ saturation) ammonification and DNRA may produce higher NH_4^+ concentrations. The work of Ullman et al. (2003) supports this finding that nitrification occurs at the top of beach groundwater where there is aeration from tidal pumping and wave swash, while ammonification and DNRA are dominant processes in the deeper groundwater and these processes sustain elevated NH_4^+ concentrations in deeper zones.

There were two hotspots in the beach transect where nutrient concentrations were much higher or

lower than in neighbouring wells, first at the end of summer in Well C1 and then during mid-winter in Well D1 (Fig. 4). At these locations there was a pool of elevated NO_x^- (Fig. 4b, c), and low NH_4^+ (Fig. 4e, f) relative to the neighbouring wells. An outside source at this well was unlikely as there was no evidence of additional impacts in the immediate vicinity of C1, and C1 appeared as the same as the rest of the transect: an undisturbed vegetated sand dune. These nutrient hotspots coincided with a pool of increased oxygen, relative to the other wells. This patchiness indicated a potential conversion between NH_4^+ and NO_x^- via oxidation, however, there was loss in TN around this patchiness, and so it seems that there may have been coupled nitrification–denitrification where there is a surplus of organic matter and changing oxygen concentrations.

In a study of variable nutrient concentrations in shallow groundwater discharging from an agricultural catchment (Susanna Brook, approximately 100 km north-east of Cockburn Sound), Ocampo et al. (2006) demonstrated that a changing flow velocity of the groundwater drives change of the two-dimensional nutrient profile in subterranean groundwater, and in shallow sandy soils of Cape Cod (USA), Kroeger and Charette (2008) showed that short residence times in a fast flowing groundwater layer may prevent nutrient reaction or attenuation. To estimate the role of transport versus reaction time in our beach transect, we calculated the groundwater discharge velocity (as specific discharge, Q , $\text{m}^3 \text{day}^{-1}$ in the fresh layer) using Darcy's Law

$$D = KA \frac{dh}{dl} \quad (1)$$

where K is the hydraulic conductivity (m day^{-1}) of the aquifer material, A is the cross-sectional area of flow and dh/dl is the hydraulic gradient (m) (Fetter 1994). Due to the high dependency on the K , we applied a range of reported K estimates for the Safety Bay Sands and present mid-range, minimum and maximum results. The minimum applied K value was 4.5 m day^{-1} , obtained from an unpublished study of sands at the same location (James Point) by Bodard in 1991 and cited Smith and Nield (2003). A maximum K value of 50 m day^{-1} was applied, obtained from a study by Appleyard and cited in Smith and Nield (2003). A mid-range value of $K = 10$ was selected as a conservative estimate of K within this range. The

pore velocity, v_{pw} (m day⁻¹), of the groundwater flow was calculated using

$$v_{pw} = K \frac{dh}{dl} n \quad (2)$$

where v_{pw} is the velocity of water through the pores, using the effective porosity ($n = 0.3$) to account for microscale interactions (such as adsorption) between the sand and porewater (Fetter 1994).

For the conservative estimate of K (10 m day⁻¹) we arrive at a minimum summertime seepage velocity of $v_{pw} = 0.14$ m day⁻¹ and a discharge of $Q = 4.8$ m³ day⁻¹ m⁻¹ and maximum wintertime seepage of $v_{pw} = 0.18$ m day⁻¹ and $Q = 5.8$ m³ day⁻¹ m⁻¹ (Table 2). Across the range of K values, the v_{pw} ranged from 0.06 to 0.77 m day⁻¹ (23–281 m year⁻¹) and Q ranged from 2 to 30 m³ day⁻¹ m⁻¹ (Table 2). These discharge estimates agreed with published regional-scale estimates of discharge (2.5–8 m³ day⁻¹ m⁻¹, Smith and Nield 2003), and are an order of magnitude higher than cited estimates for the SBS (0.1–0.6 m³ day⁻¹ m⁻¹, Bodard and Appleyard, as cited in Smith and Nield 2003). We expected more agreement between the Bodard and Appleyard values and ours, as both estimates used parameters that were specific to the James Point superficial sands, rather than regional parameters that incorporate sand and limestone aquifers. This disparity may be due to inter-annual variability of rainfall and groundwater flow.

