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List of Conference Presentations

Australian Marine Sciences Association, Fremantle, 10-12 Jul 02, “The Development and Validation of Algorithms for Remotely Sensing Case II Waters”

Australian Meteorological and Oceanographic Society, UWA, 10-12 Feb 03, “Hyperspectral Remote Sensing of Western Australian Coastal Waters”

SPIE - The International Society for Optical Engineering, San Diego, 3-8 Aug 03, “Hyperspectral Remote Sensing of Western Australian Coastal Waters”

Ocean Optics, Fremantle, 25-29 Oct 04, “Bottom Type Classification using Hyperspectral Imagery”

Australian Remote Sensing and Photogrammetry Conference, Fremantle, 18-21 Oct 04, “Characterisation of Seagrass Beds using HyMap Imagery”

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Publications

Klonowski, W., (2003). Hyperspectral remote sensing of Western Australian coastal waters, The International Society for Optical Engineering *5515,* 201-210.

2.2.6 Spatial, temporal and biogeochemical dynamics of submarine groundwater discharge in a semi-enclosed coastal basin

Investigator / Institution

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Executive Summary

This PhD study applied a variety of field sampling techniques in conjunction with surface water hydrodynamic modelling to achieve a process-based understanding of spatial, temporal and biogeochemical dynamics of groundwater discharge in marine waters. Field investigations were carried out in Cockburn Sound, a semi-enclosed marine basin located approx. 12 km south of Fremantle, Western Australia. This site was selected in part for its topical relevance to Western Australian marine health, but also for the complexity of groundwater discharge dynamics that arises from complex interactions between chemistry, hydrogeology, bathymetry and oceanography.

Results indicated that groundwater discharge was highly spatially and temporally heterogeneic. Additionally, the availability of post-discharge groundwater in marine surface

waters was seasonally dependant on coastal conditions and hydrogeologic forcing. Biogeochemical studies of groundwater nutrient dynamics prior to discharge also indicated that, an understanding of the groundwater nutrient climate was essential for estimating groundwater input of dissolved materials to marine waters. The seasonal and spatial dynamics discovered by this work suggest that mid-winter is a key time of contaminant availability to surface water biota.

Introduction

This study aimed to traverse land and marine hydrogeology in order to examine biogeochemical and oceanography dynamics at the convergence of groundwater and marine water. A two-year groundwater and surface water sampling program was applied to capture the spatial, seasonal and biogeochemical dynamics of SGD in a sheltered, oligotrophic marine basin.

Objectives

Objective 1: Quantify groundwater discharge volume into a marine basin. This estimate will improve on past estimates of SGD by accounting for geological heterogeneity and unknown sources of groundwater input.

Objective 2: Identify if nutrient concentrations are altered on the pathway to discharge in the subterranean predischarge environment. Understanding nutrient biogeochemistry enables confident estimation of nutrient input to surface waters via groundwater discharge.

Objective 3: Identify spatial and temporal patterns of groundwater availability in the surface environment.

Study Site

The seasonal climate and occurrence of contaminated groundwater discharge in Cockburn Sound, Western Australia (Figure 2.21a) made this location an ideal site to study groundwater biogeochemistry. Superficial groundwater flows westerly from recharge zones to discharge into Cockburn Sound (Figure 2.21a). The superficial aquifer consists of an unconfined 5-10 meter surface layer of sand, underlain by a ~10 m layer of Tamala limestone (Figure 2.21b). Discharge from the sand aquifer occurs at the beach on the eastern shoreline, through a narrow (~5m wide) discharge zone (Smith *et al.*, 2003).

