

SOURCE, FATE AND MOBILITY OF GROUNDWATER NUTRIENTS,
METALS/METALLOIDS AND 4-NONYLPHENOL IN THE UNCONFINED BROOME
AQUIFER

By

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Abstract

Submarine groundwater discharge (SGD) contributes significant nutrient loads to coastal waterways. When groundwater is impacted by anthropogenic disturbances, the SGD of nutrients is generally increased, causing coastal eutrophication. Roebuck Bay, located on the southern boundary of Broome in north Western Australia, has recently been impacted by blooms of *Lyngbya majuscula*. This disturbance has been linked to changes in benthic invertebrate population dynamics and shorebird feeding behaviour. It has been theorised that SGD from the Broome peninsula contributes significant nutrient loads to Roebuck Bay, driving subsequent environmental impacts. In this study concentrations of groundwater nitrogen (N) and phosphorus (P) were assessed throughout the Broome unconfined aquifer, to identify the key sources of nutrients, the capacity for natural attenuation, and the quantity of nutrients discharge into Roebuck Bay seasonally.

The wastewater treatment plant (WWTP) and sites irrigated with wastewater effluent were found to be the primary source of N and P to the aquifer. Similarly sites impacted by heavy fertiliser application were identified as a major source of P. Natural attenuation processes are likely to be significantly reducing groundwater nitrate from wastewater irrigated ovals prior to SGD. The primary sources of N and P to Roebuck Bay were found to be the WWTP and the Broome golf course. Annual nutrient loads were estimated to be 32,826 Kg and 455 Kg for N and P respectively. Consequently N was identified as the most significant nutrient contributing to eutrophication.

The groundwater concentration of metals/metalloids and 4-nonylphenol, a common organic wastewater contaminant, were also assessed. 4-nonylphenol was found to be below detectable levels at all sites, including samples of treated wastewater effluent. Several metals/metalloids violated drinking water guidelines at a number of bores, and occurred in bioavailable and mobile forms. Although groundwater from these sites should not be consumed, these metals/metalloids are not likely to threaten Roebuck Bay biota, as concentrations were generally below relevant guidelines. Attenuation processes may further reduce concentrations prior to SGD.

Keywords: Broome, Broome Sandstone Aquifer, Groundwater Nutrients, *Lyngbya majuscula*, Metals/Metalloids, Natural Attenuation, Roebuck Bay, Submarine Groundwater Discharge, 4-nonylphenol

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1. Introduction

Groundwater resources are being increasingly impacted by contamination due to agricultural, industrial and domestic activities (Florke *et al.* 2013; Hu and Cheng 2013). Broome, situated on Western Australia's Kimberly coast, has experienced local impacts to the underlying unconfined aquifer (Wright 2013). This has resulted in changes to the groundwater chemistry, causing ecological disturbances, and threatening biodiversity throughout the region (Estrella 2013; Estrella 2011; Vogwill 2003).

Roebuck Bay, located to the south of Broome, is of international significance, being recognised under the Ramsar convention (Piersma *et al.* 2006). The wetland is an important stopover site for migratory shorebirds using the East Asian Australian Flyway (Department of the Environment 2011; Estrella 2013). The region is also regarded as one of the most biodiverse tropical mudflats in the world, boasting a particularly high benthic invertebrate biomass and species richness (Piersma *et al.* 1998; Estrella 2011). Since 2005 Roebuck Bay has experienced blooms of *Lyngbya majuscula*, threatening the local ecology (Estrella 2013).

Lyngbya majuscula (Oscillatoriaceae) is a filamentous, non-heterocystous marine cyanobacteria species that inhabits the intertidal zone of tropical coastal waters, attaching to organic and inorganic substrates (Osbourne *et al.* 2001; Jones 1990; Dennison *et al.* 1999). Recent studies have linked the presence of *Lyngbya* to reductions in benthic invertebrate species richness and abundance, and altered shorebird feeding behaviour throughout Roebuck Bay (Estrella 2011; Estrella 2013). The presence of the algal species also has negative implications for human health (Osbourne *et al.* 2007).

Lyngbya produces a suite of toxic compounds, most notably debromoaplysiatoxin and aplysiatoxin. These toxins cause a number of health issues including dermatitis, repository irritation, and burning of the upper gastrointestinal tract (Osbourne *et al.* 2007). As Roebuck Bay is situated proximal to the Broome town site the presence of *Lyngbya* puts residents and visitors at risk. Similarly these toxins effect the health of marine macrofauna, causing fibropillomatosis in juvenile green sea turtles and ulcerative dermatitis in dugongs (Quackenbush 1998; Harr 2008). These species frequent Roebuck Bay and are of conservation significance, being listed under the Environmental Protection and Biodiversity Conservation Act 1999 (Smyth 2005; EPBCA 2014).

Lyngbya naturally occurs in discrete quantities within Australian coastal waters, however under optimal conditions blooms rapidly intensify (Watkinson *et al.* 2005). Warm water

temperature, low turbidity, and long periods of light are the major environmental parameters controlling bloom initiation (Hamilton *et al.* 2007). Macronutrient availability, most notably phosphorus, nitrogen, and chelated iron, is also essential for *Lyngbya* proliferation (Ahern *et al.* 2008; Taylor *et al.* 2014).

Within Roebuck Bay surface water runoff and submarine groundwater discharge (SGD) have been identified as significant contributors of nutrients (Gunaratne *et al.* 2014; Wright 2013). SGD of nutrients has previously been quantified at the end of the 2013 dry season, however it is yet to be constrained at the end of the wet season (Wright 2013). As Broome experiences most of its rainfall during this period nutrient transport to the unconfined aquifer is likely, as is groundwater recharge (Bureau of Meteorology 2014(a)). It has been theorised that natural attenuation could act to mitigate groundwater contamination throughout the peninsula (National Research Council 2000).

Treated wastewater effluent is used for the irrigation of council ovals and parks throughout Broome. Wastewater effluent can contain a number of organic contaminants, having negative environmental effects (Ternes *et al.* 2004). 4 – nonylphenol (NP) has been identified to be one of the most pervasive (Schaidler *et al.* 2014). NP acts as an endocrine disrupter, interfering with the hormonal system. (Soares *et al.* 2008; Maenpaa and Kukkonen 2006). At low concentrations, less than 6µmol/L, NP has been found to cause physiological defects and mortality in benthic invertebrate populations (Maenpaa and Kukkonen 2006). Furthermore NP bioaccumulates and biomagnifies up trophic levels (Diehl *et al.* 2012; Preuss *et al.* 2008). As NP poses a significant threat to ecologic function as well as human health it was investigated in groundwater throughout Broome peninsula (Centeno *et al.* 2000; Lemly 2002).

During the early 2000's high concentrations of metals, most notably As, Hg, and Se, were identified within the unconfined aquifer at Broome (Vogwill 2003). These contaminants have been linked to neurological disorders, cancer, and keratosis in humans (Ratcliffe *et al.* 1996; Liu *et al.* 2013; Senanayake and Mukherji 2014). Similarly they have detrimental effects on benthic invertebrates, causing reductions in abundance and species richness (Beltman *et al.* 1999; Lemly 2002). Metal and metalloid contaminants were investigated in this study as high concentrations may continue to occur within the Broome unconfined aquifer. Additionally the spatial scale of the investigation in Vogwill (2003) was limited, being focussed primarily on tidal creek margins.

To address the environmental issues outlined above it is imperative for groundwater contamination to be further investigated. Recent studies have been successful in identifying key pathways of nutrients into Roebuck Bay and in recognizing ecological disturbances (Gunaratne *et al.* 2014; Wright 2013; Estrella 2011; Estrella 2013). Past research has led to the development of improved management strategies throughout the region (Griffiths 2009). The following investigation has been formulated to expand on the above studies, in order to provide pertinent information for use in future management practices.

1.1 Study Area

Broome is located in the Kimberly region approximately 1700 km north-north east of Perth, Western Australia and borders the northern margin of Roebuck Bay (Figure 1). Over the past 30 years the town has developed from a small settlement into a large regional centre, with a current population of 26,000 permanent residents (Mullholland and Piscicelli 2012). During the dry season this figure doubles due to the large influx of tourist (Cambell 2013). This has put increasing pressure on the local groundwater resources and surrounding ecosystem.



Figure 1: Location Map of Broome, Western Australia

1.2 Hydrogeological Setting

Geologically the Broome peninsula sits within the northern Canning Basin, which contains a deformed sedimentary sequence ranging in age from the Ordovician to Cainozoic. The Canning Basin is the largest in Western Australia (Laws 1991). Groundwater occurs in three major and two minor aquifers within the region, with the Broome Sandstone being the most significant (Vogwill 2003; Laws 1991). The Pindan Sands, Broome Sandstone, and Jarlemai Siltstone form the upper most units of the sequence underlying the Broome Peninsula (Laws 1991).

The recent increase in urban development has led to significant reductions in groundwater recharge due to the channelling of storm water runoff into Roebuck Bay (Gunaratne *et al.* 2014). Similarly abstraction has caused aquifer salinization (salt water incursion and interface upcoming) and a reduction in groundwater levels over the past decades (Vogwill 2003; Wright 2013). These disturbances limit the development and utilisation of groundwater throughout Broome (Groth 2011).

1.2.1 Pindan Sand

Pindan Sand forms the primary surficial cover throughout the Broome town site and much of the Kimberly (Emery *et al.* 2003; Vogwill 2003). These sands are composed of well graded silty sand or well graded clayey sands and have a deep red colouration, attributed to a haematite (Fe_2O_3) coating around the quartz sand and silt particles (Emery *et al.* 2003). The unit is Quaternary in age and was formed through both aeolian and alluvial processes (Vogwill 2003). Pindan sands unconformably overly the Broome Sandstone and can form minor perched aquifers (Laws 1991).

1.2.2 Broome Sandstone

The Broome Sandstone is the most utilised aquifer through the Canning Basin and is the primary fresh water source for Broome. It is typically composed of poorly consolidated friable, fine – coarse grained quartzose sandstone, with minor beds of siltstone, claystone, organic matter, and conglomerate. The unit has an average thickness of 280m, is early Cretaceous in age and lies conformably on the Jarlemai Siltstone (Laws 1991). The aquifer is largely unconfined, so recharge occurs mainly through infiltration from rainwater.

Groundwater flow is predominantly south - west, south of the Baskerville Anticline, located north-north east of Broome, due to the unit's south-westerly dip and the topography. As this unit is highly utilised throughout Broome it is the most threatened water resource in the region, with impacts typically being local (Vogwill 2003).

1.2.3 Jarlemai Siltstone

The Jarlemai Siltstone is Late Jurassic in age, light grey to black in colour and composed mainly of black puggy silt and clay, with minor amounts of sand and rare sandstone interbeds (Holder and Rozlapa 2009). The unit lies conformably between the Alexander Formation, a minor sandstone aquifer, and the Broome Sandstone. The Jarlemai Siltstone is primarily an aquiclude, inhibiting through flow between the Broome Sandstone and the underlying Alexander formation (Laws 1991). It effectively forms an impermeable basement for the unconfined aquifer (Vogwill 2003).

1.3 Climate

Broome is located at the boundary of three climatic zones; the Northern, Dry Interior, and North-western (Laws 1991). The climate at Broome displays features of all three regimes, however is classified as tropical, due to its distinct wet (October to February) and dry (March to September) seasons (Wharton 2008; Laws 1991). These are characterised by hot wet summers and warm dry winters (Wharton 2008). Daily average minimum and maximum temperatures during the wet season are 26.5 °C and 34.3 °C, while average minimum and maximum temperatures during the dry season are 13.7 °C and 31.8 °C (Bureau of Meteorology 2014 (a)). In the wet season monsoonal conditions are prevalent with high tropical cyclone and thunderstorm activity producing significant rainfall and humidity (Wharton 2008). Mean rainfall during this period is 530.2 mm (Figure 2), representing close to 90% of yearly precipitation (Bureau of Meteorology 2014(a)).

Rainfall during the wet season is highly variable due to the random, episodic and spatially limited nature of storm events (Holder and Rozlapa 2009). In some years over nine cyclones can occur, while in others there may be less than three. This has a major control over groundwater recharge throughout the region (Qi *et al.* 2005). Annual potential evaporation throughout Broome is 2700mm (Bureau of Meteorology 2014 (a)), 5 times more than that of annual precipitation (Figure 2). Large rain events are therefore critical for the replenishment of groundwater resources throughout the region.

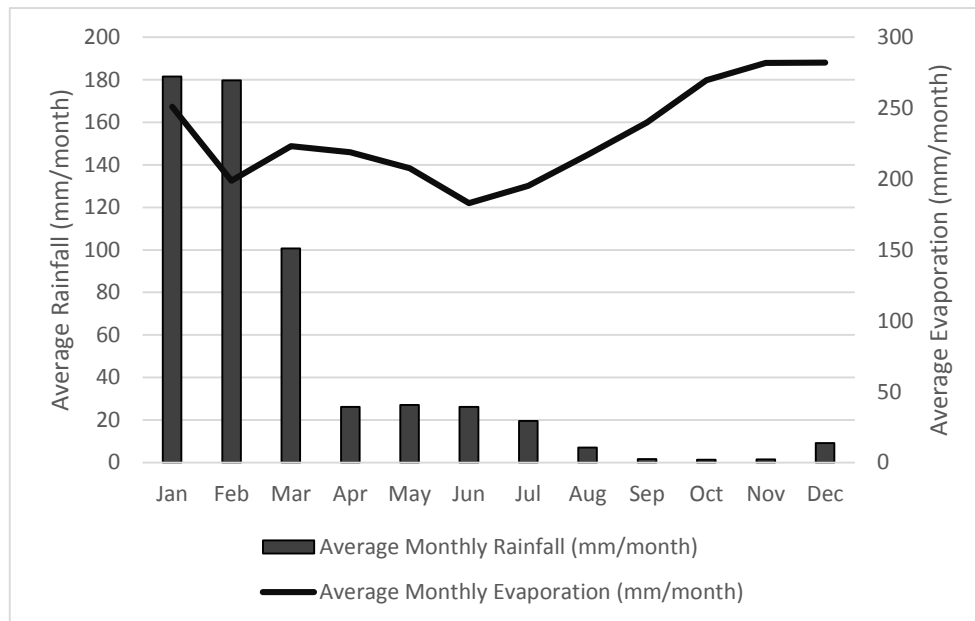


Figure 2: Average monthly rainfall and evaporation for Broome Western Australia (Bureau of Meteorology 2014 (a)).

2. Materials and Methods

2.1 Groundwater Sampling Protocol

Groundwater samples were collected from eight UWA monitoring bores (A – H), and four council bores (Bedford Park (BP), Cable Beach (CB), Kimberly Region Offices (KRO), Town Oval (TO)) which are located throughout the Broome town site (Figure 3). Each of the UWA monitoring bores consisted of both shallow and deep wells, which were constructed in order to collect groundwater samples from the upper (0 – 6m) and lower (20 – 26m) portion of the saturated aquifer. Total bore depths were between 15m and 20m, and 30m and 35m for shallow and deep wells respectively (Wright 2013). Each bore was purged, using a 12 volt submersible pump, for more than three casing volumes before samples were taken and field parameters read. During pumping water was lifted via a length of plastic tubing and injected into a flow cell (Sundaram *et al.* 2009). Treated waste water effluent was also collected from storage tanks, located at Haynes Park (HP) and Bracks Oval (BO).



Figure 3: Broome Bore Location Map

2.2 Groundwater Sample Collection

Samples for total nutrients, dissolved nutrients, anions, cations, NP and trace metals were collected at each location. A 1L amber glass bottle was used to collect the NP samples, while all other samples were collected in 50mL plastic vials. Dissolved nutrients, anions and cations, and trace metals were filtered through a 45 micron membrane in the field, while total nutrients and NP were collected without filtration. NP, cation, anion, and trace metal/metalloid samples were refrigerated at 4°C during storage. Supplementary to this ultra-pure nitric acid was added to trace metal/metalloids samples, producing a 5% acid solution (Sundaram *et al.* 2009). Total nutrients and dissolved nutrient samples were immediately refrigerated at 4 °C after collection, and frozen at the end of each day.

2.3 Field Parameter Measurements

Electrodes measuring pH, EC, dissolved oxygen, redox potential and temperature were inserted into a flow cell and readings taken once levels had stabilized. Electrodes were calibrated using the appropriate techniques and standard solutions (Sundaram *et al.* 2009). These methods are described in detail in Appendix 4. It is necessary to measure environmental parameters in the field as they control the mobility and fate of groundwater contaminants and can change rapidly once groundwater is removed from its natural setting (Alvarez 2006; Weidmeier *et al.* 1999).

2.4 Groundwater Head Measurements

Groundwater head (level) was measured using an electronic depth meter and tape measure prior to purging and sampling at each site (Sundaram *et al.* 2009). Water levels were measured relative to ground level. A differential global positioning system was used to survey each site prior to sampling, determining the ground level height above sea level. The error associated with these measurements was <40mm (Portz 2013). Groundwater head measurements were subtracted from the surveyed ground level height to determine their height relative to sea level.

2.4 Delineation of the Near Shore Groundwater Discharge

Groundwater discharge was assessed along Town Beach proximal to the waste water treatment plant. Samples were taken systematically at 50m intervals along several transects throughout the upper part of the intertidal zone. At each location an EC probe was used to assess salinity to determine the presence of freshwater. When a zone of fresh water discharge was detected measurements were taken at smaller intervals to delineate the extent of the zone. NP and total nutrient samples were taken at sites with low EC.

2.5 Nutrient Analysis

Nutrient samples were sent to the University of Western Australia's Water Quality Laboratory for analysis. All nutrient samples were analysed using a Lachat Flow Injector (Lachat 2008). Concentrations of total nitrogen and total phosphorus were determined using in-line UV/persulfate digestion and oxidation, while nitrate, ammonium, and reactive phosphorus were analysed using the QuickChem Method 31-107-04-1-A, QuickChem Method 31-107-06-1-B, and the QuickChem Method 31-115-01-1-G respectively (Eaton *et al.* 2012; Lachat 2008). These procedures are described in detail in Appendix 4.

2.6 Anion and Cation Analysis

Anion and cation groundwater samples were analysed at the Environmental Inorganic Geoscience Group's laboratory located in the Myer Street Building at the University of Western Australia. High Performance Ion Chromatography (HPIC) was used to assess the concentration of these analytes (Appendix 4).

2.7 Nonylphenol Analysis

4-nonylphenol samples were sent to the ChemCentre in Bentley for analysis. Triple Quadrupole Gas Chromatography/Mass Spectrometry (GC/MS) and High Performance Mass Spectrometry (HP-MS) were used to determine concentrations (Appendix 4).

2.8 Trace Metal/Metalloid Analysis

Groundwater samples were analysed for 53 trace metal contaminants at TSW Analytical. Initially samples were diluted with Type II deionised water and nitric acid (2% v/v) according to their respective electrical conductivity. Samples were then injected into the Agilent 7700 x ICP – MS using a MicroMist nebuliser and Peltier Colled spray chamber. The ICP – MS was optimised prior to analysis. Rhobidium and iridium were used as internal standards.