Using our measured concentrations of NO_x⁻, NH₄⁺ and FRP in the nearest beach wells (and neglecting any further biogeochemical effect on nutrient concentrations from the last well to the discharge point) we estimate an annual nutrient load of 0.4–13 kg day⁻¹ of NO_x⁻, 0.2–24 kg day⁻¹ of NH₄⁺ and 0.004–0.8 kg day⁻¹ of FRP. We arrive at an estimated TN load of 2.5–43 kg day⁻¹ which is 1–2 orders of magnitude less than past estimates. This difference may be due to the site-specificity of our estimate and our account for nutrient attenuation in the beachface.

Based on our sampling resolution and load estimates, FRP supply was greater in late summer than in the early summer (mid-winter estimate was not available) and NO_x⁻ and NH₄⁺ supply to the coastal ocean was greater in mid-winter and early summer. As different biogeochemical processes determine NO_x⁻, NH₄⁺ and FRP levels in the groundwater, it would be worthwhile investigating SGD nutrient fluxes over a higher seasonal resolution to understand the implications of seasonal variability in the beach aquifer on marine organisms. As highlighted by the biogeochemical modelling of Spiteri et al. (2008a, b), highly variable N:P ratios can result from variable redox conditions in the beach aquifer and this differential in N and P supply, both in timing and in magnitude, may impede or deliver ideal conditions for nutrient uptake by marine primary producers.

Table 2 Specific groundwater discharge Q , velocity v and porewater velocity v_{pw} over a range of hydraulic conductivities, K

Season	Δh m	i	K m day ⁻¹	Q m ³ day ⁻¹ m ⁻¹	v_{pw} m year ⁻¹	Q NO _x ⁻ kg day ⁻¹	Q NH ₄ ⁺ kg day ⁻¹	Q TN kg day ⁻¹	Q FRP kg day ⁻¹
Early summer	1.775	0.051	10	5.1	56	2 ± 0.1	5 ± 0.05	8 ± 1	0.01
			4.5	2.3	25	0.8 ± 0.05	2 ± 0.02	3 ± 0.5	0.004
			50	26	281	9 ± 0.5	24 ± 0.3	38 ± 5	0.05
Late summer	1.565	0.047	10	4.7	52	0.9 ^a	5 ^a	6 ^a	0.8 ^a
			4.5	2.1	23	0.4 ^a	2 ^a	3 ^a	0.3 ^a
			50	24	260	5 ^a	23 ^a	31 ^a	4 ^a
Mid-winter	2.205	0.059	10	5.9	29	2 ± 0.2	0.5 ± 0	7 ± 0.9	NA
			t	2.7	0	1 ± 0.08	0.2 ± 0	3 ± 0.4	NA
			50	30	56	12 ± 0.9	2 ± 0.02	34 ± 5	NA

Δh = Watertable height at well B1 above surveyed low tide mark -0.98 m Australian Height Datum, this study, November 2004

i = Hydraulic gradient fitted regression for dh/dl across all wells

NA samples not collected

^a Replicate samples were omitted and variability can not be estimated

Conclusion

Our study presented further evidence of the emerging complexity of describing nutrient loads from submarine groundwater. Marine water oscillation in the aquifer increased the concentration of P by ion exchange or by dissolution of iron-bound phosphorus from the beach sediments, and a slow groundwater velocity (0.14–0.18 m day⁻¹) and low oxygen conditions presented a suitable environment for biologically mediated reduction of nitrogen to occur. Based on the decreased concentration of nitrogen, the estimated nitrogen load to the marine environment was 1–2 orders of magnitude less than past regional estimates, reflecting the heterogeneity of regional groundwater and influence of the biogeochemical environment in the beach aquifer. Of the three sampled occasions, the greatest load of N to marine waters occurred when freshwater discharge was greatest and it is possible that a greater load of P occurred when saline flows from the aquifer are highest. This uncomplicated snapshot study demonstrates a relatively simple approach to refining estimates of N and P discharge to marine waters.

Acknowledgments We thank Dr. Rod Lukatelich, Dr David Reynolds, Dr. Ian Eliot, and Ms Ailbhe Travis for site-related and logistical support, and appreciate the field assistance of Deb Read and Nikki Grieve. The manuscript benefited from comments by Dr. Anas Ghadouni, UWA. This study was supported by grants from CSIRO SRFME, Kwinana Industries Council and the Centre for Groundwater Studies. The constructive comments of four anonymous reviewers are appreciated, as are those provided by Dr M. Charette, Dr A. Payton and Dr J. Turner on this manuscript in its form within a PhD thesis. This paper is School of Environmental Systems Engineering report ED1789AL.