West Australian ocean waters are nitrogen limited, with some elevation of nutrient concentrations occurring at the coast. Natural regional groundwater nutrient concentrations are near analytical detection limits, however up to 11,000 μmol.N/L of NO_x and 27,000 μmol. N/L of NH_4^+ have been measured in contaminated groundwater in the Cockburn Sound industrial strip (this study, and Smith et al., 2003). Nitrogen contamination of the surface waters from point and non-point sources have caused significant water quality decline and seagrass mortality. Despite removal of point-sources and the re-establishment of low surface water DIN concentrations, chlorophyll-*a* (Chl-*a*) concentrations still indicate elevated phytoplankton, and no recovery of seagrasses (Pearce et al., 2000, Kendrick et al., 2002). This uncoupling between remediation effort and ecosystem response prompted this study of the dynamics of contaminated groundwater discharge in Cockburn Sound.

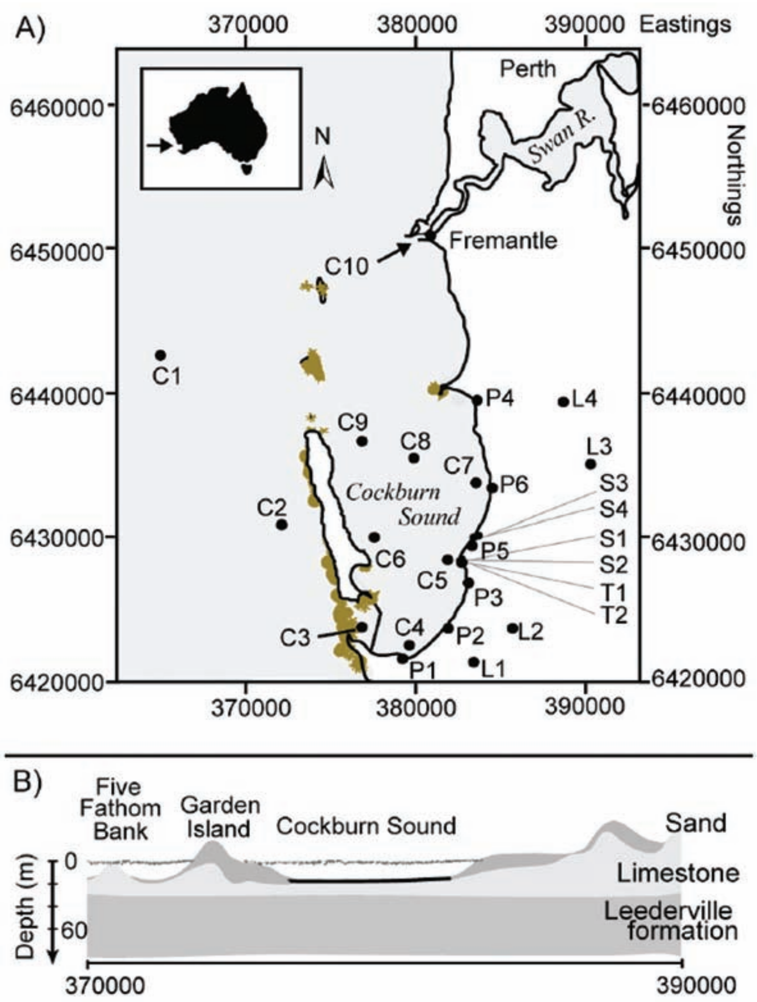

Figure 2.21: Surface water and groundwater sampling locations for geochemical tracers.

Methods

Geochemical Tracers in surface and ground waters

A seasonal sampling program of 10 marine (C1-C10, 2m depth) and 15 groundwater stations (4 'S' Sand aquifer, 2 'T' Limestone, 3 'L' Leederville and 6 'P' beach porewater) was conducted for radium and nutrient analysis (Figure 2.22a). Sampling dates were 22-24 Sept 2003 (End of Winter), 30 Nov-2 Dec 2003 (Early Summer), 8-10 Mar 2004 (Late Summer), and 15-20 Jul 2004 (Mid Winter). Salinity, temperature, pH and DO were measured at all marine and groundwater sampling stations. Ratios of short and long lived Ra isotopes were examined to identify sources and regions of groundwater discharge, and a Ra mass-balance was applied to estimate volume flux to surface waters.