2.9 Trace Metal/Metalloid Speciation

Eh and pH were identified as key factors influencing the speciation of metal contaminants within groundwater systems (Basu *et al.* 2007; Ryu *et al.* 2002; Mok *et al.* 1988). When groundwater bores did not comply with the drinking water standards outlined by the ANZECC, NHMRC, and USEPA they were considered to be of significance. These sites were plotted on Eh – pH diagrams sourced from *NIAIST* (2005) to determine the chemical speciation of each contaminant under the measured environmental conditions. PHREEQC was also used to determine speciation, as it considers several other input parameters, giving a more robust analysis (USGS 2014 (a)). This investigation was deemed imperative as mobility, toxicity and bioavailability of metal contaminants are strongly associated with chemical speciation (McGeer *et al.* 2004; Nolan *et al.* 2003).

2.10 Data Interpolation

2.10.1 Groundwater Head Contours

Groundwater contours for the end of the 2014 wet season and end of the 2013 dry seasons were plotted with ArcMap 10.2.1 using water level data from the eight UWA bores (A –H). Interpolations were performed and contour lines approximated accordingly. The kriging interpolation method was applied due to its common use in hydro-geologic studies (Srinivasan and Natesan 2012; Kurtzman, Navon, and Morin 2009; Kumar and Remadevi 2006). The settings used in the interpolation are described in Appendix 5.

2.10.2 Nutrient Interpolation

Groundwater nutrients were interpolated using kriging and concentration contours determined for the end of both the wet and dry seasons. Data acquired by *Wright* (2013) and collected during this study were used for the interpolation. This has been termed UWA data. In addition publically available data was sourced to further constrain the nutrient interpolation at the WWTP and Broome golf course (Wright 2013). Total nitrogen, nitrate, ammonium, total phosphorus, and orthophosphate were interpolated. These settings are described in Appendix 5.

2.11 Statistical Analysis

2.11.1 Univariate Data

Descriptive statistics were explored for nutrient data collected during the 2014 wet and 2013 dry season. The IBM SPSS Statistic 22 software package was utilised and boxplots developed. Extreme outliers occurred when data was more than three interquartile ranges from the box (Wang and Bushman 1999). These were considered to be significantly different from the median and mean. IBM SPSS Statistic 22 was also used to explore the descriptive statistics for EC measurements taken throughout Town Beach. Extreme outliers were considered to represent areas of fresh water/seawater mixing (Appendix 7). These zones were plotted using ArcMap 10.2.1.

2.11.2 Bivariate Data

The IBM SPSS Statistic 22 software package was used to test the significance of differences between data groups. Normality was tested and log transformations implemented where datasets were highly skewed (Weinberg and Abramowitz 2008). The One-way ANOVA was used to assess the significance of differences between the means for parametric nutrient data in shallow and deep wells, and for wastewater effluent, waste water irrigated and non-wastewater irrigated sites for both the wet and dry season. Tukey Honest Significant

Difference (HSD) post hoc tests were implemented to identify where differences occurred (Warner 2013; Sanford *et al.* 2003). When data was non-parametric a Kruskal-Wallis analysis was utilised. Mean rankings were used in combination with the chi square to identify where the significant difference occurred (Appendix 7).

2.11.3 Multivariate Data

A Principal Component Analysis (PCA) was performed using the XLSTAT software package, identifying relationships between water quality variables and groundwater depth/disturbance at eight UWA monitoring bore sites. PCA has been utilised in a number of studies concerning nutrient contamination (Gunaratne *et al.* 2014; Buschmann *et al.* 2007; Critto *et al.* 2003). In this study ten environmental and nutrient factors measured over four bore depth/disturbance groups formed the inputs for the PCA for wet season data. These groups were as follows; deep wells at sites not irrigated with wastewater (Non Wastewater Irrigated Deep or NWWID), shallow wells at sites not irrigated with wastewater (Non Wastewater Irrigated Shallow or NWWIS), deep wells at sites irrigated with wastewater (Wastewater Irrigated Deep or WWID), and shallow wells irrigated with wastewater (Wastewater Irrigated Shallow or WWIS). For dry season data seven environmental and nutrient factors were used as redox, dissolved oxygen, and temperature measurements were not taken. A biplot was produced for each sampling period. The principal components PC1 and PC2 were selected for the biplot as they described the greatest amount of variance.

2.12 Submarine Groundwater Nutrient Discharge into Roebuck Bay

Roebuck Bay SGD was estimated using Dupuit's revision of Darcy's Law (Kasenow 2010), as demonstrated by Wright (2013). There is potential variability in the parameters required for these calculations particularly for hydraulic conductivity and the depth of the freshwater lens for the Broome Sandstone. For hydraulic conductivity the most conservative values were less than 1m/day, whilst the least conservative greater than 25m/day (Vogwill 2003). A hydraulic conductivity value of 7.5 m/day for the upper facies of the aquifer was considered the best approximation (Wright 2013). The depth of fresh water lens has been estimated to be between 30m and 50m. A depth of 40m was considered the most appropriate (Wright 2013). Nutrient discharge into Roebuck Bay from the Broome peninsula was calculated using the method outlined by Wright (2013). The peninsula was split into several sections and bores BP, C, F, H, and G used to estimate nutrient concentration and hydraulic gradients (Appendix 15). To estimate SGD and nutrient discharge from the WWTP and Golf Course publically

available data from 2013 was used, as access to these sites was not granted during either sampling period (current study and *Wright (2013)*).

2.13 Quantify Natural Attenuation

The velocity and travel time of nutrients migrating from groundwater bores to Roebuck Bay was calculated using Darcy's Law, as outlined by *Fetter (1999)*. The range of values previously defined for hydraulic conductivity were adopted, with a K value of 7.5 m/day considered the best estimate. The denitrification rates determined by *Tesoriero and Pucket (2011)* were used to calculate natural attenuation of groundwater migrating from each bore. These values ranged from 0.186 mg/L/year to 6.2mg/L/year, with a value of 3.1 mg/L/year considered the best approximation. Total denitrification times were estimated for each bore discharging into Roebuck Bay. For the WWTP and Golf Course publically available data from 2013 was used (*Wright 2013*). This was compared to the overall travel time and nitrate discharge concentrations. SGD was re-evaluated for nitrate, taking the potential range in natural attenuation into consideration.

2.14 Groundwater Recharge

Groundwater recharge was estimated for areas surrounding each of the eight private bores using the following equations:

$$\Delta S = S_y \times \Delta h$$

where ΔS = change in groundwater storage; S_y = specific yield; and Δh = fluctuation in water table height (*Marechal et al. 2006*)

Specific yield was estimated as follows:

$$S_y = \phi - S_r$$

where S_y = specific yield; ϕ = porosity; and S_r = specific retention (*Healy and Cook 2002*)

Vogwill (2003) determined that the specific retention (S_r) and effective porosity for the upper facies of the Broome Sandstone were 0.05 and 0.25 respectively (*Vogwill 2003*). Total seasonal recharge was estimated for the southern proportion of the Broome peninsula as bores were constrained within this zone. To achieve this several polygons were created in ArcMap 10.2.1 and their total area calculated (Appendix 11). Each polygon was generated to encapsulate bore locations which best represented recharge. The groundwater kriging interpolation was used to guide the extent and boundaries of polygons (Appendix 11)

2.15 Groundwater Chemistry

Groundwater chemistry was assessed for the twenty bores sampled at the end of the wet and dry seasons. A piper diagram was generated using the GW_Chart program (USGS 2014 (b)). Alkalinity was plotted against EC and compared to trends typical of freshwater - ocean water. An ion balance was calculated for each site, identifying the charge balance error (Appendix 14).

3. Results

3.1 Nutrient Interpolation

3.1.1 Total Nitrogen and Nitrate

The distribution of groundwater nutrients throughout the Broome peninsula varied between the wet and dry season. During the wet season the highest concentrations of total nitrogen in groundwater occurred at the WWTP and Broome golf course, when both UWA data and publically available data were considered. Concentrations were greater than 60,000 ug/L (Figure 4). In contrast when only UWA data was considered, the highest concentrations of total nitrogen and nitrate occurred at the centre of the study site, within areas irrigated with treated wastewater effluent. Concentrations for total nitrogen and nitrate at these sites were as high as 27,884 ug/L and 21,368 ug/L respectively. The interpolated concentrations of these contaminants were far less for the remaining extent of the peninsula, generally plotting 1 to 2 orders of magnitude lower than these values (Figure 4 - 5).

During the dry season, when both UWA data and publically available data were considered, the highest total nitrogen concentrations occurred at the centre of the town site, in areas irrigated with treated wastewater effluent, and proximal to Roebuck Bay, at the WWTP and the Broome golf course. Concentrations in groundwater below the WWTP and golf course exceeded 60,000 ug/L (Figure 4). When only UWA data was considered the greatest levels of total nitrogen and nitrate occurred at wastewater irrigated ovals, and at bore C, proximal to the WWTP (Figure 4). Concentrations for total nitrogen and nitrate at wastewater irrigated sites were as high as 20,429 ug/L and 18,751 ug/L, while concentrations proximal to the WWTP were 34,360 ug/L and 34,200 ug/L respectively. Interpolated contaminant levels were far less for the remaining peninsula, generally plotting 1 to 2 orders of magnitude lower than these values (Figure 4 - 5).

3.1.2 Ammonia

Ammonia concentrations at the WWTP and golf course are unknown. At the end of the wet season the highest ammonia concentration occurred at Bedford Park with a value of 584 ug/L. All other sites throughout the peninsula displayed levels 1 to 2 orders of magnitude less than this value. In contrast ammonia during the dry season was largest proximal to bore E with a concentration of 144 ug/L. Levels were also elevated throughout the south west of the study site and at the KRO bore. Concentrations ranged from 50 - 100 ug/L. The remaining extent of the study area was characterised by low ammonia concentrations, generally between 5 ug/L - 30 ug/L (Figure 6).

3.1.3 Total Phosphorous and Orthophosphorus

At the end of the wet season total phosphorus concentrations were greatest at the WWTP and the Broome golf course, when both UWA data and publically available data were considered. Concentrations at the WWTP exceeded 500 ug/L, while levels at the Broome golf course were greater than 50 ug/L. When only UWA data was considered total groundwater phosphorous was highest proximal to bore E, Town Oval, Bedford Park, and sites irrigated with wastewater effluent, occurring at concentrations of 80 ug/L (Figure 7). Orthophosphorus was highest proximal to the Town Oval bore, while sites irrigated with treated waste water had moderate concentrations. Concentrations for total phosphorus and orthophosphorous were generally between 20 ug/L - 40 ug/L and 10 – 20 ug/L throughout the Broome peninsula respectively.

At the end of the dry season groundwater at the WWTP and Broome golf course were found to have high total phosphorus concentrations, when publically available data was considered. Levels at these sites exceeded 500 ug/L and 50 ug/L respectively. Bores E and D were also found to have high levels of total phosphorus (Figure 7). When only UWA data was considered the greatest total phosphorus and orthophosphorous groundwater concentrations occurred at sites E and D. Concentrations for total phosphorus were as high as 292 ug/L, while orthophosphorous exceeded 105 ug/L. Groundwater occurring proximal to the wastewater treatment plant generally had a low – moderate concentration of these contaminants. Throughout much of the Broome peninsula total phosphorus levels were generally between 50 ug/L - 150 ug/L while orthophosphorous ranged from 30 ug/L - 70 ug/L (Figure 7 – 8).

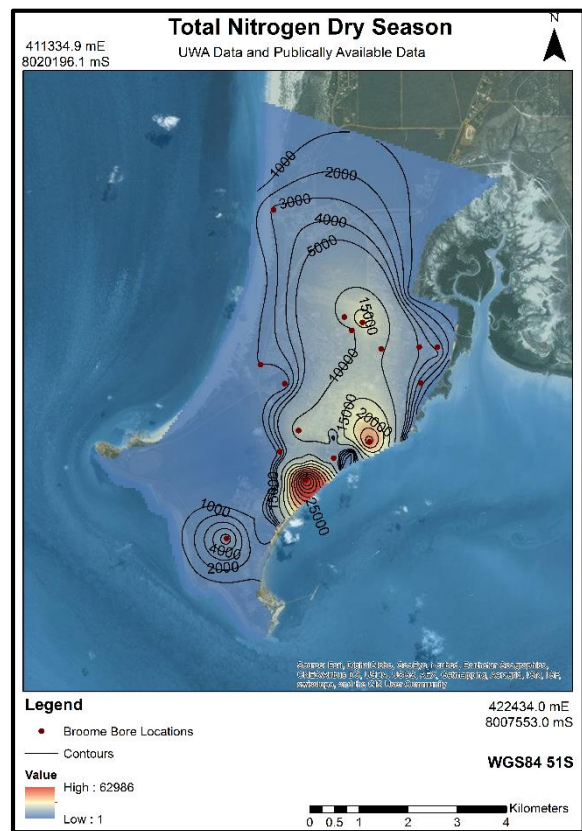
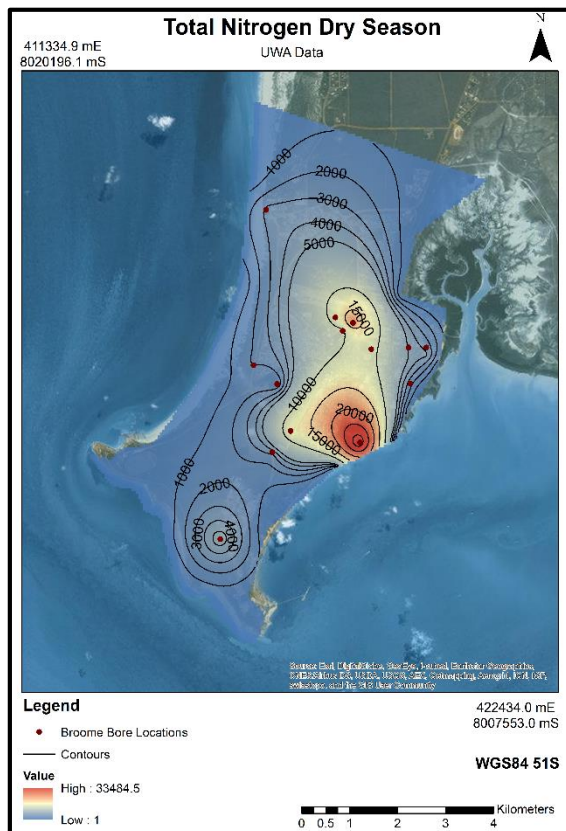
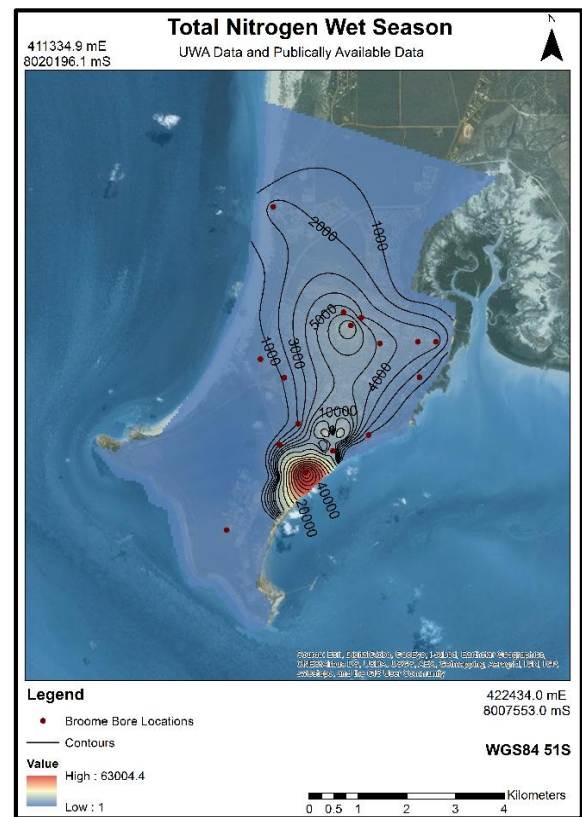
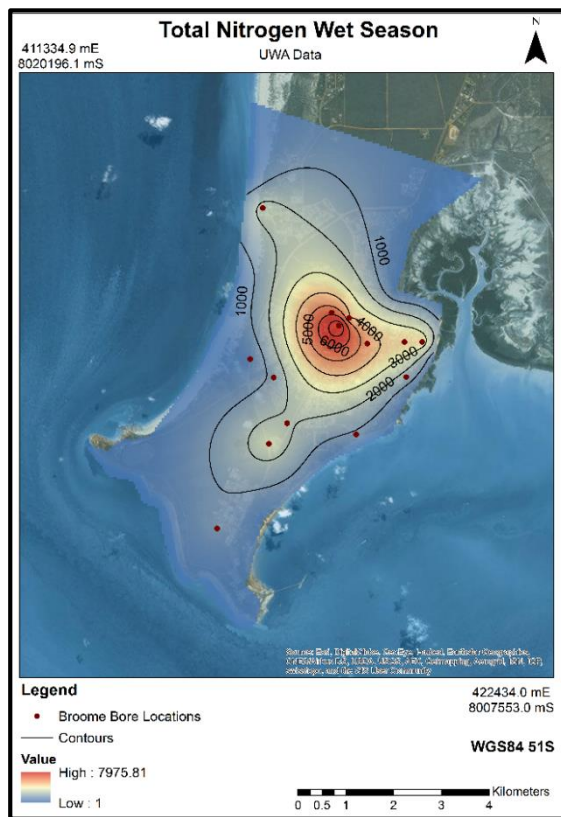


Figure 4: Interpolation maps for total groundwater nitrogen in the Broome unconfined aquifer at the end of the 2014 wet and 2013 dry season.

*Please note that due to software limitations different colour scales were used for each map in this section

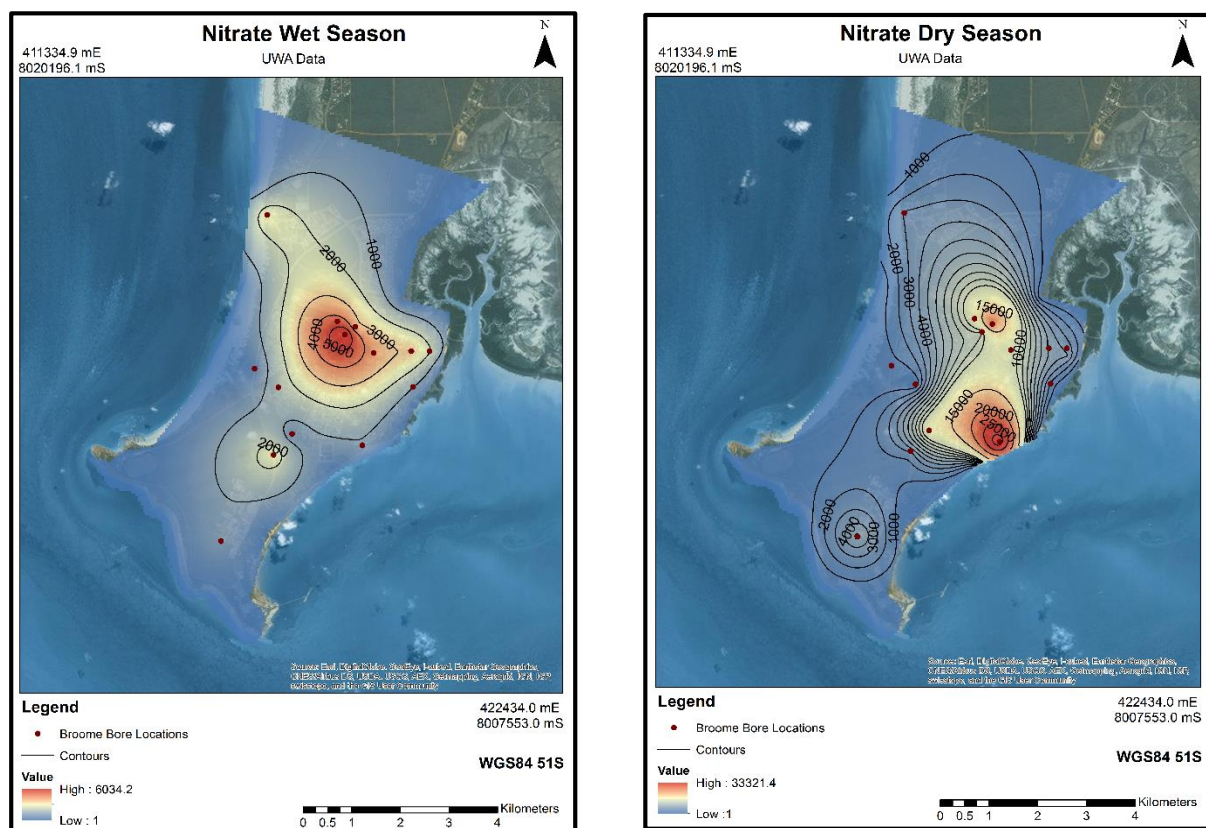


Figure 5: Interpolation maps for nitrate in the Broome unconfined aquifer at the end of the 2014 wet and 2013 dry season.