References

- Andersen MS, Baron L, Gudbjerg J, Gregersend J, Chapellier D, Jakobsen R, Postma D (2007) Discharge of nitrate-containing groundwater into a coastal marine environment. *J Hydrol* 336:98–114
- Appleyard S (1994) The discharge of nitrogen and phosphorus from groundwater into Cockburn Sound, Perth, Metropolitan region. Geological Survey of Western Australia hydrogeology report 1994/39, Perth
- Bureau of Meteorology (2005) Weather station data. <http://www.bom.gov.au/climate/data/weather-data.shtml> cited Sep 2005. Australian Government site
- Burnett WC, Dulaiova H (2003) Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *J Environ Radioact* 69:21–35
- Chanton JP, Burnett WC, Dulaiova H, Corbett DR, Taniguchi M (2003) Seepage rate variability in Florida Bay driven by Atlantic tidal height. *Biogeochem* 66:187–202
- Charette MA, Sholkovitz ER (2002) Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophy Res Lett* 29. doi: 10.1029/12001GLO145I2
- Charette MA, Sholkovitz ER (2006) Trace element cycling in a subterranean estuary: part 2. Geochemistry of the pore water. *Geochim Cosmochim Acta* 70:811–826
- Charette MA, Buesseler KO, Andrews JE (2001) Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. *Limnol Oceanogr* 46:465–470
- Charette MA, Splivallo R, Herbold C, Bollinger MS, Moore WS (2003) Salt marsh submarine groundwater discharge as traced by radium isotopes. *Mar Chem* 84:113–121
- Charette MA, Sholkovitz ER, Hansel C (2005) Trace element cycling in a subterranean estuary: part 1. Geochemistry of the permeable sediments. *Geochim Cosmochim Acta* 69:2095–2109
- Corbett DR, Chanton J, Burnett W, Dillon K, Rutkowski C, Fourqrean JW (1999) Patterns of groundwater discharge in Florida Bay. *Limnol Oceanogr* 44:1045–1055
- Corbett DR, Kump L, Dillon K, Burnett W, Chanton J (2000) Fate of wastewater-borne nutrients under low discharge conditions in the subsurface of the Florida Keys, USA. *Mar Chem* 69:99–115
- D'Adamo N, Mills DA (1995) Field measurements and baroclinic modelling of vertical mixing and exchange during Autumn in Cockburn Sound and adjacent waters. Western Australia Department of Environmental Protection, Perth, Western Australia, 6000, technical series no. 71
- Department of Environment (2004) Perth groundwater atlas, 2nd edn. Western Australian Department of Environment, hydrogeology report no. 202, Perth, Australia
- Destouni G, Prieto C (2003) On the possibility for generic modeling of submarine groundwater discharge. *Biogeochem* 66:171–186
- Drever JI (1982) The geochemistry of natural waters: surface and groundwater environments. Prentice-Hall, New Jersey
- Duarte CM (2002) The future of seagrass meadows. *Environ Cons* 29:192–206
- Fetter CW (1994) Applied hydrogeology. Prentice Hall, New Jersey
- Gibbs RJ, Matthews MD, Link DA (1971) The relationship between sphere size and settling velocity. *J Sediment Petrol* 41:7–18
- Giblin AE, Gaines AG (1990) Nitrogen inputs to a marine embayment: the importance of groundwater. *Biogeochem* 10:309–328
- Gobler CJ, Boneillo GE (2003) Impacts of anthropogenically influenced groundwater seepage on water chemistry and phytoplankton dynamics within a coastal marine system. *Mar Ecol Prog Ser* 255:101–114
- Hays RL, Ullman WJ (2007) Direct determination of total and fresh groundwater discharge and nutrient loads from a sandy beachface at low tide (Cape Henlopen, Delaware). *Limnol Oceanogr* 52:240–247
- Herrera-Silveira JA, Medina-Gomez I, Colli R (2002) Trophic status based on nutrient concentration scales and primary