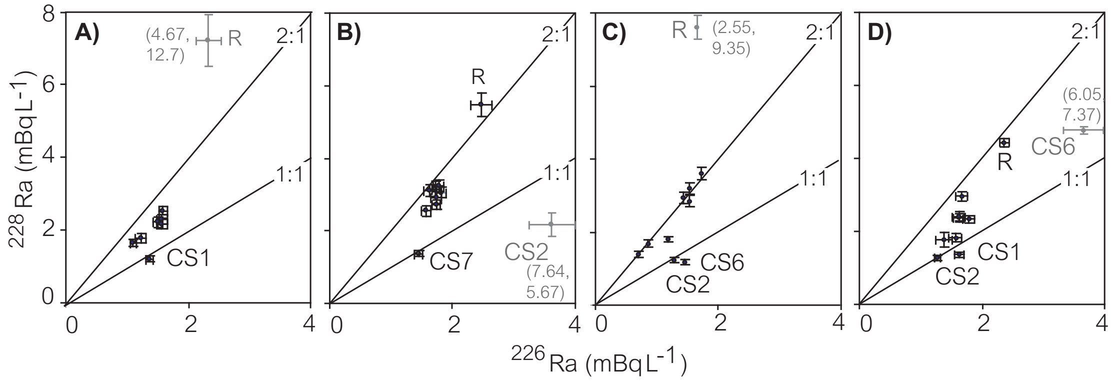

Figure 2.22: Spatial separation of surface water $^{226}Ra/^{228}Ra$ at different times of the year: A) end of winter, B) early summer, C) late summer, D) mid-winter. Riverine signal denoted by large R. Error bars are one standard error of instrumental counts. Off-scale values are written in grey type and are shown relative to ratio lines.

Nutrient chemistry in surface and ground waters

A 50 m transect of groundwater monitoring wells and nested beach piezometers were installed perpendicular to the shore and normal to the groundwater flow at an identified site of nitrogen groundwater contamination at Cockburn Sound. The transect facilitated a two-dimensional study of the predischarge environment, sampling groundwater from 2 or 3 depths beneath the water table in the unconfined sand aquifer (Figure 2.21b) at 5 inland locations and one surface water sampling location. Groundwater samples were collected during low tide on November 15 2004, April 8 and August 15 2005. These months correspond to an early summer, late summer and mid-winter seasonal sampling regime. Water samples were collected for nutrient and physical-chemical concentrations. A conservative mixing model and Dämkohler calculations were applied to the chemical data obtained in the sampling program to investigate the role of transport and biogeochemical reaction with discharge.

Hydrodynamic modelling of surface waters

A HAMSOM (Hamburg Shelf Ocean Model, Backhaus 1985, Stronach et al. 1993) model had been previously written for Cockburn Sound (Pattiaratchi, pers. comm.). HAMSOM is a three dimensional model employing Navier Stokes equations at Z coordinates and an hourly forcing (wind direction and speed). Hourly wind data was obtained from the meteorological station at Garden Island. The Cockburn HAMSOM model domain is a grid size of 100x100m, through 10 layers of 2m thickness. We applied this model to determine the surface water flow regimes for the four field-sampling periods, and to determine the origin and fate of water at the field stations.

Results

Geochemical Tracers in surface and ground waters

Groundwater from different geological sources display different ratios of Ra ($^{228}Ra/^{226}Ra$) and different ratios of these isotopes in marine surface waters act as a fingerprint of different groundwater inputs. Shallow groundwater and embayment surface water had a similar $^{228}Ra/^{226}Ra$ fingerprint of 2, while samples outside the marine embayment demonstrated a $^{228}Ra/^{226}Ra$ fingerprint of 1 (Figure 2.22). The $^{228}Ra/^{226}Ra$ ratios of water samples collected from deeper in the sand and limestone aquifers (1-20 m below the water table) were variable and did not indicate a clear origin of the $^{228}Ra/^{226}Ra$ = 1 groundwater (Figure 2.23). Vertical mixing between aquifers may be extensive and responsible for the spatially and temporally variable ratios. The presence of $^{228}Ra/^{226}Ra = 1$ at a number of sites within the embayment in summer also suggested that groundwater discharge pathways change seasonally.