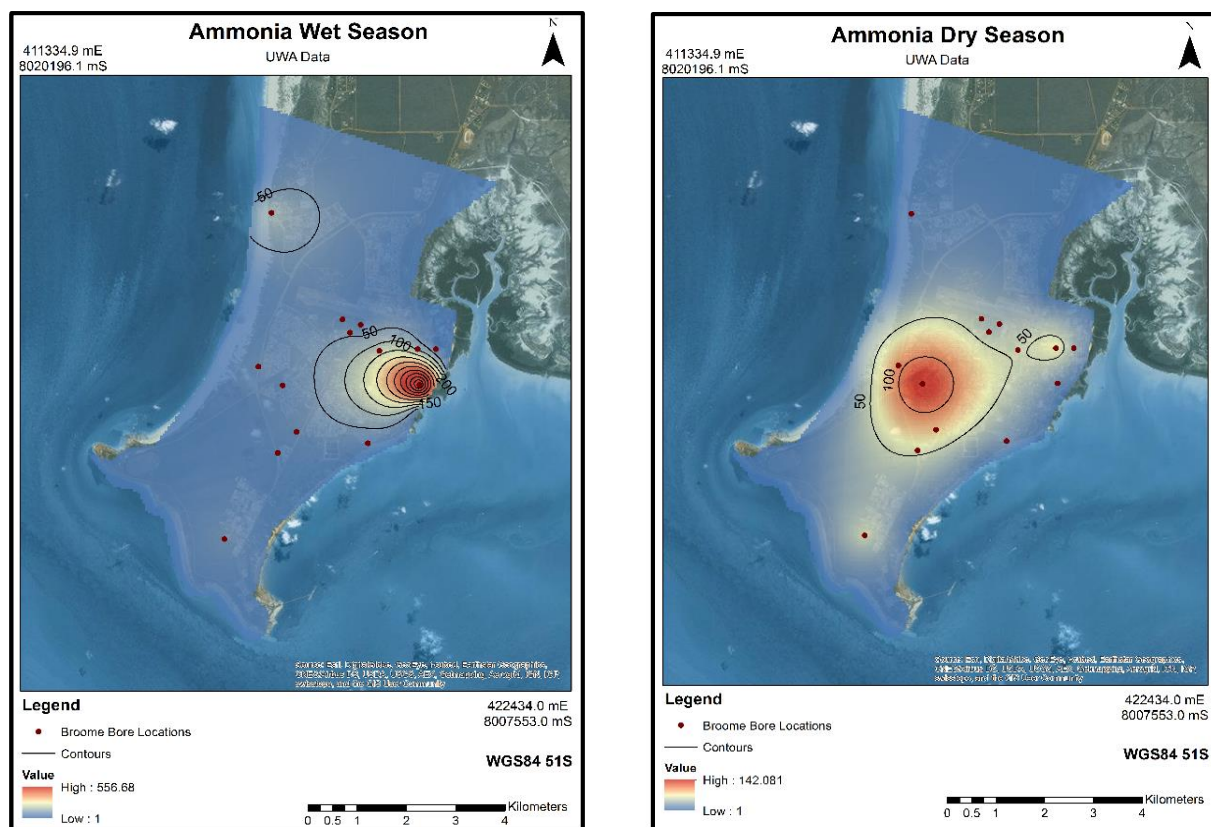


Figure 6: Interpolation maps for ammonia in the Broome unconfined aquifer at the end of the 2014 wet and 2013 dry season.

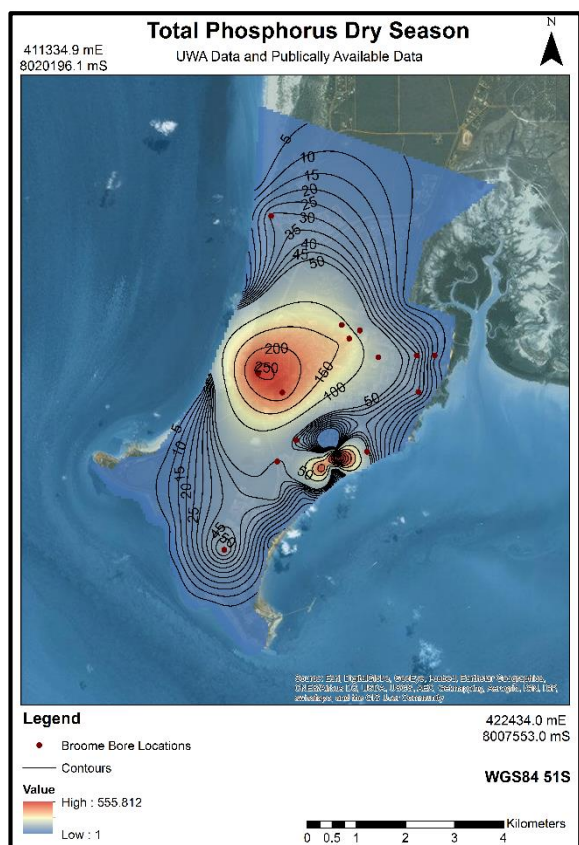
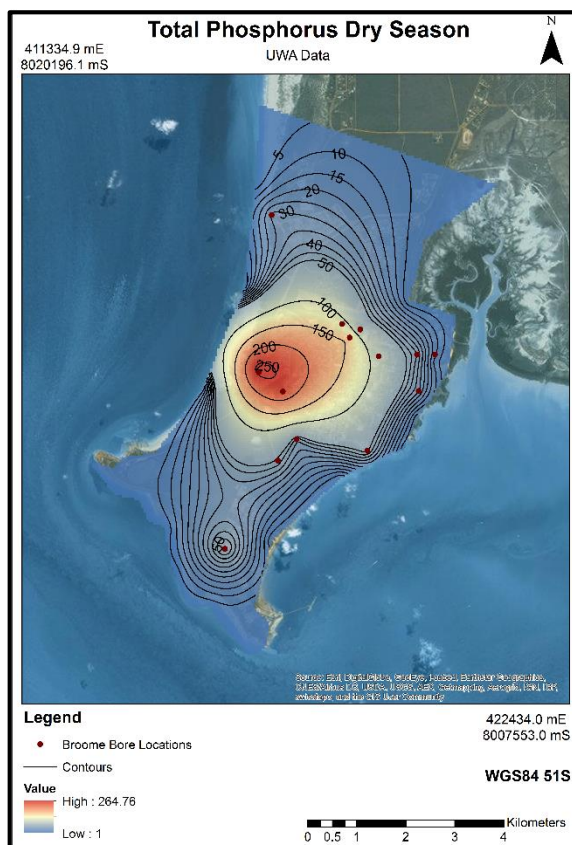
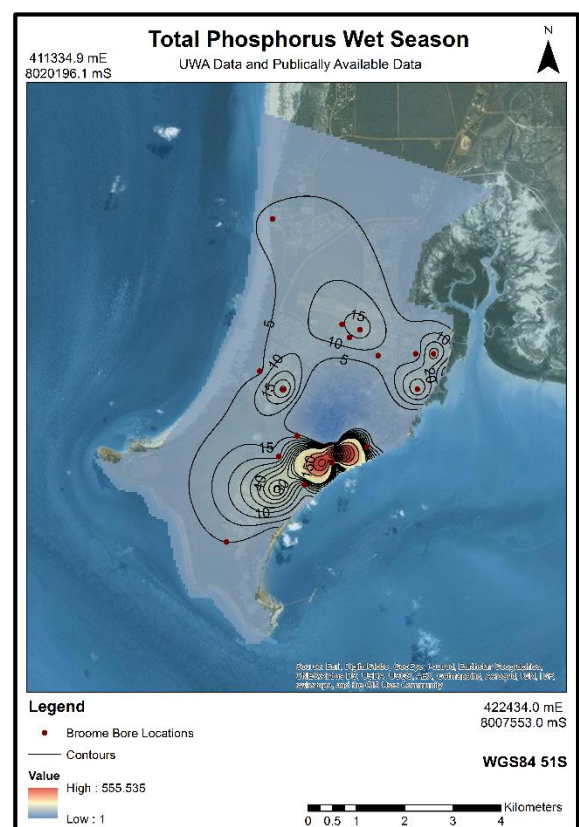
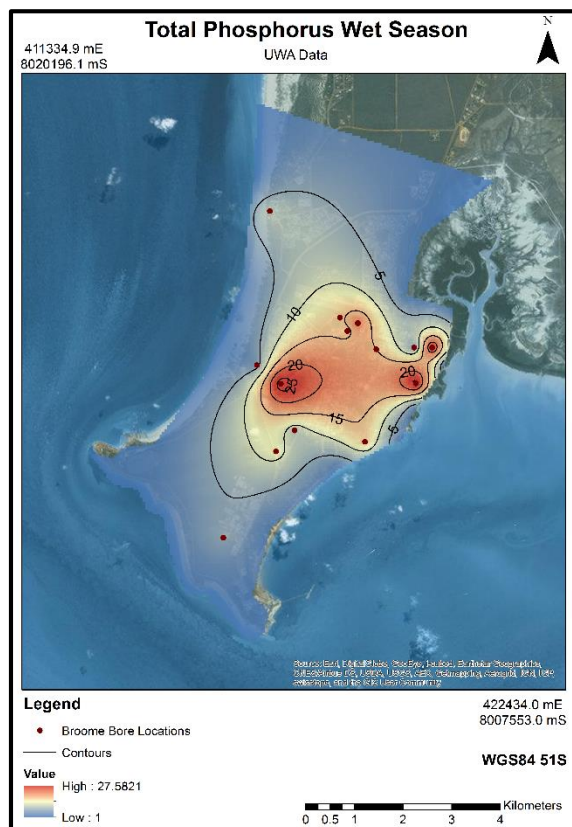


Figure 7: Interpolation maps for total groundwater phosphorus in the Broome unconfined aquifer at the end of the 2014 wet and 2013 dry season.

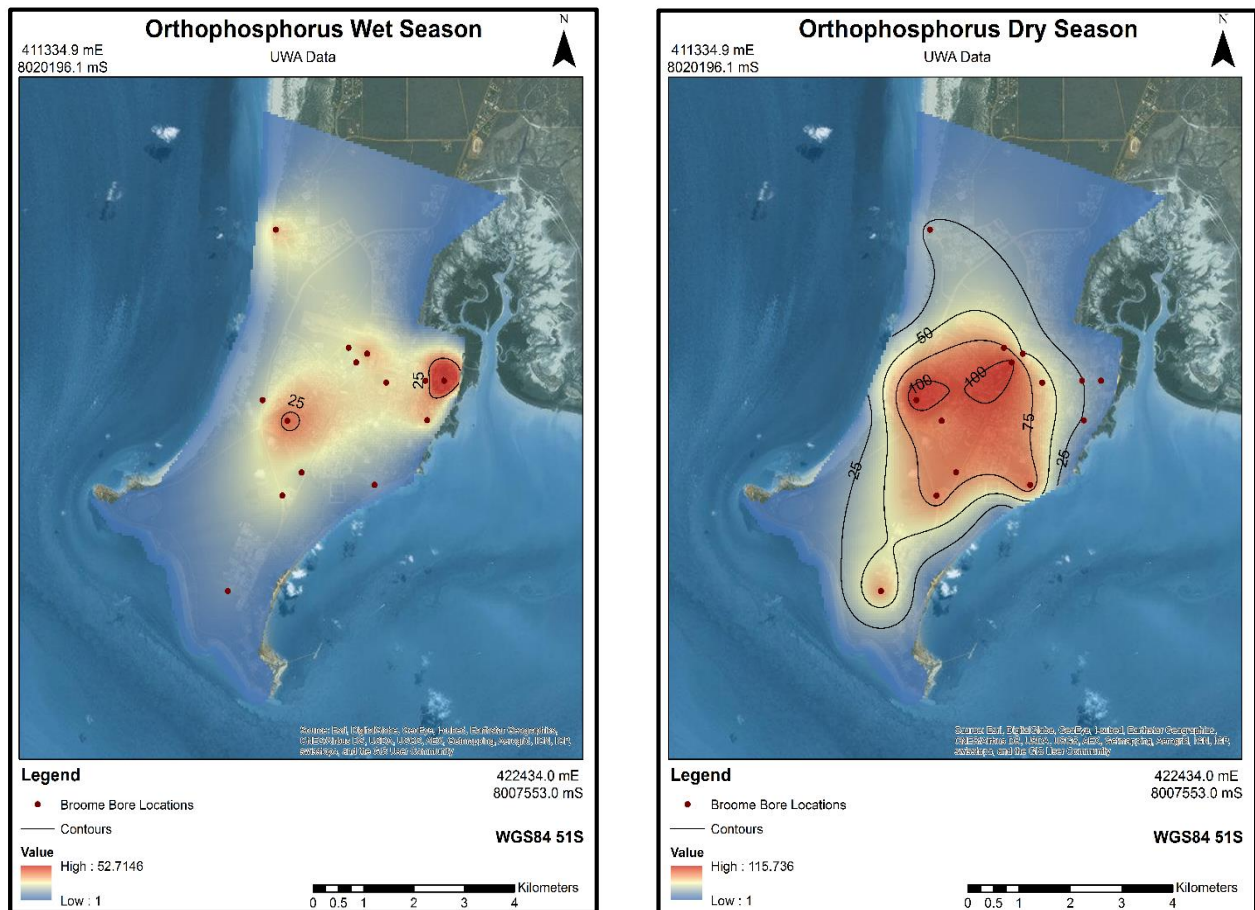


Figure 8: Interpolation maps for orthophosphorus in the Broome unconfined aquifer at the end of the 2014 wet and 2013 dry season.

3.2 Statistical Validation of Source of Nutrients within the Aquifer

3.2.1 Nutrient Concentrations throughout the Wet Season

The mean concentrations of total nitrogen, total phosphorus, ammonium, nitrate, and orthophosphorus at the end of the 2014 wet season in the Broome unconfined aquifer were 4016.32 $\mu\text{g/L}$, 17.37 $\mu\text{g/L}$, 61.22 $\mu\text{g/L}$, 3405.48 $\mu\text{g/L}$, and 23.36 $\mu\text{g/L}$ respectively. Extreme outliers from seasonal average concentrations existed in shallow water bores at sites A, C, E and at the Bedford Park and Town Oval council bores. At site A total nitrogen and nitrate was 27884.86 $\mu\text{g/L}$ and 21368.45 $\mu\text{g/L}$ respectively, at site C nitrate and orthophosphorus was 13952.28 $\mu\text{g/L}$ and 71.85 $\mu\text{g/L}$ respectively, at site E total phosphorus was 80.37 $\mu\text{g/L}$, at Bedford Park ammonium was 584.17 $\mu\text{g/L}$, and at Town Oval orthophosphorus was 55.17 $\mu\text{g/L}$. These concentrations were significantly greater than their respective means (Appendix 7).

3.2.2 Nutrient Concentrations throughout the Dry Season

The mean concentrations of total nitrogen, total phosphorus, ammonium, nitrate, and orthophosphorus at the end of the 2013 dry season in the Broome unconfined aquifer were 6381.49 µg/L, 105.64 µg/L, 40.69 µg/L, 6065.59 µg/L, and 61.58 µg/L respectively (Appendix 7). Extreme outliers, significantly different from these average concentrations, occurred in the deep bores at site A and C. Total nitrogen and nitrate at site A was 20429.20 µg/L and 18751.59 µg/L respectively, while at site C total nitrogen and nitrate were 34359.54 µg/L and 34200.00 µg/L respectively. No outliers existed for ammonium, total phosphorus and orthophosphate.

3.2.3 Nutrient Concentrations in Shallow and Deep Bores in both the Wet and Dry Season

The One-way ANOVA showed that there was a significant difference in the means of total phosphorus (*df*: 30; *F*: 20.893; *p*: 0.000), orthophosphate (*df*: 31; *F*: 19.985; *p*: 0.000), and ammonium (*df*: 30; *F*: 20.893; *p*: 0.002) in at least one of the four sample groups. The post hoc Tukey HSD test indicated that for total phosphorus, shallow and deep bores were statistically similar during wet season with means of 9.77 µg/L and 10.58 µg/L respectively. Likewise shallow and deep bores were statistically alike during the dry season with the respective means of 165.92 µg/L and 87.78 µg/L. However means for total phosphorus during the wet and dry season were not the same, with dry season bores containing groundwater with higher average concentrations.

Post hoc analysis showed that mean orthophosphate concentrations were statistically similar for shallow and deep bores during the wet season with the respective means of 30.14 µg/L and 14.13 µg/L. Likewise during the dry season shallow and deep bores were statistically alike with means of 75.42 µg/L and 86.15 µg/L respectively. However, as with the total phosphorous data, mean orthophosphorous concentrations for the wet and dry season were not the same, being greater at the end of the dry season.

The post hoc test for ammonium showed that means for shallow and deep bores at the end of the wet season and shallow bores at the end of the dry season were statistically similar with the respective means of 23.016 µg/L, 17.77 µg/L, and 26.74 µg/L. However, deep dry season bores were significantly greater than these groups with a mean concentration of 78.53 µg/L. The One-way ANOVA indicated that there was no difference in means for total nitrogen (*df*: 31; *F*: 1.877; *p*: 0.156) and nitrate (*df*: 31; *F*: 0.866; *p*: 0.47) between the four sample groups.

3.2.4 Nutrient Concentrations in the Context of Wastewater

Statistical analysis using a One-Way ANOVA indicated that means were significantly different for at least one of the three data groupings (waste water effluent, waste water irrigated sites, and sites not irrigated with wastewater) for both total nitrogen ($df: 22; F: 14.646; p: 0.000$) and nitrate ($df: 22; F: 6.627; p: 0.006$). The post hoc Tukey HSD test showed that for total nitrogen waste water irrigated sites were statistically similar to the waste water effluent with means of 8,853 $\mu\text{g/L}$ and 29,040 $\mu\text{g/L}$ respectively. Sites that were not irrigated with wastewater had significantly less total nitrogen with a mean of 1,620 $\mu\text{g/L}$. The post hoc tests for nitrate showed that non- waste water irrigated sites were not significantly different to waste water irrigated sites. These groups had respective means of 1,463 $\mu\text{g/L}$ and 3,259 $\mu\text{g/L}$ and were found to have significantly larger mean nitrate concentrations than the waste water effluent, which had a mean of 96.52 $\mu\text{g/L}$.