- producers community of tropical coastal lagoons influenced by groundwater discharges. *Hydrobiologia* 475(476):91–98
- Johannes RE (1980) The ecological significance of the submarine discharge of groundwater. *Mar Ecol Prog Ser* 3:365–373
- Johnson KS (1982) Determination of phosphate in seawater by flow injection analysis with injection of reagent. *Anal Chem* 54:1185–1187
- Johnson KS (1983) Determination of nitrate and nitrite in seawater by flow injection analysis with injection of reagent. *Limnol Oceanog* 28:1260–1266
- Kendrick GA, Aylward MJ, Hegge BJ, Cambridge ML, Hillman K, Wyllie A, Lord DA (2002) Changes in seagrass coverage in Cockburn Sound, Western Australia between 1967 and 1999. *Aquat Bot* 73:75–87
- Korom SF (1992) Natural denitrification in the saturated zone: a review. *Water Resour Res* 28:1657–1668
- Kroeger K, Charette M (2008) Nitrogen biogeochemistry of submarine groundwater discharge. *Limnol Oceanog* 53:1025–1039
- Lourey MJ, Dunn JR, Waring J (2006) A mixed-layer nutrient climatology of Leeuwin Current and Western Australian shelf waters: seasonal nutrient dynamics and biomass. *J Marine Syst* 59:25–51
- Loveless AM, Oldham CE, Hancock GJ (2008) Radium isotopes reveal seasonal groundwater inputs to Cockburn Sound, a marine embayment in Western Australia. *J Hydrol* 351:203–217
- Michael HA, Lubetsky JS, Harvey CF (2003) Characterizing submarine groundwater discharge: a seepage meter study in Waquoit Bay, Massachusetts. *Geophys Res Lett* 30:1297
- Michael HA, Mulligan AE, Harvey CF (2005) Seasonal oscillations in water exchange between aquifers and the coastal ocean. *Nature* 436:1145–1148
- Moore WS (1996) Large groundwater inputs to coastal waters revealed by ²²⁶Ra enrichments. *Nature* 380:612–614
- Moore WS (2003) Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. *Biogeochem* 66:75–93
- Ocampo CJ, Oldham CE, Sivapalan M (2006) Nitrate attenuation in agricultural catchments: shifting balances between transport and reaction. *Water Resour Res* 42:W01408
- Pearce A, Hellen S, Marinelli M (2000) Review of productivity levels of Western Australian coastal and estuarine waters for mariculture planning purposes. Fisheries Research Division research report no. 123, Department of Fisheries Western Australia, p 67
- Robinson C, Gibbes B, Carey H, Li L (2007a) Salt-freshwater dynamics in a subterranean estuary over a spring-neap tidal cycle. *J Geophys Res* 112:C09007
- Robinson C, Li L, Prommer H (2007b) Tide-induced recirculation across the aquifer–ocean interface. *Water Resour Res* 43:W07428
- Santos IR, Burnett WC, Chanton J, Mwashote B, Suryaputra IG, Dittmar T (2008) Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. *Limnol Oceanog* 53:705–718
- Simpson CJ (ed) (1996) Southern metropolitan coastal waters study, 1991–1994. Department of Environmental Protection report 17, Perth, Western Australia, p 288
- Slomp CP, Van Cappellen P (2004) Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *J Hydrol* 295:64–86
- Smith AJ, Nield SP (2003) Groundwater discharge from the superficial aquifer into Cockburn Sound Western Australia: estimation by inshore water balance. *Biogeochem* 66:125–144
- Smith AJ, Turner JV, Herne DE, Hick WP (2003) Quantifying submarine groundwater discharge and nutrient discharge into Cockburn Sound Western Australia. Technical report no. 01/03, Commonwealth Scientific and Industrial Research Organisation, Floreat, Western Australia, p 185
- Spiteri C, Slomp CP, Charette MA, Tuncay K, Meile C (2008a) Flow and nutrient dynamics in a subterranean estuary (Waquoit Bay, MA, USA): field data and reactive transport modelling. *Geochim Cosmochim Acta* 72:3398–3412
- Spiteri C, Slomp CP, Tuncay K, Meile C (2008b) Modeling biogeochemical processes in subterranean estuaries: effect of flow dynamics and redox conditions on submarine groundwater discharge of nutrients. *Water Resour Res* 44:W02430
- Suzumura M, Ueda S, Sumi E (2000) Control of phosphate concentration through adsorption and desorption processes in groundwater and seawater mixing at sandy beaches in Tokyo Bay, Japan. *J Oceanog* 56:667–673
- Switala K (1993) Determination of ammonia by flow injection analysis colorimetry dialysis. Lachat Instruments, Milwaukee
- Taniguchi M, Burnett WC, Cable JE, Turner JV (2002) Investigation of submarine groundwater discharge. *Hydrol Process* 16:2115–2129
- Turner I, Coates B, Acworth RI (1997) Tides, waves and the super-elevation of groundwater at the coast. *J Coast Res* 13:46–60
- Ullman WJ, Chang B, Miller DC, Madsen JA (2003) Groundwater mixing, nutrient diagenesis, and discharge across a sandy beachface, Cape Henlopen, Delaware, USA. *Estuar Coast Shelf Sci* 57:539–552
- Valderrama J (1981) The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Mar Chem* 10:109–122