From a mass-balance of ^{228}Ra activities in the embayment and groundwater, we calculated lower seasonal estimate of SGD ($0.27 – 0.87 \times 10^7$ L day^{-1}) than previous hydraulic groundwater calculations (Smith et al., 2003). We propose that we detected lower SGD than inland hydraulic calculations due to heterogeneic discharge: a proportion of the regional groundwater bypasses the embayment via preferential pathways/conduits in limestone, and discharges through limestone reefs and islands beyond the embayment.

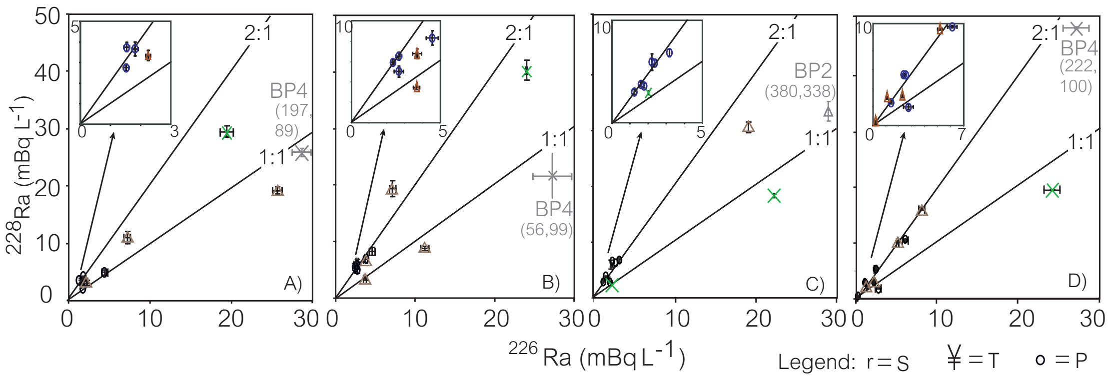

Figure 2.23: Mixed $^{226}Ra/^{228}Ra$ signal in groundwater from Safety Bay Sand aquifer (S), Tamala Limestone aquifer (T) and beach pore water (P) samples at different times of the year: A) end of winter, B) early summer, C) late summer, D) mid-winter. Error bars are one standard error of instrumental counts. Off-scale values are written in grey type and are shown relative to ratio lines.

Nutrient chemistry in surface and ground waters

An analysis of predischarge groundwater chemistry identified shifting gradients of dissolved inorganic nitrogen (DIN) species (nitrate + nitrite, NO_x, and ammonium, NH_4^+) in a sandy beach. Nutrient concentrations decreased with distance toward discharge. Elevated NO_x concentrations at the water table and elevated NH_4^+ in the mid-depths (Figure 2.24) corresponded to high and low oxygen conditions respectively, and suggested that both oxidation and reduction of DIN occurred prior to discharge. A two end-member mixing model revealed non-conservative behaviour of the DIN and identified regions of NO_x and NH_4^+ production and removal. Dissimilatory nitrate reduction to ammonium (DNRA) may be the dominant microbial process utilising N in the suboxic predischarge groundwater. Nitrification was limited to the top layer and denitrification only potentially occurred in winter. Dämkohler calculations reveal that the beach biogeochemistry was controlled by reaction processes at all times.