Total Phosphorus, orthophosphorus, and ammonium were found to be non-parametric. A Kruskal-Wallis statistical analysis was used to assess differences in the means of the three data groupings. For both total phosphorus ($X^2: 5.81; df: 2; p: 0.061$) and ammonium ($X^2: 5.288; df: 2; p: 0.071$) means were not found to be significantly different, however means for orthophosphorus were not the same ($X^2: 6.761; df: 2; p: 0.034$). Post hoc analysis cannot be performed with non-parametric data. However, mean ranks could be produced.

Waste water effluent, wastewater irrigated sites, and non- waste water irrigated sites had respective mean ranks of 22.5, 14.75, and 10.12 for orthophosphorus. The difference between the mean ranks of the waste water effluent and wastewater irrigated sites was larger than the difference between the mean rank of the wastewater irrigated sites and sites not irrigated with wastewater. It was presumed that this was where the significant difference occurred. The orthophosphorus concentration in wastewater was therefore significantly greater than that of both the wastewater irrigated and non-wastewater irrigated sites.

3.3 Multivariate Analysis

3.3.1 Wet Season Data

The bi-plot produced from the PCA describes the relationship between water quality variables and groundwater depth/disturbance at the end of the wet season for two principal components (Figure 9). The first two principle components (PC1 and PC2) were found to describe 91% of the data variance occurring between the groups. PC1 described 71% of this variance, while PC2 described 20%. This was deemed to be more than adequate, with PCA values greater than 60% being acceptable (Sodre *et al.* 2005). The strength of correlations

between water quality variables and groundwater depth/disturbance is inversely related to the angles of the lines. Variables that correlate most strongly are located proximal to each other (Sodre *et al.* 2005).

Deep waste water irrigated sites were associated with the highest total nitrogen, nitrate, and orthophosphorus levels and consequently plotted proximal to these environmental factors. The other nutrient variables, total phosphorus and ammonium, plotted in opposite quadrants, showing that there is little correlation between these variables and deep groundwater concentrations at waste water irrigated sites. Shallow waste water irrigated sites were found to show little correlation with either of the nutrient variables. Of the other environmental variables redox correlated most closely. Both shallow and deep bores at sites not irrigated by waste water correlated closely with total phosphorus. For the other environmental factors the non-wastewater irrigated deep bores were found to be associated most closely with dissolved oxygen and temperature.

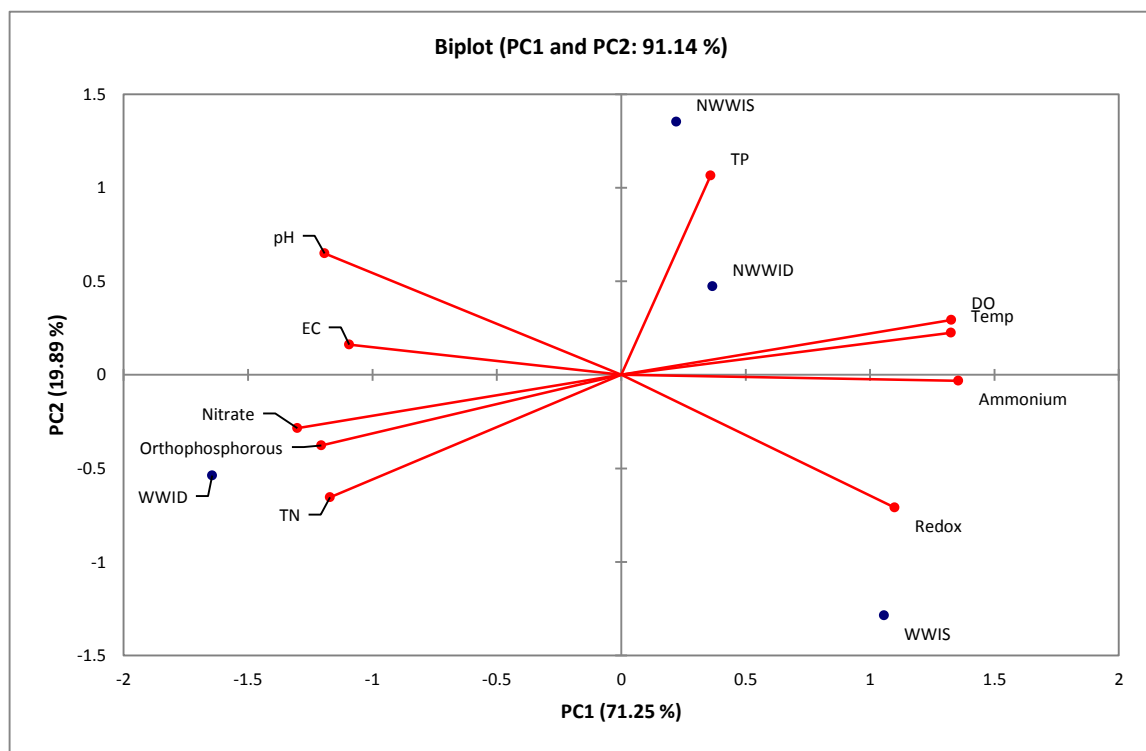


Figure 9: Bi-plot for the first two principal components describing the correlation between water quality variables and groundwater depth/disturbance during the wet season

3.3.2 Dry Season Data

The bi-plot produced from the PCA describes the relationship between water quality variables and groundwater depth/disturbance at the end of the dry season for two principal components (Figure 10). The first two principle components (PC1 and PC2) were able to describe 83% of the data variance cumulatively. PC1 described 52% of this variance, while PC2 described 31%. As with the wet season this analysis was deemed to be acceptable (Sodre *et al.* 2005).

Deep bores from waste water irrigated sites were found to correlate strongly with total nitrogen and nitrate. pH was also weakly associated with these sites. Of the groundwater nutrient variables total phosphorus was most strongly related with shallow bores situated on sites irrigated with wastewater. No other environmental variables correlated with this depth/disturbance group. Deep bores on sites not irrigated with wastewater were found to correlate most closely with ammonium and orthophosphorous. Shallow bores from sites not irrigated with wastewater did not correlate strongly to any of the environmental variables.

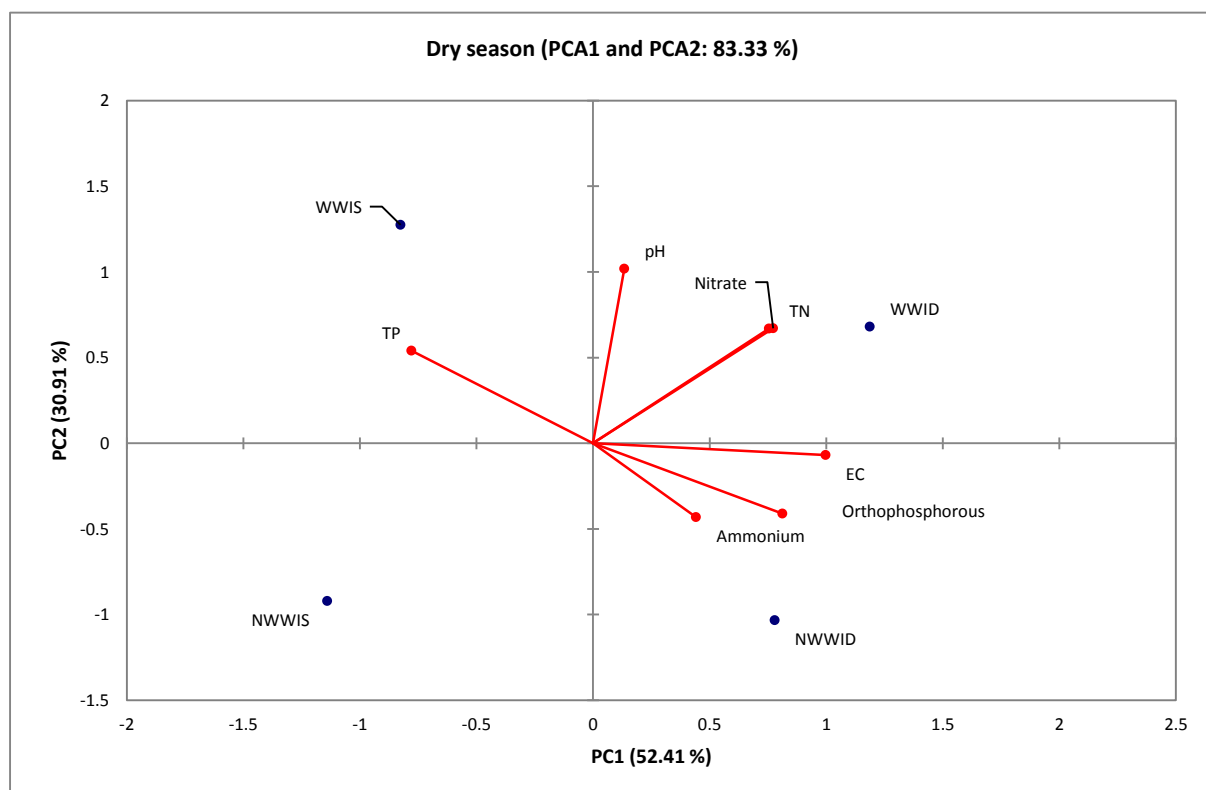


Figure 10: Bi-plot for the first two principal components describing the correlation between water quality variables and groundwater depth/disturbance during the dry season

3.4 Submarine Groundwater Nutrient Discharge into Roebuck Bay

Using the most appropriate estimates for hydraulic conductivity and the extent of the fresh water lens, SGD during the wet season was estimated to be 0.01006 GL/day, giving total discharge of 1.835 GL throughout the season. In contrast SGD during the dry season was estimated to be 0.00867 GL/day, with a total seasonal discharge of 1.582 GL. These estimations were made using data acquired by *Wright* (2013) and data obtained during this study. SGD coming from the WWTP and Broome golf course were estimated to be 0.006336 GL/day and 0.001599 GL/day respectively, using the most appropriate values.

Estimates varied when the total range of values for hydraulic conductivity and fresh water lens depth were considered. During the wet season discharge rates ranged from 0.001013 GL/day to 0.04169 GL/day, while discharge rates during the dry season ranged from 0.000923 GL/day to 0.03597 GL/day. Discharge from the WWTP ranged from 0.0006528 GL/day – 0.02592 GL/day, while discharge coming from the Broome golf course ranged from 0.0001612 GL/day – 0.000663 GL/day. The total range of estimates are shown in Appendix 15.

The best estimate for discharge of total nitrogen, nitrate, and total phosphorus during the wet season were 50.0 kg/day, 46.5 kg/day, and 0.255 kg/day respectively, when attenuation rates were not considered. In contrast discharge rates during the dry season were larger with the respective values of 107.6 kg/day, 104.5 kg/day, and 0.64 kg/day for total nitrogen, nitrate, and total phosphorus. These estimations were made using data acquired by *Wright* (2013) and sampled for the purpose of this study. During 2013 nutrient discharge rates from the WWTP for total nitrogen, nitrate, and total phosphorus were 44.62 kg/day, 33.87 kg/day, and 0.72 kg/day respectively. Discharge rates from the Broome golf course were 43.65 kg/day, 42.75 kg/day, and 0.0745 kg/day for total nitrogen, nitrate, and total phosphorus during 2013. The total range of estimated values for nutrient discharge is displayed in Appendix 15.

3.5 Natural Attenuation of Groundwater Nutrients

Under the estimate for natural nitrogen attenuation used in this study, total denitrification of groundwater at all sites, is expected to occur, except at bore C, the WWTP and the Broome golf course. At all other sites the transport time was far greater than the associated total denitrification time (Table 1), even when the full range of denitrification and hydraulic conductivity values were considered (Table 3 and 4). Proximal to bore C the estimated discharge concentrations into Roebuck Bay, when a denitrification rate of 3.1 mg/L/year was

considered, were 3.82 mg/L and 13.71 mg/L at the end of the wet and dry season respectively (Table 2). This equates to a total nitrate SGD of 13,627 Kg during the dry season and 3,796 Kg during the wet season, using the best approximations for K and freshwater lens depth. The estimated discharge concentrations of nitrate for the WWTP and the Broome golf course were 3.13 mg/L and 13.99 mg/L respectively when a denitrification rate of 3.1 mg/L/year was considered (Table 2). This equates to a total annual nitrate discharge of 7,238 Kg from the WWTP and 8,165 Kg from the Broome golf course. The full range of estimates are displayed in Appendix 15.

Table 1: Total transport time (years) of groundwater migrating from each bore (K=7.5 m/day) to Roebuck Bay, and total denitrification time (denitrification rate = 3.1 mg/L/year) for nutrients at each bore location. Bold text identifies sites with N discharge after natural attenuation was taken into account.

	Wet		Dry	
	Transport time (years)	Total denitrification time (years)	Transport time (years)	Total denitrification time (years)
A	154.25	3.98	203.46	5.05
B	171.99	1.03	214.99	3.04
C	1.16	2.39	1.16	5.58
D	368.74	0.14	536.35	0.21
E	236.16	0.34	302.81	0.03
F	60.75	0.53	74.44	2.59
G	55.75	0.51	71.48	1.40
H	50.09	0.65	52.54	1.09
BP	9.07	0.33	9.43	0.59
KRO	41.79	0.98	43.77	1.55
TO	15.61	0.68		
WWTP	0.713	1.72	0.713	1.72
Golf Course	6.85	8.62	6.85	8.62

Table 2: Estimated final nitrate concentration of groundwater discharging into Roebuck Bay from Bore C, WTTP and the Golf Course.

	Denitrification Rate (mg/L/year)	0.186	3.1	6.2
Bore C -Wet	Nitrate (mg/L)	7.20	3.82	0.25
Bore C - Dry	Nitrate (mg/L)	17.09	13.71	10.12
WWTP	Nitrate (mg/L)	5.21	3.13	0.92
Golf Course	Nitrate (mg/L)	25.97	13.99	1.26

Table 3: Estimated velocity, transport time, and total denitrification time for nitrate migrating from groundwater bores to Roebuck Bay during the 2014 wet season and the WWTP and Golf Course during the 2013 sampling period.

	Velocity (m/day)				Transport time (years)				Total denitrification time (years)		
Hydraulic Conductivity (m/day)	1	7.5	15	25	1	7.5	15	25	-	-	-
Denitrification Rate (mg/L/year)	-	-	-	-	-	-	-	-	0.19	3.1	6.2
A	0.00512	0.03842	0.07684	0.12806	1157	154	77	46	66.25	3.98	1.99
B	0.00479	0.03592	0.07184	0.11973	1290	172	86	52	17.18	1.03	0.52
C	0.04579	0.34345	0.6869	1.14483	8.7	1.16	0.578	0.347	39.89	2.39	1.20
D	0.00328	0.02462	0.04925	0.08208	2766	368	184	111	2.39	0.14	0.07
E	0.004	0.03002	0.06005	0.10008	1771	236	118	71	5.60	0.34	0.17
F	0.00732	0.05493	0.10985	0.18309	456	61	30	18	8.91	0.53	0.27
G	0.00724	0.0543	0.1086	0.181	418	56	28	17	2.88	0.51	0.26
H	0.00662	0.04961	0.09923	0.16538	376	50	25	15	10.89	0.65	0.33
BP	0.01852	0.13891	0.27783	0.46304	68	9	4.5	2.7	5.44	0.33	0.16
KRO	0.00787	0.059	0.118	0.19667	313	41	21	12.5	16.38	0.98	0.49
TO	0.01287	0.09655	0.19309	0.32182	117	15	7.8	4.7	11.40	0.68	0.34
WWTP	0.128	0.96	1.92	3.2	5.35	0.71	0.36	0.21	28.74	1.72	0.86
Golf Course	0.016	0.12	0.24	0.4	51.4	6.85	3.42	2.05	143.75	8.62	4.31

Table 4: Estimated velocity, transport time, and total denitrification time for nitrate migrating from groundwater bores from groundwater bores to Roebuck Bay during the 2013 dry season and the WWTP and Golf Course during the 2013 sampling period.

	Velocity (m/day)				Transport time (years)				Total denitrification time (years)		
Hydraulic Conductivity	1	7.5	15	25	1	7.5	15	25	-	-	-
Denitrification Rate (mg/L/year)	-	-	-	-	-	-	-	-	0.19	3.1	6.2
A	0.00388	0.02913	0.05825	0.09709	1525	203	101	61	84.13	5.05	2.52
B	0.00383	0.02874	0.05747	0.09579	1612	215	107	65	50.62	3.04	1.52
C	0.04579	0.34345	0.6869	1.14483	8.7	1.16	0.578	0.347	93.06	5.58	2.79
D	0.00226	0.01693	0.03386	0.05643	4022	536	268	161	3.42	0.21	0.10
E	0.00312	0.02342	0.04683	0.07805	2271	302	151	91	0.46	0.03	0.01
F	0.00598	0.04483	0.08966	0.14943	558	74	37	22	43.20	2.59	1.30
G	0.00565	0.04235	0.08471	0.14118	536	71	35	21	1.62	1.40	0.70
H	0.00631	0.0473	0.0946	0.15766	394	52	26	16	18.22	1.09	0.55
BP	0.01783	0.1337	0.26739	0.44565	70.7	9	4.7	2.8	9.79	0.59	0.29
KRO	0.00751	0.05633	0.11267	0.18778	328	43	22	13	25.89	1.55	0.78
WWTP	0.128	0.96	1.92	3.2	5.35	0.71	0.36	0.21	28.74	1.72	0.86
Golf Course	0.016	0.12	0.24	0.4	51.4	6.85	3.42	2.05	143.75	8.62	4.31

3.6 Town Beach Fresh Water Discharge Zone

Three freshwater discharge zones were identified throughout Town Beach. Two zones comprised of a single EC measurement deemed to be significantly lower than the median. The first area was situated proximal to the Town Beach access track (418334 mE, 8012405 mS) and had an EC reading of 42.3 mS/cm, considerably lower than the median of 52.45 mS/cm. The second small discharge zone was located approximately 50m into the intertidal zone from the beach (417510 mE, 8011718 mS), proximal to the largest discharge zone. The EC reading at this site was 44.2 mS/cm and was deemed to be significantly lower than the median of 47.56 mS/cm.

The largest freshwater discharge zone was located approximately 500m south south -west of the WWTP and contained eleven samples which were significantly less than their respective medians. EC measurements at this discharge zone ranged from 43.3 mS/cm – 33.3 mS/cm and were significantly less than the medians of 52.45 mS/cm and 47.8 mS/cm, determined during two periods of sampling (Figure 11). Given the position of these discharge sites (located at the top of the intertidal zone) it is unlikely that they represent regional discharge, which is more likely to occur at the base of the intertidal zone due to the large tidal regime at Broome (Robinson *et al.* 2007; Bureau of Meteorology 2014 (b)). The observed zones are most likely related to discharge occurring from the perched aquifer in the beach dune system.

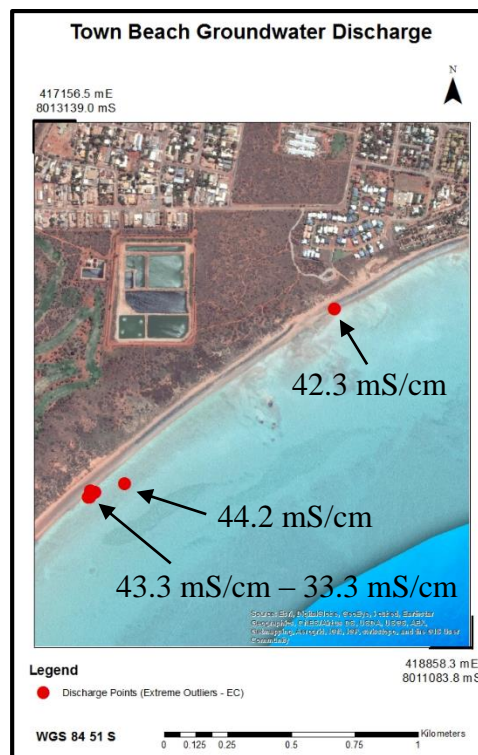


Figure 11: Groundwater discharge zones identified throughout Town Beach.

3.7 Nonylphenol Concentrations within the Broome Unconfined Aquifer

NP concentrations at all groundwater bores, wastewater storages and throughout Town Beach were found to be below detectable levels (<5 µg/L). It can therefore be presumed that this organic contaminant is not present within the Broome unconfined aquifer. NP does not appear to pose as an environmental threat to the Broome peninsula or Roebuck Bay.

3.8 Groundwater Metal/Metalloid Contaminants

Several metal/metalloid contaminants were found to be above the maximum acceptable levels outlined by the United States Environmental Protection Authority (USEPA), Australian and New Zealand Environment and Conservation Council (ANZECC), and the Australian National Health and Medical Research Council (NHMRC). Nickel, arsenic, and selenium violated all three drinking water guidelines, while uranium was above the level acceptable under the ANZECC and NHMRC. Similarly vanadium, manganese and strontium were above the levels acceptable under the USEPA guidelines (Table 5). Manganese, selenium, and uranium were above the recommended levels outlined by ANZECC for recreational water. Each of these contaminants can have harmful biological effects at relatively low levels, so are of environmental significance (Bissen and Frimmel 2003; Maraldi *et al.* 2011; Venkataraman and Sudha 2005; Cempel and Nickel 2006; ATSDR 2004; ATSDR 1997).

Table 5: Concentrations of metal contaminants (mg/L) of environmental significance which violate drinking water quality standards according to the USEPA, ANZECC and NHMRC guidelines.

Element	Vanadium	Manganese	Nickel	Arsenic	Selenium	Strontium	Uranium
AD1	0.002	0.001	0.001	0.0156	0.055	3.34	0.0141
AS1	0.00664	0.0109	0.001	0.001	0.00126	0.0578	0.001
BD1	0.00691	0.00168	0.001	0.00373	0.014	0.373	0.00153
Bedford Park	0.00288	0.446	0.0247	0.00514	0.00598	0.725	0.00237
Bracks Oval	0.001	0.0174	0.00473	0.00123	0.00226	0.266	0.001
BS1	0.00395	0.00331	0.001	0.001	0.00276	0.0981	0.001
Cable Beach A	0.0026	0.001	0.001	0.001	0.00502	0.251	0.001
Cable Beach B	0.00298	0.001	0.001	0.001	0.00581	1.51	0.00437
CD2	0.00271	0.001	0.001	0.00181	0.0121	1.33	0.00656
CS2	0.0409	0.001	0.001	0.00427	0.00157	0.635	0.00569
DD2	0.00299	0.001	0.001	0.00228	0.00967	1.94	0.021
DS2	0.0134	0.00555	0.001	0.00548	0.014	2.36	0.0204
ED2	0.001	0.0242	0.001	0.00262	0.0163	0.807	0.00352
ES3	0.001	0.02	0.001	0.001	0.00571	0.497	0.001
FD3	0.00135	0.001	0.00479	0.0153	0.0601	5.9	0.001
FS3	0.00418	0.0166	0.001	0.00696	0.0289	1.75	0.001

GD4	0.001	0.001	0.00582	0.0176	0.0639	6.14	0.00464
GS4	0.0136	0.001	0.001	0.00173	0.00924	0.124	0.001
Haynes Park	0.001	0.0172	0.001	0.00116	0.00267	0.257	0.001
HD4	0.0124	0.0122	0.00474	0.0198	0.0736	7.29	0.0164
HS4	0.00829	0.001	0.001	0.00145	0.001	0.07	0.001
KRO	0.00769	0.001	0.001	0.00219	0.0086	0.382	0.00275
Town Oval	0.001	0.001	0.001	0.00182	0.00736	0.372	0.001



Violates USEPA Drinking Water Guidelines exclusively

0.001

Violates USEPA Drinking Water Guidelines



Violates ANZECC and NHMRC Drinking Water Guidelines

0.001

Violates ANZECC and NHMRC Recreational Water Guidelines

3.9 Speciation of Metal/Metalloid Contaminants

Eh – pH plots and PHREEQC were used to determine the chemical speciation of metal/metalloid contaminants violating drinking water guidelines (Appendix 9). As was found to exist as H_2AsO_4^- at all four sites, Mn and Ni were present as Mn^{2+} and Ni^{2+} within the Bedford Park well and V was present as VO_3^- at the site C shallow well. Se was present as Se (s) at the E, A, G and F deep wells and the F and D shallow wells, SeO_3^{2-} at the site B deep well, and as HSeO_3^- at the site H and C deep wells. Sr was present as Sr^{2+} at the F, G, and H deep wells, while U occurred as UO_2^{2+} at both the shallow and deep wells at site D.

3.10 Groundwater Interpolation

Groundwater levels at the end of the 2014 wet season were found to be considerably greater than those measured during the end of the 2013 dry season, as was expected (Figure 12). This flux in hydraulic head causes a small variation in the hydraulic gradient between the middle of the peninsula and the coast. This may have implications for the seasonal variability in groundwater migration velocity (Nonner 2006). In general groundwater is predicted to migrate predominantly outwards towards Roebuck Bay and Cable Beach from the centre of the southern extent of the peninsula.

Table 6: Seasonal groundwater recharge at each private groundwater bore.

Bore	Water table height (<i>h</i>) fluctuation (m)	Sy	Δ S (m)	Δ S (mm)
A	0.67	0.2	0.134	134
B	0.54	0.2	0.108	108
C	-0.3	0.2	-0.06	-60
D	0.85	0.2	0.17	170
E	0.57	0.2	0.114	114
F	0.41	0.2	0.082	82
G	0.44	0.2	0.088	88
H	0.07	0.2	0.014	14

The Broome peninsula was divided into several different areas in order to estimate total seasonal recharge (Table 7). The total area considered for recharge calculations covered the southern proportion of the peninsula, which was calculated to encapsulate an area of approximately 20.89 km². The total seasonal recharge occurring between the wet and the dry season for this area was estimated to be approximately 1.176 GL. Seasonal recharge was not calculated for the northern extent of the Broome peninsula due to the lack of data.

Table 7: Seasonal recharge for the southern Broome Peninsula

Recharge Extent	Bores within recharge area	Recharge Area (km ²)	Average Δ S (mm)	Seasonal Regional Recharge (GL)
North	A, B	2.82	121	0.3412
North West	D	2.77	170	0.4709
Middle	E, F, G	4.8	94.6	0.4541
South East	C	3.21	-60	-0.1926
South West	H	7.29	14	0.10206
Total	-	20.89	67.92	1.17566

3.12 Groundwater Chemistry

Variations in groundwater composition were useful for identifying the extent of contamination throughout the Broome peninsula. Most bores had an alkalinity to electrical conductivity ratio greater than levels typical of the freshwater - seawater mixing line (Figure 13). Bores which plotted close to the expected values were generally situated away from

areas affected by wastewater contamination. Similarly the piper diagram displayed two general data groupings (Figure 14). Those with a groundwater chemistry typical of the peninsula historically (circled in blue) and those with anomalous carbonate and bicarbonate concentrations (circled in red), relative to the other ions. These anomalous concentrations generally occurred at sites proximal to wastewater affected regions.

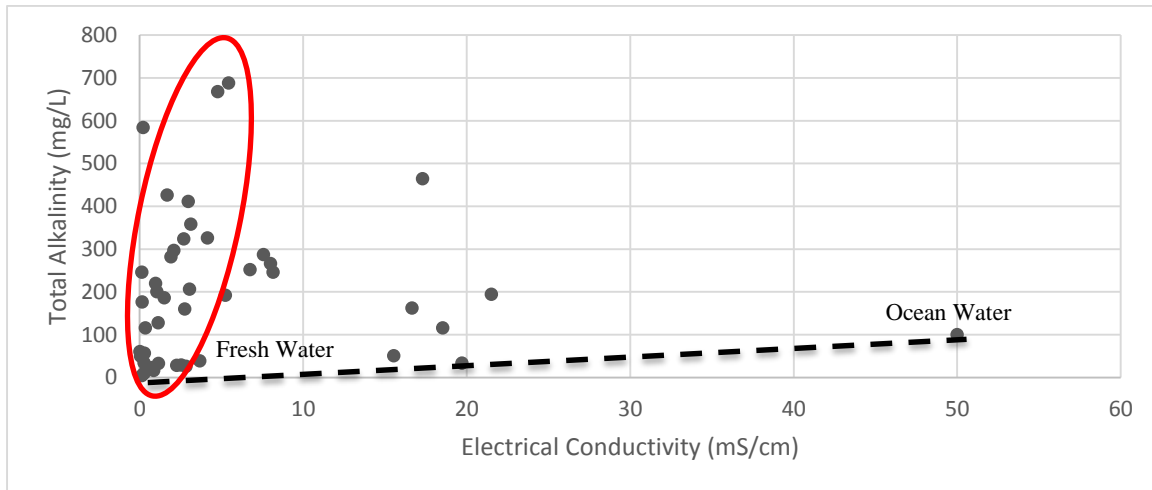


Figure 13: Alkalinity vs salinity for samples collected during the 2013 dry and 2014 wet seasons.

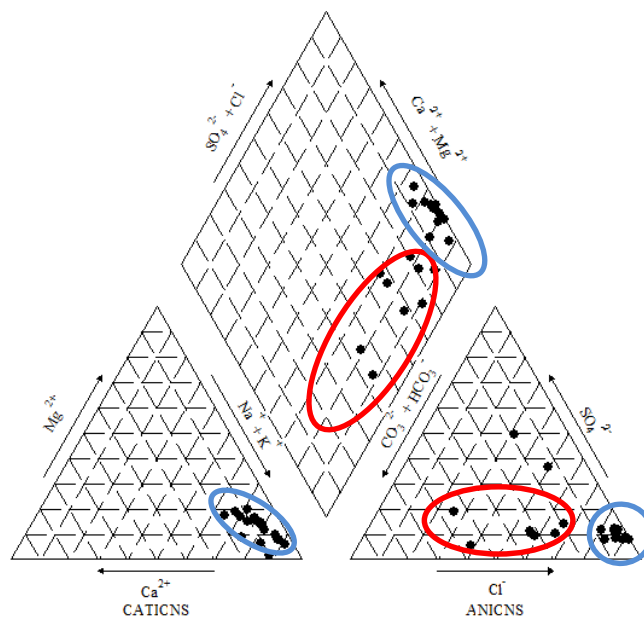


Figure 14: Piper diagram of groundwater chemistry for twenty bores sampled throughout the 2014 wet season throughout the Broome peninsula. (Blue = Groundwater chemistry historically typical of the peninsula; Red = Anomalous carbonate and bicarbonate concentrations (typically wastewater effected sites))

4. Discussion

4.1 Nutrient Source, Fate, and Environmental Significance

4.1.1 Total Nitrogen and Nitrate

Nitrogen is one of the most ubiquitous groundwater contaminants (DeSimone and Howes 1998). Primary sources include human and animal waste disposal, sewage leakages, landfill leachate, and the overuse of nitrogenous fertilisers in agricultural and domestic practices (Gu *et al.* 2013; DeSimone and Howes 1998). The effluent from WWTP's has been identified as a significant point source of excess nutrients (Carey and Migliaccio 2009; Ahearn *et al.* 2005; Migliaccio *et al.* 2007). In Florida it was estimated that 1.2×10^{10} g – N/year is released to the environment from WWTP facilities alone (Badruzzaman *et al.* 2012). This leads to nutrient loading in waterways, causing eutrophication, currently one of the most significant water quality issues globally (Smith *et al.* 1999). High levels of nitrogen in drinking water also causes a number of human health issues (Yang *et al.* 2007). Birth defects, such as infant methemoglobinemia, and cancer development, from nitrosamine synthesis in the body, are two of the most concerning (Fan *et al.* 1987; Khanfar 2010).

Throughout the Broome peninsula the highest levels of total nitrogen (TN) and nitrate occurred in areas proximal to the WWTP, golf course and wastewater irrigated ovals. Concentrations at these sites were significantly greater than seasonal means for the peninsula. TN at sites irrigated with wastewater were found to be statistically similar to that of the wastewater effluent, while non-wastewater irrigated sites were significantly different. Deep bores at wastewater irrigated sites correlated closely with TN and nitrate in the multivariate analysis. Non-irrigated sites were not associated with these nutrient variables. These trends indicate that the elevated TN and nitrate concentrations throughout the Broome peninsula are explicitly linked with the wastewater treatment plant and effluent discharge sites.

In many of these areas total nitrogen was found to be above the 10 mg N L⁻¹ maximum level outlined by the World Health Organization (Gu *et al.* 2013). Groundwater sourced from these regions should not be consumed, as the human health effects previously outlined can occur (Khanfar 2010). Groundwater also exceeded the recommended maximum concentration of TN and nitrate for tropical wetlands and marine ecosystems, by several orders of magnitude, throughout the Broome peninsula (ANZECC 2000). As aquatic systems are generally nutrient limited, increased nutrient loads can cause a number of ecological issues. These include reduced species diversity, increased biomass of benthic and epiphytic algae, greater toxin

synthesis from bloom forming algal taxon, and reduced aesthetic value of the water body (Rabalais 2002; Scheffer *et al.* 2001; Smith 1999).

During this study several freshwater/saltwater mixing zones were identified throughout Town Beach. This confirms that SGD is occurring into the intertidal zone of Roebuck Bay from the Broome peninsula. The discharge sites identified are at the top of the tidal range so are unlikely to represent regional groundwater discharge where wastewater nutrient contamination will be present. These sites are more likely to relate to groundwater stored in the perched aquifer in dunes immediately behind the beach. Unfortunately it was outside the scope and budget of this study to complete a comprehensive investigation of groundwater discharge across the whole of the intertidal zone. Regional groundwater discharge is likely to occur at the base of the intertidal zone (Robinson *et al.* 2007). The identification of zones of freshwater discharge in this study proves that groundwater discharge is occurring in the intertidal zone and that its distribution is likely discontinuous, hence it was difficult to find with opportunistic and spatially limited surveys.

Some of the highest concentrations of total nitrogen and nitrate occurred at bore C, the WWTP and the Broome golf course. Denitrification was found to be ineffective in eliminating all groundwater nitrate from these areas before reaching Roebuck Bay. The annual discharge of nitrate, coming predominantly from the WWTP and the golf course, irrigated with treated wastewater effluent, was estimated to be 32,826 Kg/yr. This is likely to be significant in terms of impacts to Roebuck Bay. Consequently the SGD of N is likely to be a key factor driving with the recent increases in *Lyngbya majuscula* blooms (Estrella 2013). The levels of TN/nitrate in the aquifer and the level of natural attenuation warrant additional monitoring and a more detailed assessment.

4.1.2 Ammonia

Ammonia is a nitrogenous molecule that exists in either an ionised (NH_4^+) or unionized form (NH_3). Unionized ammonia is extremely toxic to aquatic organisms, while ionized ammonia is nontoxic (Camargo and Alonso 2006). High levels of ammonia in natural environments causes eutrophication, soil acidification, and reductions in biodiversity (Shen *et al.* 2011). In humans several health issues can occur due to high levels of ammonia. In general it is an irritant that affects the eyes, skin, and respiratory passages, causing a burning sensation (Harte *et al.* 1991). In some cases hepatic encephalopathy can occur due to a rise of ammonium in circulating plasma (Walsh *et al.* 2008). The primary pathway of ammonium

into the environment is through release from land fill and septic tanks, discharge from WWTP's, and by the anaerobic degradation of organic matter (Umezawa *et al.* 2009).

Throughout the Broome peninsula groundwater ammonia was not directly related to the WWTP or discharge sites. The greatest concentrations occurred proximal to Bedford Park during the wet season. This value was significantly greater than the seasonal mean. During the dry season ammonium concentrations were greatest at bore E. Neither Bedford Park, nor the area surrounding bore E were directly impacted by the WWTP or WWTP discharge sites. Anomalous ammonia concentrations generally correlated most closely with non-wastewater irrigated deep bores in the multivariate analysis. These sites were also found to correlate closely with the redox potential variable.

The speciation of nitrogenous products is a redox mediated process (Reddy and DeLaune 2008). Under reducing conditions the formation of ammonium is favoured (Pyne 1995). Bedford Park had the lowest redox potential of any site sampled throughout the peninsula at the end of the wet season. When the environmental conditions for the site were plotted, using an Eh-pH diagram, it was predicted that the major nitrogenous species was ammonia (Pyne 1995). This correlated with the anomalous ammonium concentration detected at the site. As nitrogen from wastewater is driven into the reduced parts of the aquifer, ammonia is subsequently being formed. Redox potential was not measured at bore E at the end of the dry season. It is likely that this site also had a low Eh, accounting for the high groundwater ammonia concentration.

The US EPA outline that ammonium levels in human drinking water should be less than 35 mg/L (Harte *et al.* 1991). Ammonium concentrations did not exceed these levels at any of the sites sampled throughout the Broome peninsula. However, ammonia did violate the maximum recommended concentrations for tropical wetland and marine ecosystems (ANZECC 2000). Although this is concerning, ammonia concentrations throughout the peninsula were generally several orders of magnitude less than those observed for nitrate and TN. Natural attenuation is also likely to reduce ammonium levels prior to SGD (Buss *et al.* 2004). Bedford Park was found to have a greater concentration of nitrate in the underlying aquifer than ammonium at the end of the wet season. Natural attenuation was predicted to eliminate all groundwater nitrate from this site prior to SGD. If attenuation rates are similar for ammonium it is unlikely that SGD will contribute significant loads of ammonia to

Roebuck Bay. Consequently the SGD of TN/nitrate presents a far greater threat to biodiversity and environmental processes throughout Roebuck Bay.

4.1.3 Total Phosphorus and Orthophosphate

Since the early 1960's concentrations of groundwater P have risen globally due to increased fertiliser application and wastewater discharge (Spiteri *et al.* 2007; Wilhelm *et al.* 1994). The release of P contaminated groundwater into coastal waters causes eutrophication, altering the limiting nutrient in primary production and stimulating toxic algal blooms (Slomp and Cappellen 2004). Although elemental P is toxic, it is extremely rare in the environment, so P is generally considered to be non – toxic (Gibson *et al.* 2000). Nausea, gastrointestinal haemorrhage, and cardiovascular collapse can occur in extreme cases where concentrated elemental P is ingested (Bateman *et al.* 2014). As P discharge causes reductions in water quality and ecological disturbance, these are the primary concerns associated with the contaminant (Badruzzaman *et al.* 2012).