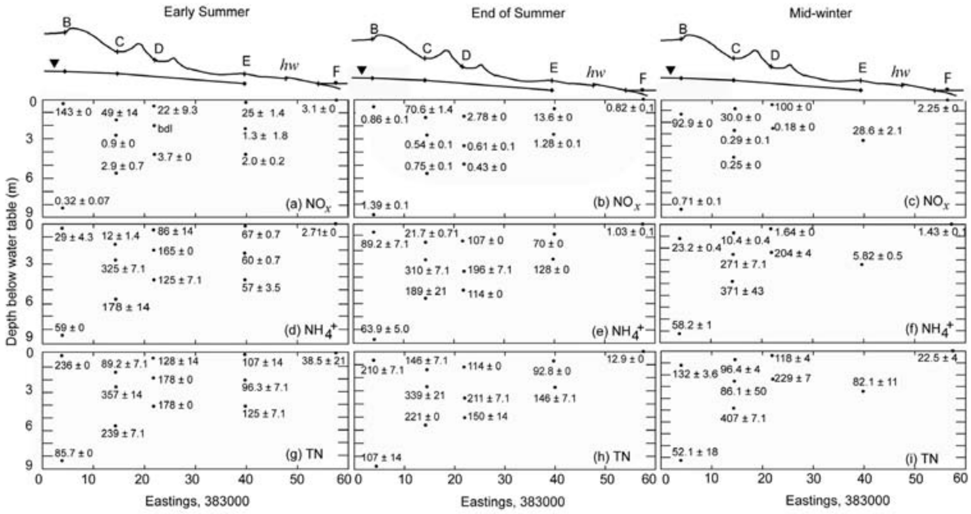

Figure 2.24: Seasonal groundwater predischarge nitrogen concentrations a-c) NOx (μmol N L^{-1}) at the end of winter, end of summer and mid-winter; d-f) NH_4^+ (μmol N L^{-1}) at the end of winter, end of summer and mid winter; g-i) TN (μmol N L^{-1}) at the end of winter, end of summer and mid winter.

Hydrodynamic modelling of surface waters

Activities of short-lived Ra geochemical tracers (^{224}Ra and ^{223}Ra) in 10 surface water sampling locations indicated a greater presence of groundwater at the eastern shoreline and on the west side of the island and limestone reefs. This spatial pattern was observed during the end of winter, early summer and late summer. In mid-winter the tracers demonstrated an opposite spatial pattern, with high levels away from shorelines and lower "marine-like" signals at groundwater discharge localities. Surface water circulation modelling showed that the same northward-flowing current regime dominated in the embayment during the end of winter, early summer and late summer, while southward flowing currents dominated surface currents in mid-winter. Particle tracking modelling of tracer movement away from sampling stations indicated that surface water currents at the end of winter, early summer and late summer would confine discharged groundwater at the shoreline, to be flushed northward out of the system (Figure 2.25 A-C). In mid-winter, westerly tracer movement away from the shoreline and across the embayment (Figure 2.25 D) suggests groundwater and contaminants are made more widely available across the system at this time.