Throughout the Broome peninsula groundwater phosphorus and orthophosphorus was likely to come from a number of sources. At the end of the dry season total phosphorus (TP) and orthophosphorus were greatest at wastewater irrigated ovals and at bores E and D. The multivariate analysis showed that shallow bores at wastewater irrigated sites correlated with TP, while orthophosphorus correlated most closely with deep bores at non-wastewater irrigated sites. At the end of the wet season the greatest concentrations of TP occurred at bore E, while orthophosphorus was greatest at Town Oval, bores proximal to the WWTP, and ovals irrigated with treated wastewater effluent. In the multivariate analysis TP correlated most closely with shallow and deep non-wastewater irrigated bores, while orthophosphorus was most closely associated with deep bores on wastewater irrigated sites. This variability in contaminant sources indicates that the WWTP, wastewater discharge sites, and areas not irrigated with wastewater all contribute to anomalous TP and orthophosphorus concentrations in the Broome unconfined aquifer.

The application of fertilisers is a major contributor of phosphorus to the environment. In the south east of coastal USA this contaminant source was estimated to contribute 13 – 840 kg of P/ha/year (MacDonald *et al.* 2011). Similarly throughout the European Union P application was estimated to contribute 3,849, 873 tons P/year to the environment (Toth *et al.* 2014). Only 1 – 2.5% of the available P can be absorbed by plants. A large proportion of P is therefore lost to the environment, contributing to groundwater contamination (Yu *et al.*

2013). Throughout Broome the application of fertiliser is likely to be a significant contributor of P to the unconfined aquifer. Discharge of wastewater effluent has also been identified to be a key source of P to groundwater. Secondary treatment facilities, such as the WWTP located at Broome, typically release P at concentrations of 3 to 10 mg/L. This is significant for nutrient loading in aquifers (Chang 2010; Canter and Knox 1985).

Currently little qualitative information is available regarding the attenuation of groundwater P in field studies (Spiteri *et al.* 2007). However, the predominant mechanisms are well known. P retention in aquifers is largely controlled by sorption, with P having the greatest affinity for Fe oxides and calcium carbonate (Krom and Berner 1980). Sorption generally occurs in two steps; the rapid adsorption of P onto high affinity mineral surfaces, and slow diffusion into micropores (Slomp *et al.* 1998). Phosphate also forms several reasonably insoluble secondary minerals including strengite, vivianite, variscite and hydroxyapatite, limiting P migration through the subsurface (Nriagu and Moore 1984).

These mechanisms are often successful in limiting P migration to groundwater. This was observed in field studies at a site which had been affected by wastewater for 10 years. P was found to be attenuated within a 10m radius of the area (Spiteri *et al.* 2007). Sorption sites can however become occupied, rapidly increasing the movement of P through the subsurface (Heckrath 1995). Attenuation is also affected by grain size. It is most rapid and effective in soils with a fine (0.1 – 0.25 mm) particle size (Canter and Knox 1985). These factors are likely to affect P migration in the Broome unconfined aquifer.

The amount of P estimated to enter Roebuck Bay annually through SGD from the Broome peninsula was 455 Kg. As attenuation was not considered this value is likely to be an over estimation. The grain size in the upper facies of the Broome sandstone aquifer ranges from 0.0016 mm to 2mm (Wright 2013). Attenuation through sorption will be effective in areas containing finer sediment fractions (Canter and Knox 1985). P has a high affinity for Fe oxide minerals, limiting P migration through the soil into aquifers (Krom and Berner 1980). Pindan soils, forming the upper unit of the unconfined aquifer, have a high haematite (Fe_2O_3) content (Emery *et al.* 2003). The Broome Sandstone has some Fe oxides in the upper deltaic facies, but the fact that elevated P concentrations exist in the groundwater suggests that the capacity to adsorb the loads of P being applied is being at least partially overwhelmed. The discharge of P into Roebuck Bay may however be less than the estimated figure, even if a

proportion of sorption sites are occupied, limiting retention. N discharge through SGD appears to be far more significant in terms of nutrient loading throughout Roebuck Bay.

4.2 Seasonal Variability in Groundwater Nutrient Loads

Throughout the Broome peninsula TP and orthophosphate were significantly greater at the end of the dry season, while ammonia was greatest in deep bores at the end of the dry season. Similarly TN and nitrate were greater at the end of the dry season, however this difference was found to not be significant. As 1.469 GL of seasonal recharge occurred throughout the southern portion of the peninsula, contaminant dilution may account for the overall reduction in concentrations between the 2013 dry season and 2014 wet season.

Contaminants are diluted in aquifers primarily through dispersion, as contaminant plumes migrate longitudinally and transversely away from the contaminant source (Beaver 1996). Changes in groundwater velocities are influenced by recharge intensity in areas where rainfall infiltration occurs (Serrano 2010). Molecular diffusion also contributes to reductions in groundwater contaminant concentrations. This process involves the movement of solutes from areas of high to low concentration (Rushton 2003). As dispersion and diffusion are non-destructive, they do not cause a net loss of contaminants, only a reduction in the concentration (Beaver 1996).

4.3 4-nonylphenol

Throughout the Broome peninsula NP was found to be below detectable levels in all samples taken from groundwater bores, wastewater facilities and throughout Town Beach.

Consequently NP does not pose a threat to benthic invertebrate populations throughout Roebuck Bay, and is unlikely to be responsible for the recent drop in abundance and biodiversity. However, a number of other synthetic organic contaminants may be present in effluent discharged by the WWTP. A study sampling 47 sites across 18 states throughout the USA found that synthetic organic contaminants were present at 81% of the sites. Of the 65 organic contaminants sampled N,N-diethyltoluamide, bisphenol, sulfamethoxazole, and 4 – octylphenol monethoxylate were found at 35%, 30%, 23%, and 19% of the sites respectively (Barnes *et al.* 2008). It is therefore critical that a suite of synthetic organic compounds be sampled throughout the Broome peninsula in wastewater, groundwater, and throughout Town Beach to identify if these contaminants are present, posing a threat to the local ecology and population who consume intertidal biota.

4.4 Metals/Metalloids

As, Mn, Ni, Se, Sr, U, and V were found to be above USEPA, ANZECC and NHMRC drinking water guidelines in at least one of the groundwater bores sampled throughout the Broome peninsula. At all contaminated sites, excluding deep bores situated at sites A, E, F, and G containing Se, metals/metalloids were present in bioavailable and mobile forms (Hutzinger 2009; Alloway 2010). Groundwater should not be extracted from these sites for drinking purposes. The only sites that did not violate guideline levels for metals/metalloids were Cable Beach, the Kimberly Regional Offices and Town Oval. Groundwater from these sites is safe for human consumption.

Generally the metals/metalloids violating drinking water guidelines were only slightly higher than the recommended concentrations. Of these seven metals/metalloids only Mn, Se, and U were found to be above the ANZECC recreational water quality guidelines (ANZECC 2008). As with groundwater nutrients, metals can be removed from groundwater through natural attenuation processes (Surampalli *et al.* 2004). As and Se can be transformed and concentrations reduced via volatilization, precipitation, and sorption (Mulligan and Yong 2004). Ni readily sorbs to metal hydroxide minerals, predominantly Fe and Mn oxides, reducing contaminant concentrations in groundwater (Webber *et al.* 2009). Sr can be removed from groundwater through inorganic ion exchange, and V is immobilised primarily through microbial mediated processes (Sylvester and Clearfield 1998; Ortiz - Bernad 2004). Mn concentrations in groundwater are reduced through precipitation and sorption, while U is generally removed through precipitation (Mulligan and Yong 2004). These processes are likely to reduce concentrations of metal/metalloids to environmentally insignificant levels prior to SGD. Consequently the metal/metalloids identified throughout the Broome unconfined aquifer are unlikely to pose a substantial threat to biodiversity and ecological function throughout Roebuck Bay. However metal/metalloids may present a health risk for residents consuming large quantities of Roebuck Bay invertebrates, due to bioaccumulation.

Conclusions

The WWTP and sites irrigated with treated wastewater effluent were found to be major contributors of TN and nitrate to groundwater throughout the Broome peninsula. These sites were also key contributors of P, as were sites impacted by heavy fertiliser application. Ammonia was not associated with wastewater affected areas and was found to be a product of redox processes (Pyne 1995), where pervasive groundwater nitrate was transformed to ammonia once it encountered the reducing conditions of the deep aquifer.

Nitrate was identified to be the primary nutrient contaminant effecting Roebuck Bay. When attenuation processes were considered the amount of nitrate entering Roebuck Bay annually through SGD was estimated to be 32,826 Kg. This is significant in terms of eutrophication (Scheffer *et al.* 2001). The SGD of nitrate is likely to be contributing to the recent increase in Lyngbya blooms throughout Roebuck Bay (Estrella 2013).

Attenuation processes were estimated to be significant for the removal of all groundwater nutrients from ovals irrigated with treated wastewater effluent prior to SGD. However this is based on a simple attenuation estimate. The attenuation capacity of the aquifer may be less than this as the aquifer may be overwhelmed with nitrogen, inhibiting denitrification processes such as N_2 gas synthesis (Blackmer and Bremner 1978). In contrast large concentrations of nitrate can facilitate extensive microbial mass development, assimilating significant loads of nitrate (Hu *et al.* 2000). The attenuation capacity of the aquifer therefore requires a dedicated mechanistic investigation to assess these factors.

The primary contributors of nitrate to Roebuck Bay were identified to be the WWTP and the neighbouring golf course, even if total attenuation is not occurring. Mitigation measures should be put in place to reduce the amount of nitrate reaching Roebuck Bay from these sources. Near shore fresh water discharge occurred in several areas throughout Town Beach, showing that SGD from the Broome peninsula impacts Roebuck Bay. A dedicated study of SGD is required to understand the concentrations of nutrients in regional groundwater discharge.

Seven metals/metalloids were found to exceed recommended drinking water guidelines outlined by the USEPA, ANZECC, and NHMRC. These contaminants were generally present in bioavailable and mobile forms. Groundwater sourced from these areas should not be utilised for drinking purposes. In contrast these contaminants were unlikely to cause environmental impacts to Roebuck Bay. Mn, Se, and U were the only contaminants which violated ANZECC recreational guidelines. Furthermore these metals/metalloids did not exceeded these levels by substantial amounts. Attenuation processes may further reduce concentrations prior to SGD. The metals/metalloids present in groundwater are unlikely to threaten organisms occurring within Roebuck Bay but could be an issue for locals consuming large amounts of biota from the intertidal zone.

NP was found to be below detectable levels at all sampled sites. Consequently NP does not pose a threat to residents or biota occurring at Roebuck Bay. However a number of other

synthetic organic contaminants are often present in WWTP effluent. A suite of these, most notably N,N-diethyltoluamide, bisphenol, sulfamethoxazole, and 4 – octylphenol monethoxylate, should be analysed in wastewater effluent, groundwater, and along Town beach to identify if they pose a threat to biodiversity throughout Roebuck Bay.

Recommendations

The following recommendations have been made based upon the outcomes of this study:

- Undertake a comprehensive survey of seasonal groundwater discharge chemistry from the stretch of coast between Town Beach and Port Beach.
- Develop a detailed groundwater model, including explicit contaminant reactive transport modelling, for the Broome peninsula to identify the total nutrient load being discharged into Roebuck Bay through SGD.
- Sample Water Corporation bores at the WWTP and golf course, at least seasonally, to accurately quantify nutrient loads entering Roebuck Bay from this source.
- Develop management strategies to inhibit groundwater nutrient contamination coming from the Broome WWTP and Broome golf course.
- Use a suite of N, S, C, and O isotopes to constrain the capacity for natural attenuation throughout the Broome unconfined aquifer.
- Sample for a suite of organic wastewater contaminants at the WWTP, treated effluent holding tanks, groundwater bores, and near shore discharge zones at Town Beach to detect if contaminants are present, discharging into Roebuck Bay.
- Analyse cations and anions at the Town Beach freshwater/seawater mixing zones to assess if water chemistry is consistent with freshwater discharge.

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Appendix:

Appendix 1: Research Proposal

Research Proposal

Fate and Mobility of Groundwater Nutrients, Metals and Organic Wastewater Contaminants in the Unconfined Broome Aquifer

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Research Proposal

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1. Introductory Statement

Roebuck Bay is located on North Western Australia's Kimberly coast, bordering the Broome town site. The area is recognized as a significant stopover site for migratory shorebirds using the East Asian Australian Flyway, due to the regions high invertebrate biomass and diversity (Department of the Environment 2011; Estrella 2013). Consequently it is registered under the Ramsar convention. Blooms of *Lynbya majuscula* currently affect the area, causing ecological disturbance (Piersma *et al.* 2006). Groundwater eutrophication has been identified as a significant factor controlling blooms (Vogwill 2003; Wright 2013). Reductions in benthic invertebrate abundance and species richness have been observed within Roebuck Bay (Estrella 2013). This may be partially attributed to the presence of organic waste water contaminants (OWCs), heavy metals, and the previously identified groundwater nutrients (Barber *et al.* 2009; Matthiessen *et al.* 2002; Wright 2013). The current study aims to assess the level of contamination from OWCs and heavy metals occurring within the Broome Sandstone aquifer, track groundwater nutrient migration/attenuation, delineate groundwater discharge at Town Beach and quantify seasonal groundwater recharge.

2. Background

2.1 *Lynbya majuscula*

Lyngbya majuscula (Oscillatoriaceae) is a non-heterocystous, filamentous marine cyanobacterium species which inhabits the intertidal zone of tropical and sub-tropical coastal waters and estuaries (Osbourne *et al.* 2001; Jones 1990). It grows in fine 10 – 30cm strands, forming clusters of loosely bound mats, attaching to organic and inorganic surfaces (Dennison *et al.* 1999). As blooms propagate they create blankets which turn substrates and water proximal to the substrate anoxic (Al-Shehri and Mohamed 2007). This can cause seagrass loss and altered community structure of marine plants (Watkinson 2005). During rapid photosynthesis air pockets develop in the filamentous matrix of *L. majuscula* allowing it to float and form large surface aggregations (Hewson *et al.* 2001). This has negative economic implications, reducing both the quality and quantity of commercial fish catches and impacts tourism through reduced beach aesthetics (Al-Shehri and Mohamed 2007).

2.1.1 *Lynbya majuscula* Toxicity

L. majuscula produces a suite of toxic compounds including debromoaplysiatoxin (DAT) and aplysiatoxin (AT). These are responsible for a number of health issues in humans including dermatitis, respiratory irritation, and burning of the upper gastrointestinal tract (Osbourne *et al.* 2007). Furthermore these toxins discourage feeding in marine species, impacting ecologic function (Osbourne *et al.* 2001). Intertidal habitats affected by *L. majuscula* blooms were found to have reduced benthic invertebrate biomass and diversity (Estrella 2013). Changes in shorebird foraging behaviour were also associated with the occurrence of *L. majuscula*, as was fibropillomatosis in juvenile green sea turtles and ulcerative dermatitis in manatees (Estrella 2013; Quackenbush 1998; Harr 2008). This is significant as both are protected species (Alves *et al.* 2013; Buitrago 2008). Nonmarine organisms also come in contact with *L. majuscula* when mats wash to shore. A number of horse deaths throughout Sri Lanka have occurred due to consumption of this algae species (Osbourne *et al.* 2001). The presence of the toxic cyanobacterium in coastal waters therefore has profound effects on human health, ecosystem function, and threatens the conservation of protected species.

2.1.2 Bloom Initiation

L. majuscula naturally occurs in discrete quantities, however over the past few decades blooms have increased in both extent and severity throughout Australian coastal environments (Watkinson *et al.* 2005). Roebuck Bay, located in Western Australia, has experienced notable increases in *L. majuscula* blooms since 2005, while bloom intensification has occurred in Morton Bay since the early 1990's (Estrella 2013; Albert *et al.* 2005). These temporal changes correlate with increased anthropogenic nutrient input and changes in land use (Taylor *et al.* 2014; Johnson *et al.* 2010; Albert *et al.* 2005). Key sources include urban and rural wastewater, agricultural activities (ie. fertilizer application and animal waste products), and discharge of nitrogen enriched groundwater (Paerl 1997). Bloom intensification in Morton Bay has been linked to changes in land use. Harvesting/clearing of pine plantations and native forest, urban development, and the expansion of agricultural activities such as livestock and poultry farming have led to increased net nutrients reaching the bay (Ahern *et al.* 2008). This trend is a global phenomenon with human activities responsible for a 3 fold increases in nitrogen and phosphorus availability worldwide (Howarth *et al.* 2002).

2.1.3 Submarine Groundwater Discharge

Submarine groundwater discharge (SGD) is a major contributor of nutrients in coastal environments (Boehm *et al.* 2006; Slomp and Cappellen 2004). Across the northern Perth coastline SGD is predicted to contribute three times more nitrate than surface run off (Johannes and Hearn 1985). Similarly in Geographe Bay, Western Australia groundwater discharge is estimated to be as much as 80 million m³/yr, facilitating the release of large nutrient loads (Varma *et al.* 2010). SGD occurs primarily as diffuse seepage along the shoreline, offshore and through springs. The magnitude of seepage is generally largest near shore, decreasing with water depth and distance from the coast. For coarse grained, shallow, unconsolidated aquifers near shore diffusion is most common (Fig 1), while offshore seepage results from breaches in restraining layers (Slomp and Cappellen 2004).

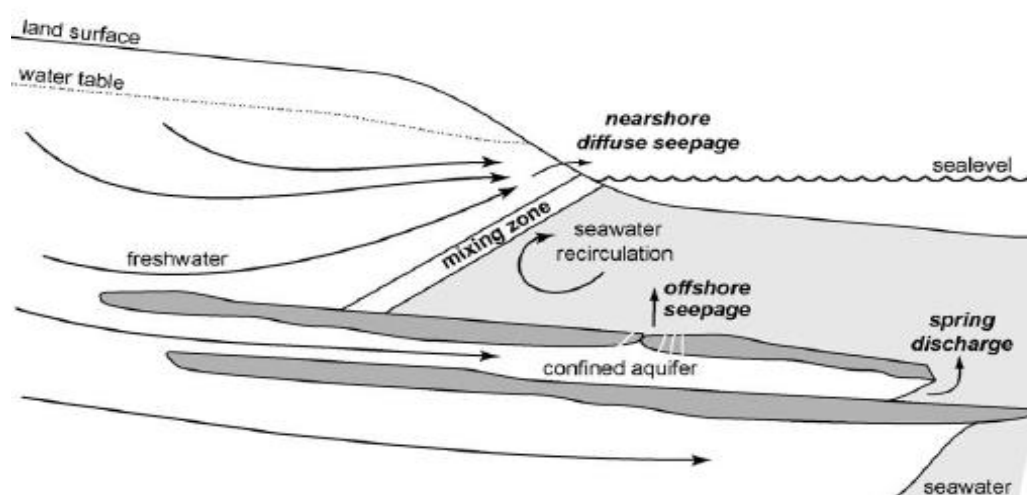


Fig 1- Diagram showing relationships between coastal aquifers and the different types of submarine groundwater discharge. (Slomp and Cappellen 2004)

Groundwater begins as meteoric water, precipitating from the atmosphere and infiltrating permeable sediments and rocks. Water is driven to near shore coastal environments through onshore hydraulic gradients and gravitational convection, where buoyant fresh pore water is driven up over denser saline pore water (Burnett *et al.* 2003). This interaction occurs at the fresh water/ salt water interface also termed the mixing zone (Fig 1), and contributes significantly to coastal eutrophication due to nutrient enrichment of groundwater from anthropogenic sources (Slomp and Cappellen 2004). In intertidal areas, fluctuations in tidal

and wave activity induce groundwater discharge by generating pressure gradients between the land and sea (Waska and Kim 2011; Li *et al.* 2009). At Hasaki Beach, Japan these processes were found to be significant for the mass transport of nutrients (Uchiyama *et al.* 2000). Likewise endogenic drivers such as osmotic pressures, thermal gradients, and inverted density stratification influence groundwater discharge. On the Florida platform geothermal convections were found to induce large scale convection currents in submarine groundwater, influencing seawater – pore water exchange (Moore and Wilson 2005). Terrestrial, oceanic, and endogenic mechanisms act in concurrence, controlling the input of nutrients and other solutes into coastal environments (Burnett *et al.* 2003).

2.1.4 Macronutrients Controlling Blooms

The macronutrients phosphorous, nitrogen and chelated iron have the strongest controls over *L. majuscula* propagation (Ahern *et al.* 2008; Taylor *et al.* 2014). A field experiment conducted in Morton Bay found that of these products organically chelated iron had the most notable effect on *L. majuscula* biomass. However, algae grown in elevated phosphorus and nitrogen were found to have significantly larger biomass than the controlled replicate (Fig 2). Furthermore *L. majuscula* biomass grown with increased macronutrients of all three elements had the largest biomass (Ahern *et al.* 2008). Limiting factors controlling bloom propagation are likely to be different at other locations. The Broome Peninsula is cover by Pindan Sands, rich in iron oxide minerals and contains nitrogen fixing vegetation (Wright 2013; Lamont 1982). Nitrogen fixation is a physiological mechanism developed to cope with nutrient poor soils (Turnbull *et al.* 1996). This ecosystem is therefore nitrogen limited so nitrogen availability is likely to have the strongest control over *L. majuscula* blooms, rather than iron which is more freely available in Roebuck Bay.

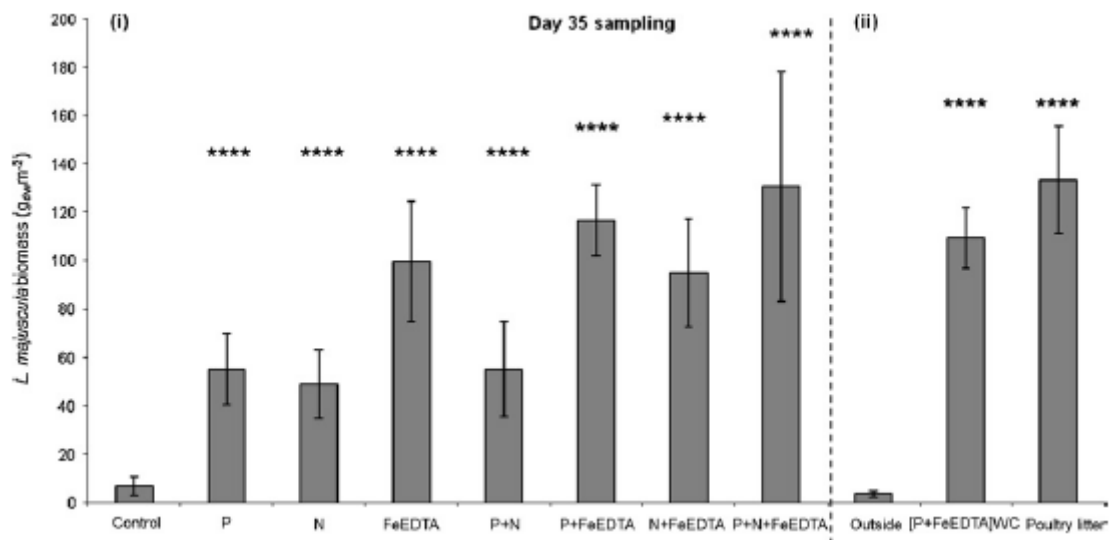


Fig 2 – Mean *L. majuscula* biomass on day 35 for numerous treatments grown in situ in Morton Bay (Ahern *et al.* 2008).

2.1.5 Environmental Parameters Controlling Blooms

Environmental factors have a strong control over *L. majuscula* blooms (Ahern *et al.* 2008; Taylor *et al.* 2014; Johnson *et al.* 2010). Bloom initiation occurs in early summer and expands aggressively during the following 2 -3 months, eventuating in population collapse as conditions change (Ahern *et al.* 2008). Water temperature, turbidity, and light have the strongest environmental controls over bloom initiation (Hamilton *et al.* 2007; Thacker and Paul 2001). Modelling of *L. majuscula* blooms was undertaken by Hamilton *et al.* 2007 using a Bayesian Network and data collected over the six years prior to the study. Using this model it was predicted that bloom initiation would not occur at low temperatures, regardless of other variables. When low turbidity was modelled in association with high light, temperature, and nutrients the probability of bloom initiation rose to 100%. Although modelling is not representative of all conditions controlling bloom initiation it highlights the significant key environmental drivers (Recknagel *et al.* 1997).

2.2 Groundwater Contaminants

Demand for water has increased globally due to high rates of population growth, leading to elevated domestic, industrial and agricultural uses (Florke *et al.* 2013; Hu and Cheng 2013). This has a number of implications, including augmented waste water production and exposure of natural water systems to various contaminants such as nitrates and phosphates, heavy metals, and synthetic organic products (Meffe and Bustamante 2014). Leakage from septic tanks and sewerage systems, fertilizer application during agriculture and urban use, discharge of industrial and waste water effluent, and storm water runoff contribute significantly to the reduction of groundwater quality (Meffe and Bustamante 2014; Chen *et al.* 2010). The environmental and human health impacts of several groundwater contaminants will be discussed below.

2.2.1 Impacts of Nutrient Contamination

Ecosystem function and biodiversity are impacted when nutrient enriched groundwater is discharged into coastal water bodies (Slomp and Cappellen 2004). Cyanobacteria proliferation is one of most significant problems related to anthropogenic eutrophication (Loza *et al.* 2014). This has been discussed previously with regards to *Lynbya majuscula*.

The broader effects of coastal eutrophication on seagrass habitats will now be explored. Seagrass meadows represent important habitats in coastal ecosystems, harbouring species such as green sea turtles, providing food and shelter for numerous fish and invertebrate species, and offering essential habitat for the development for juvenile biota (Lal *et al.* 2010; Nordlund and Gullstrom 2013). Impacts related to eutrophication are caused due to a number of factors.

Light reduction due to the high biomass of algal overgrowths was found to cause declines in seagrass abundance. Likewise algal drift assemblages were found to reduce advective water exchange around the base of seagrass shoots, promoting hypoxia/anoxia and hydrogen sulphide stress. Direct physiological responses such as ammonium toxicity are also related with seagrass loss. It was found that prolonged uptake of water column nitrate stimulated significant internal carbon imbalances, causing the discharge of cellular material in order to prevent the internal accumulation of toxic products (Burkholder *et al.* 2007). Roebuck Bay in Broome has extensive seagrass meadows, providing habitat for green sea turtles and dugongs. These meadows are impacted by eutrophication, thought to be induced through wet season surface water run-off (Laurie 2010). Broome stormwater systems have also been identified in contributing significant loads of nutrients to the intertidal zone (Gunaratne *et al.* 2014). Nutrient enriched groundwater discharge from the Broome aquifer may also be a significant contributor causing seagrass decline.

2.2.2 Organic Contaminants

Synthetic organic compounds are used globally for medical purposes, food production, and industrial processes (Lapworth *et al.* 2012). They can enter the environment through a number of pathways; however the primary and most significant contaminant source is through direct discharge from waste water treatment plants (Barnes *et al.* 2008; Ternes *et al.* 2004). In 2000 groundwater from 47 sites across 18 states in the USA was analysed, finding synthetic organic contaminants present at 81% of the sites. The wastewater contaminants sulfamethoxazole and 4- nonylphenol were found at 23% and 2% of sites respectively (Barnes *et al.* 2008). In another study, 20 public wells were analysed throughout the US for 92 organic waste water contaminants. Sulfamethoxazole and 4- nonylphenol were found at 60% and 14% of sites respectively (Schaidler *et al.* 2014). These compounds have significant environmental and human health related impacts (Jiang *et al.* 2014; (Barnes *et al.* 2008).

Nonylphenol is an endocrine disrupting compound, while sulfamethoxazole has pathogenic affects. Currently treated waste water effluent is being flushed into the Broome Sandstone aquifer and discharged into Roebuck Bay (Water Corporation 2014). Changes in benthic invertebrate abundance and biodiversity have been observed (Estrella 2013). These changes may be related to the occurrence of synthetic organic compounds. Furthermore the presence of sulfamethoxazole may pose a health risk to persons using Roebuck Bay for recreational purposes. The occurrence and environmental impact of both nonylphenol and sulfamethoxazole are discussed below.

2.2.3 Endocrine Disruptor Compounds

Many synthetic organic compounds are endocrine disruptors which have negative effects on the reproduction and development of both humans and wildlife (Jurado *et al.* 2012). They act to alter regulatory function of the nervous, immune, and endocrine system by mimicking or inhibiting hormones (Crisp 1998). Human health issues related to endocrine disrupting compound (EDC) exposure include increased risk of developing breast, prostate and testicular cancer, immune suppression, and abnormal thyroid gland and neurobehavioral function (Bolong *et al.* 2009; Crisp 1998). EDC's have detrimental effects on other organisms. The freshwater snail species *Marisa cornuarietis* displayed enlarged pallial sex glands and malformations of the pallial oviduct when exposed to endocrine disrupting compounds, while the carp species *Cyprinus carpio* exhibited impaired gonadal development (Oehlmann *et al.* 2000; Wu *et al.* 2003). Furthermore exposure to EDC's has been associated to decreased hatching success in fish and altered immune and behavioural function in both birds and mammals (Crisp 1998). Synthetic organic endocrine disrupting compounds are persistent in the environment so pose a significant risk to human and ecosystem health (Jurado *et al.* 2012).

2.2.4 Nonylphenol

Nonylphenol (NP) is a toxic xenobiotic endocrine disrupter that interferes with the hormonal system (Soares *et al.* 2008). The compound is formed through the degradation of nonylphenol ethoxylate, which is widely used as a surfactant for industrial, commercial and domestic purposes. Common products containing this compound include detergents, solubilisers, shampoos, deodorants, and emulsifiers (Bozkurt and Sanin 2013). According to the China Petroleum and Chemical Industry Federation (CPCIF) the annual production of NP during 2013 was 310, 434 tonnes globally (Gao *et al.* 2013). Consequently, it is present pervasively

in groundwater, soil, sediments, food and the atmosphere. A great proportion of NP reaches the environment via sewerage systems and waste water treatment plants (Hao *et al.* 2009).

NP is of considerable concern due its chemical properties. It has a low solubility and high hydrophobicity so persists within the tissue of aquatic organisms that have high lipid contents, within sewage sludge, and throughout river sediments (Diehl *et al.* 2012; Soares *et al.* 2008). Benthic invertebrates have been shown to experience detrimental effects when exposed to nonylphenol. At concentrations of 6.264µmol/L *Lumbriculus variegatus*, a Oligochaeta worm species, experienced deaths to 50% of the study population (LC50), while larvae for the chironomid species *Chironomus riparius* displayed LC50 concentrations at 3.969µmol/L C. Typically at non-lethal concentrations larvae weight and head capsule size were found to be reduced (Maenpaa and Kukkonen 2006). Wastewater effluent discharged into aquatic environments therefore poses a significant environmental risk to invertebrates.

Bioaccumulation of nonylphenol in aquatic organisms has been shown to occur in both laboratory and field experiments. In Morro Bay (North America), bioaccumulation was observed in bivalves (mussels and oysters), otter livers and in both goby and piscivorous (sculpin and sand dab) fish livers. It was suggested that biomagnification of NP also occurs to the level of the local apex predator. This trend was observed between goby and sculpin and bivalves and otters (Diehl *et al.* 2012). *Daphnia magna*, a zooplankton species used internationally as a bio indicator, were found to bio concentrate nonylphenol in lab experiments at different levels depending on life stages. Neonates displayed significantly higher bioconcentrations when compared to adult daphnids. When exposed to nonylphenol concentrations of 75µg/L in an 80mL media for two days bioaccumulation factors in neonates and adults were 421 kg/L and 760 kg/L respectively (Preuss and Ratte 2008). The bioaccumulation, bioconcentration, and biomagnification of nonylphenol in the environment is of concern, both at an organism and ecosystem scales.

2.2.5 Sulfamethoxazole

Sulfamethaxole is among the most widely used of veterinary antibiotics, with applications in aquaculture and livestock farming. It is a water soluble and polar substance, so is readily transported to groundwater and surface water bodies (Garcia- Galan *et al.* 2009). The primary transport mechanism is through discharge by waste water treatment plants (Radke *et al.* 2009). When antibiotics are consumed by humans they are not totally metabolized so pass into the sewerage system. When they reach waste water treatment plants a proportion of the

antibiotic is degraded, with the rest discharged into the environment with the waste water effluent (Ryan *et al.* 2011). Ozonation is considered to be a suitable method for removing sulfamethaxole from wastewater; however several studies have shown that discharged effluents having undergone this process still contain significant amounts of sulfamethaxole (Rodayan *et al.* 2010).

Sulfonamides are actively biodegradable during primary and secondary treatment, but are resistant to further biodegradation in the final disinfection process applied to wastewater (Perez *et al.* 2005; Rodayan *et al.* 2010). Application of manure from medicated animals in agriculture and the addition of sulfamethaxole to aquaculture feeds are also large contributors. Close to 80% of antibiotics applied during aquaculture pass into surrounding water bodies (Garcia- Galan *et al.* 2009). The compound is toxic to microorganisms in high concentrations, however when present at low levels bacterial resistances are able to develop (Kim *et al.* 2012; Ryan *et al.* 2011). This is concerning as diseases that were once considered to be controlled are now returning with new strains that are resistant to antibiotic application (Levy and Marshall 2004). The presence of sulfamethaxole in the environment therefore poses as a risk to the health of humans.

2.2.6 Heavy Metal Contamination

Previous groundwater investigations conducted in Broome in the late 1990' have found concentrations of As, Se, and Hg above ANZECC and USEPA drinking water and recreational water quality standards (Vogwill 2003). These contaminants are associated with a various detrimental impacts in humans and aquatic organisms. There are a number of documented cases where the ingestion of high doses of arsenic have resulted in human deaths. At sublethal exposure levels pathogenic lesions such as fatty degradation of the liver, hyperemia and haemorrhages of the gastrointestinal tract, and renal tubular necrosis can occur (Centeno *et al.* 2000). Cancer development, keratosis, peripheral vascular disease, and long term neurological disorders are other common health effects related to exposure to As from contaminated groundwater (Liu *et al.* 2013; Senanayake and Mukherji 2014). Acute Se exposure can also produce negative health effects including gastrointestinal disorders, liver and spleen damage, anemia, and muscular irritation (Vinceti *et al.* 2013). At chronic exposure levels damage to the nervous and neurological system are common (Murdock 1994).

Likewise mercury can pose a significant risk to humans. When present in the form of methyl mercury exposure is particularly harmful as it bioaccumulates and is readily absorbed by the

gastrointestinal tract. At Minamata in Japan, severe neurological effects were experienced in both adults and infants when exposed to methyl mercury (Ratcliffe *et al.* 1996). The risk posed by each of these contaminants is directly related to their concentration and the chemical speciation. At the exposure levels seen at Broome the aforementioned health effects are unlikely. However as they were found to be above water quality guidelines it is important to continually monitor their levels to enable appropriate management actions, if required.

As, Se and Hg have detrimental effects on aquatic organisms, including benthic invertebrates. Drops in benthic invertebrate abundance and species richness have been seen in Roebuck Bay (Estrella 2013). Heavy metal contamination may be contributing to these changes. Reductions in the percent composition of ephemeropterans, plecopterans, and coleopterans were found due to exposure to As at levels between 10 – 75 µg/L (Beltman *et al.* 1999). Similarly at Se concentrations above 370 µg Se/g benthic invertebrate populations were found to decline (Lemly 2002), while nematode abundance in benthic sediments were found to decrease with increasing concentrations of mercury (Horne *et al.* 1999). Metal contaminants can therefore have significant effects on benthic invertebrate populations, so may be impacting benthic invertebrate composition within Roebuck Bay.

2.3 Natural Attenuation

Natural processes are being increasingly relied upon for the remediation of contaminated sites worldwide (National Research Council 2001). In Broome the elimination of significant quantities of nutrients, organic contaminants, and heavy metals is possible through natural attenuation. Natural attenuation occurs due to a number of interacting physical, chemical, and biological processes (National Research Council 2000). Predominant mechanisms include sorption, dispersion, biodegradation, chemical transformations, and volatilisation (Kresic 2007). Adsorption/sorption transpires when molecules or ions accumulate on the outer surface of adsorbants. Physical and chemical attractions occur between contaminants and the adsorbant sediment grains, allowing for affinities to develop through the action of *van der Waals forces*, hydrophobicity, electrostatic bonding, and coordinate reactions (Site 2001; Tan 2011).

Dispersion is the primary transport mechanism controlling the migration of soluble contaminants (Testa and Winegardner 2000). It is caused by differential groundwater velocities occurring in the void space of porous sediments and lithological units. This process acts to transport contaminants to areas where attenuation and transformations can occur

(Vallero 2004; Sudicky 1983). Chemical transformations mediated by microbial organisms are responsible for the biodegradation of groundwater contaminants (Delleur 2007). Heterotrophic bacteria occurring in the subsurface use organic molecules as a primary energy source, processing toxic contaminants and converting them into less toxic forms (Kresic 2007). Direct chemical transformations also contribute to attenuation through hydrolysis, redox reactions, precipitation, dissolution and complexation. These processes act to either bond contaminants to sediment particles, or convert contaminants to other forms (National Research Council 2000). The transformation of high vapour pressure liquids and solids into gaseous forms occurs during volatilisation (Alvarez and Illman 2006). This process is important for the removal of volatile organic compounds, mercury, and nitrates, which are transported through sediment pores to the atmosphere through advection and hydrodynamic dispersion mechanisms (Alvarez and Illman 2006; Sommer *et al.* 1991). These processes are all important for the removal of harmful contaminants from groundwater.

2.4 Broome Groundwater

Recent expansion has caused detrimental impacts to the groundwater regime in Roebuck Bay. Over the past 30 years Broome has developed from a small town into a large regional centre with a current population of approximately 26,000 permanent residents (Mullholland and Piscicelli 2012). This figure doubles during the dry season due to the large influx of tourists to the region (Campbell 2013). Consequently the local groundwater resources have been put under increasing pressure. Groundwater levels in the town site have dropped over the past few decades and salinization has been observed in groundwater bores proximal to the coast, due to the upconing of the saltwater interface, which has been caused by over extraction (Vogwill 2003; Wright 2013). As the major aquifer utilised by Broome is largely unconfined there is potential for contaminant and nutrient leaching. This has implications for biota accessing groundwater, the quality of groundwater discharged into surrounding coastal environments, and for human consumption. To understand groundwater dynamics in the region groundwater the major lithological units must be understood. These will be discussed below.