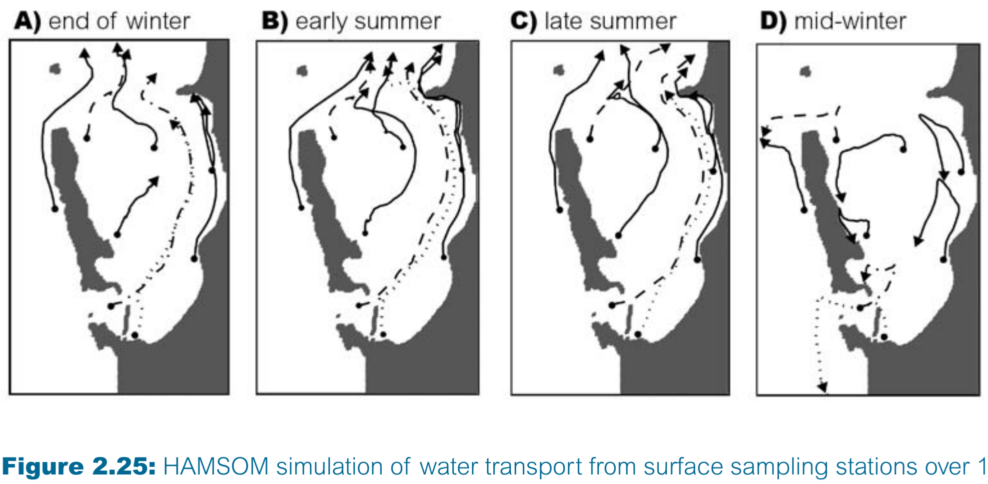

Figure 2.25: HAMSOM simulation of water transport from surface sampling stations over 10 day during: A) the end of winter, B) early summer, C) late summer , D) mid-winter.

Discussion

The outcomes of each research objective were synthesized into an overall process understanding of SGD in a marine embayment where there were multiple groundwater sources. Radium geochemical tracers from two different groundwater sources were identified in the surface waters, and the prevalence of the tracers varied spatially and seasonally. Minimum groundwater discharge was quantified at the end of winter, and a maximum in the early summer. We also showed that during summer, biogeochemical reactions in the groundwater may cause an elevation of NH_4^+, possibly by DNRA conversion of the NO_x or ammonification of organic nitrogen within the system. The end-of-summer profile of the beach groundwater showed a pool of NH_4^+ that spread out to resemble a subterranean plume again in mid-winter. From surface water modelling we demonstrated that, in mid-winter, shoreline surface waters were transported across the system prior to flushing. Calculated residence times did not vary for the different times of the year, however transport pathways and extent of availability of groundwater did vary significantly and this may be more important than flushing time to the surface water quality of this system. Groundwater nutrients may be more available to primary producers throughout the embayment in mid-winter than at other times of the year. Environmental guidelines recommend that monitoring of these marine surface waters is performed during summer, yet from this study it was apparent that groundwater source, biogeochemical composition and surface transport switched seasonally and that mid-winter may be a potentially key time of nutrient delivery within the system.

Acknowledgements

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Conference attendance and presentations

Australian Society for Limnology. Margaret River, Western Australia. October 2002

Australian Marine Sciences Association 2002: Tropical Temperate Transitions. Fremantle, Western Australia. July 2002

Gordon Research Conference Permeable Sediments. Lewiston, Maine, USA. June 2003

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Awards

2003 Postgraduate Travel Scholarship, Gordon Research Conferences – Permeable Sediments

2004 Best Presentation, CSIRO SRFME Symposium, Floreat, Western Australia

2005 Centre for Groundwater Studies International Travel Award

2006 Postgraduate Travel Scholarship, Gordon Research Conferences – Permeable Sediments

Publications

Loveless, A. and Oldham, C.E. (submitted) Biogeochemical reactions control groundwater DIN concentrations in coastal permeable sediments. *Biogeochemistry*, submitted March 2006.

Loveless, A., Oldham, C. and Hancock, G. (in prep) Radium isotopes reveal a bottom end estimate of groundwater volume flux and heterogeneic patterns of discharge in a complex semi-enclosed coastal basin.

Loveless, A. and Oldham, C.E. (in prep) Short-lived radium isotopes and HAMSOM surface water modelling reveal significant episodes of contaminant transport in a semi-enclosed marine basin.

Loveless and Moore (in prep) Scales and Assumptions of the Radium Technique for estimating Submarine Groundwater Discharge.

Evans, M., Loveless, A. and Oldham, C. (in prep) Estimation of residence time of groundwater in the marine-groundwater mixing zone using field data and modelling.

W. Burnett, W., Bokuniewicz, H., Cable, J., Charette, M., Kontar, E., Krupa, S., Loveless, A., Moore, W., Oberdorfer, J., Povinec, P., Stieglitz, T., Taniguchi, M. (submitted) Quantifying Submarine Groundwater Discharge in the Coastal Zone via Multiple Methods. *Science of the Total Environment*, submitted January 2006.