2.4.1 Major Hydrolithological Units

Broome Sandstone

The Broome Sandstone is comprised of often unconsolidated friable, fine – coarse grained quartzose sandstone, with minor beds of siltstone, claystone, organic matter, and conglomerate. The unit has an average thickness of 280m, is early Cretaceous in age and lies conformably on the Jarlemai Siltstone (Laws 1991). The Broome Sandstone is the most utilised aquifer through the Canning Basin and is the primary fresh water source for Broome. The aquifer is largely unconfined, so recharge occurs mainly through infiltration from rainwater. Groundwater flow is predominantly south and west, south of the Baskerville Anticline, which is located north-north west of Broome, due to the unit's south-westerly dip. North of the Baskerville Anticline groundwater flow is generally north and west. As this unit is highly utilised it is the most threatened water resource in the region (Vogwill 2003).

Jarlemai Siltstone

The Jarlemai Siltstone is Late Jurassic in age, light grey to black in colour and composed mainly of black puggy silt and clay, with minor amounts of sandstone (Holder and Rozlapa 2009). The unit lies conformably between the Alexander Formation, a minor sandstone aquifer, and the Broome Sandstone. The Jarlemai Siltstone is primarily an aquiclude, inhibiting through flow between the Broome Sandstone and the underlying Alexander formation (Laws 1991).

Wallal Sandstone

The Wallal Sandstone consists of fine to coarse grained sandstone, minor siltstone, and lignite (Laws 1991). Towards the base of the formation conglomerate is common, containing quartz, quartzite, jasper, and other pebbles. It has an average estimated thickness of 360m and is early to late Jurassic in age. It is confined beneath the Jarlemai Siltstone throughout most of the Canning Basin (Holder and Rozlapa 2009), and lies unconformably on several lithological units including the Liveringa Group, the Poole Sandstone and the Noonkanbah Formation. It is a major aquifer containing fresh to brackish water (Laws 1991). Artesian heads are found up to 30m above the groundwater level at the coast and groundwater flow is in a west-northwesterly direction. The majority of groundwater recharge for this unit occurs along the southern margin of the west Canning Basin (Holder and Rozlapa 2009).

Erskine Sandstone

The Erskine Sandstone is early to middle Triassic in age and consists of very fine to fine grained sandstone, which is laminated, cross bedded, and rippled marked in part. It also contains minor clay pellet conglomerates and laminated mudstone in the upper regions. It lies below the Wallal Sandstone and above the Blina Shale (Department of Water 2012).

Poole Sandstone

The Poole Sandstone is comprised of interbedded sandstone, mudstone, and minor conglomerate and is Early Permian in age. It lies conformably between the Noonkanbah formation and the Grant group and is unconformably overlain by the Wallal Sandstone. The unit holds brackish to saline groundwater (Laws 1991).

Grant Group

The Grant Group is of Late Carboniferous to Early Permian in age and is comprised largely of sandstone and mudstone, with minor conglomerate lenses. It is conformably overlain by the Poole Sandstone, unconformably overlain by the Wallal Sandstone, and unconformably overlies the Anderson Formation. It has an estimated thickness of over 1100m, and holds brackish to saline groundwater (Laws 1991).

2.5 Summary

This section has highlighted the impacts of *Lynbya majuscula* blooms on human health and the environment; primary nutrient and environmental parameters controlling blooms; and the contribution of submarine groundwater discharge in coastal nutrient cycling. It is therefore imperative to quantify levels in the aquifer to better understand its impact on the eutrophication of Roebuck Bay as well as the role of natural attenuation. The impacts of metals and synthetic organic compounds were also discussed, focussing particularly on sulfamethaxole and 4-nonylphenol. These are common contaminants discharged from waste water treatment plants and are associated with significant detrimental environmental impacts. Waste water in Broome enters the Broome sandstone aquifer both directly through leakage from the waste water treatment ponds and indirectly through irrigation using wastewater, so organic compounds may be ubiquitous. Limited studies have recently been conducted regarding heavy metal content in Broome groundwater, while synthetic organic contaminants

have never been sampled. It is therefore of paramount importance to quantify the occurrence of these contaminants within the aquifer.

3. Aims

The objectives of this study are as follows: to investigate groundwater nutrient dynamics and natural attenuation within the unconfined Broome Sandstone aquifer; to quantify groundwater heavy metal and synthetic organic contaminants within the aquifer; to determine seasonal fluctuations in groundwater head; and to identify subsurface freshwater discharge in the intertidal zone adjacent to the Broome wastewater treatment plant. This data will be used to produce maps and cross sections concerning the flow and migration of groundwater, groundwater nutrients, organic compounds, and heavy metals.

4. Significance and outcomes

Blooms of *L. majuscula* occurring in Roebuck Bay have been linked to changes in the intertidal benthic community composition as well as the foraging behaviour of migratory shorebirds (Estrella 2013). To address this issue it is essential to collect both groundwater level and geochemistry data from the unconfined Broome Sandstone aquifer. Previous studies have investigated groundwater nutrient migration proximal to the waste water treatment plant and town wide at the end of the dry season (Water Corporation 2014; Wright 2013). This study will track groundwater nutrient migration across Broome at the end of the wet season as well as attempt to constrain the levels of natural attenuation occurring within the aquifer.

Currently there are no studies in Broome and Roebuck Bay concerning the organic waste water contaminants sulfamethoxazole and 4-nonylphenol, which have negative impacts on invertebrates and microbial activity. Due to funding limitations it is only possible to analyse one of these contaminants. In this case 4-nonylphenol has taken priority over sulfamethoxazole as it has been proven to impact benthic invertebrate populations. 4-nonylphenol may be responsible for reduced invertebrate diversity and abundance at Town Beach, located adjacent to the site of the waste water treatment plant (Barber *et al.* 2009; Lye *et al.* 2008). Sulfamethoxazole should be tested at a later date as it presents a significant human health risk. Furthermore a suite of metals will be sampled to assess whether groundwater concentrations are in concurrence with ANZECC and USEPA standards, and if metals are at concentrations consistent with the levels that have been found to impact benthic invertebrate communities.

5. Methodology

This study will focus on the assessment of groundwater quality in the unconfined Broome Sandstone aquifer, with regards to nutrients, metals and the organic contaminant nonylphenol. As discussed above these pollutants have detrimental effects on the environment and human health. The following methodology will outline the steps required to quantify these groundwater contaminants and their appropriate environmental parameters.

5.1 Field Work

Groundwater samples will be collected from sixteen bores at eight locations throughout the Broome town site (Appendix 1). If permission is granted and funds permit groundwater samples will also be collected from the Water Corporation's monitoring bores surrounding the waste water treatment plant (Appendix 2). A 12 volt submersible pump will be used to purge the bores of stagnant water. Each bore will be pumped for at least three casing volumes to remove stagnant water in order obtain representative groundwater samples (Sundaram *et al.* 2009). Stagnant water within the well directly contacts the well casing and the atmosphere so is influenced by different chemical conditions then the formation water (Nielsen 1991). During pumping water will be lifted from the bore via a length of plastic tubing and ejected into a flow cell. This avoids contact between the sample and the atmosphere, producing reliable groundwater data (Sundaram *et al.* 2009).

Electrodes measuring pH, EC, dissolved oxygen, redox potential and temperature are to be inserted into the flow cell. As these physicochemical parameters change over small time intervals they must be measured in the field (Misstear *et al.* 2006). Electrodes are to be calibrated using the appropriate techniques and standard solutions. Redox probes will be calibrated using Zorbels solutions A and B which will be combined at a 1:1 ratio, dissolved oxygen will use an air calibration technique; electrical conductivity will be calibrated using a 1413 $\mu\text{S}/\text{cm}$ solution, while pH will be calibrated with two buffer solutions (Carroll *et al.* 2003, Sundaram *et al.* 2009). For groundwater that is suspected to be alkaline a neutral solution and a pH 10 solution will be used, while acidic groundwater will be calibrated with both a neutral solution and pH 4 solution. Total alkalinity will also be measured in the field using the burette titration method to assess the amount of carbonate and bicarbonate in the groundwater (Sundaram *et al.* 2009). This process will involve the titration of 0.016 mol/L sulphuric acid against 100mL aliquots of each groundwater sample, with the addition of the

indicator bromocresol green. It is of great importance to measure these environmental parameters in the field as they control the mobility and fate of groundwater contaminants (Alvarez 2006; Weidmeier *et al.* 1999).

Fresh water discharged will be assessed along Town Beach proximal to the waste water treatment plant. Samples will be taken systematically at 25m intervals along two transects, located within the intertidal zone. At each sample location an EC probe will be used to assess the salinity of the water to determine the presence of freshwater. Freshwater is generally below 1mS/cm, while saline water commonly ranges from 1 – 80mS/cm (Edmunds and Shand 2008). The EC probe will be submerged into drainage channels and small pools. If no surficial water is accessible a small well will be excavated. Nonylphenol and total nutrient sample will be taken at sites with low EC readings as they are likely to be the sites of groundwater discharge.

Samples for total nutrients, dissolved nutrients, anions and cations and trace metals will be sent to the University of Western Australia's Water Quality Laboratory for analysis. NP samples will be analysed at the Chem Centre in Bentley as they require specialist analytical methods. All samples, with the exception of total nutrients and NP, will require filtration through a 45 micron membrane in the field. Nutrient samples will be frozen, NP and the cation and anions will be refrigerated at 4°C. 5% ultra-pure nitric acid will be added to the trace metals and cation samples and refrigerated at 4°C (Sundaram *et al.* 2009). The groundwater head (level) at each bore will be measured using an automated plover and tape measure (Sundaram *et al.* 2009).

5.2 Lab Analysis

Nonylphenol is extracted and analysed through a number of methods. The most common are liquid – liquid extraction and analysis through High Performance Liquid Chromatography (HPLC), or gas chromatography/ mass spectrometry (Barber *et al.* 2009; Liao *et al.* 2014). Liquid – liquid extraction is a mass transfer technique between a raffinate liquid phase and an extract liquid phase. These two phases have very little mutual solubility. In the case of nonylphenol the contaminated groundwater is the raffinate phase, while the extract is phase is often toluene, a mono-substituted benzene derivative. Toluene has a greater affinity for phenol than groundwater, so can be used for its extraction (Rydberg *et al.* 2004). To quantifying the amount of NP present in the extracted solution either liquid chromatography or gas chromatography/mass spectrometry must be implemented. Liquid chromatography is the

most common method and involves forcing the eluent liquid, containing the contaminant, through a column packed with an extremely fine grained silica gel. Molecules/ions of different species travel through the column at different speeds due to their different chemical properties. A detector sits at the end of the column and quantifies the amount of each molecule/ion in the solution according to the timing and height of the unique peak produced (Lindsay 1997).

Gas chromatography/mass spectrometry is another method applied to quantify NP in waste water or contaminated groundwater. Typically gas chromatography uses a carrier gas, either helium, hydrogen, or nitrogen, which is introduced into a temperature regulated sample injection device. The sample is fed into the gas mixture and forced through the column in much the same way as in liquid chromatography (Karasek and Clements 2003). Mass spectrometry is used to analyse the proportions of each compound present in the gas mixture. A sample inlet introduces the analyte from the gas chromatograph into a mass analyser which has an ionization source. This separates each compound into molecular ions. The mass spectrometer then separates each ion according to its mass:charge ratio, determining the proportion of each ion in the system, and quantifying the sample analyte (Hoffman, and Stroobant 2007).

Anions and cations and metal samples are to be analysed using High Performance Ion Chromatography. Samples will be diluted to ensure elements with high concentrations do not overload the separator column. They will be run against standard solutions and the peaks of each anion/cation present in the groundwater will be quantified. Anions (F, Cl, Br, NO₃, PO₄ and SO₄) and cations (Na, K, Mg and Ca) will be measured using the Dionex Corporation Conductivity meter. Trace metals will be analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This process involves pumping the sample eluent into a nebuliser which transforms the solute into an aerosol with argon gas. The sample then migrates through a spray chamber and into a plasma torch via the sample injector. This plasma torch uses a strong magnetic field which excites the electrons of positively charged ions. This process releases photons as electrons move from their ground state to a higher energy level. A unique photon is released for each trace metal. The photon is then converted into an electrical signal with a series of metal dynodes. Measurements for each metal present in the sample are then taken (Thomas 2004).

Nutrient analysis will be completed with a Lachat flow injection analyser, where nutrients and dissolved nutrients will be assessed using the persulphate method (Wright 2013). In this method persulphate converts phosphorus to orthophosphorus and oxidises all nitrogen forms to nitrate. Analytes are then passed through an air segmented continuous flow analyser, where nitrates go through cadmium reduction also known as the Griess-reduction method, and orthophosphorus is processed using the phosphantimonylmolybdenum blue method. Concentrations of each analyte are then determined by the RFA – 300, third generation, air segmented continuous flow analyser (Patton and Kryskalla 2003).

Dissolved organic carbon will be quantified through detection using an infrared analyser, after the removal of all inorganic carbon. Samples are acidified and transported to a thin turbulent liquid film and passed through a large bore coil in order to remove carbonate. At a pumping rate of 500mL per minute as much as 500mg of inorganic carbon can be removed. The remaining solution is then mixed with potassium persulfate and subjected to UV radiation. The resultant carbon dioxide is measured using an infrared analyser, where peak heights are used to determine the concentration of dissolved organic carbon (EPA 2002).

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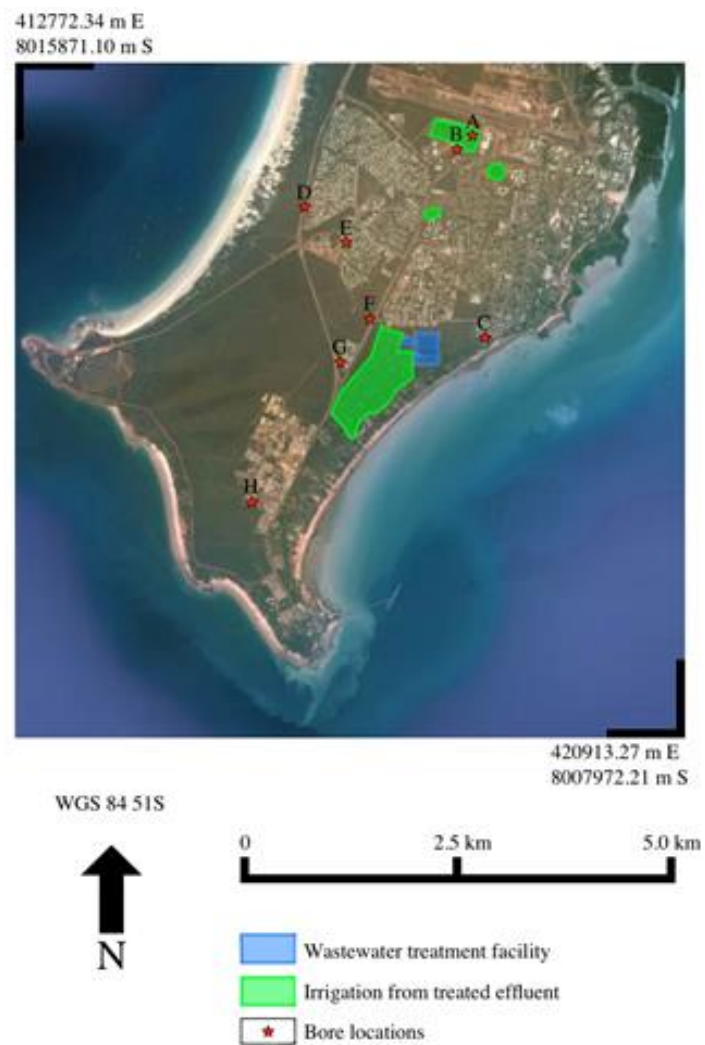
7. Budget

Task	Details	Budget
Travel	Return airfare to Broome	\$800
Accommodation	Accommodation at the Department of Parks and Wildlife	\$700
Car Hire	Transport to each monitoring bore will be provided by the use of a vehicle provided by the Department of Parks and Wildlife.	\$1000
Groundwater Sampling	Groundwater pump, probes, flow cell, filters, sample bottles and other consumables	\$1000
Groundwater Analysis	Dissolved nutrients - (\$40) Total nutrients - (\$40), Anions and Cations - (\$60) Organic waste water analysis – (4-nonylphenol (NP)) - (\$100) Metals - (\$80)	16 sites + 20 Water Corp (optional depending on funding and permission) Cost excluding analysis of Water Corp groundwater = \$5,120 Cost including analysis of Water Corp groundwater = \$11,520
Total		Excluding Water Corp bores = \$8620 Including Water Corp bores = \$15,020

8. Timetable

Task	Month							
	March	April	May	June	July	August	September	October
Research Proposal for Supervisors Comment	X	X	X					
Proposal Seminar	X	X						
Final Research Proposal	X	X	X					
Groundwater Sample Collection		X	X					
Groundwater Contaminant and Solute Analysis			X	X				
Data Analysis				X	X			
Research Thesis for Supervisors Comment				X	X	X	X	
Final Research Thesis				X	X	X	X	X
Research Seminar							X	X

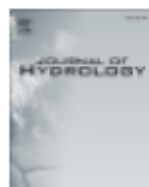
9. Appendix:



Appendix 1: Map showing the location of monitoring wells throughout Broome (Wright 2013)



**Appendix 2: Map showing the location of the Water Corporation monitoring wells
(Water Corporation 2014)**



An Interval-Deviation Approach for hydrology and water quality model evaluation within an uncertainty framework



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SUMMARY

Uncertainty assessment is becoming one of the main topics in hydrology and water resources. In this study, an Interval-Deviation Approach (IDA) was designed and incorporated into the process of model evaluation. The proposed IDA was validated in a real application of the Soil and Water Assessment Tool (SWAT) and Generalized Likelihood Uncertainty Estimation (GLUE) in the Three Gorges Reservoir Area (TGRA), China. Compared with the traditional point-to-point comparison between measured and predicted data, the main superiority of the IDA is its innovative theory that models should be evaluated by each absolute distance between the paired uncertainty intervals or probability distribution for each measured and predicted data. In addition, the IDA can be used to quantify the possible range of model performance in a real application of the SWAT. This proposed IDA can be useful for error form indicators and models by providing a substitute method to facilitate enhanced evaluation of watershed models within an uncertainty framework.

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1. Introduction

Hydrology and water quality (H/WQ) models are essential tools for developing watershed programs, such as Total Maximum Daily Load (TMDL) and the Water Framework Directive (WFD) (Stow and Borsuk, 2003; Panagopoulos et al., 2012). The confidence that we have in these models depends on how well the models match the real system that they are intended to represent (Mediero et al., 2011). However, the meteorological-, geological-, hydrological-, and ecological processes at basin scale are notably complex and are not always well known (Renard et al., 2010; Beven and Alcock, 2012). Faced with such insufficient knowledge and natural randomness, uncertainty becomes an inherent part of watershed modeling (Beven and Alcock, 2012).

Prediction uncertainty is a major concern and has been routinely incorporated as a key part of TMDL plans (Renard et al., 2010). Many researchers have focused on prediction uncertainty, specifically addressing the sources of uncertainty (Shen et al., 2012a), uncertainty propagation (Naranjo et al., 2012), evaluation methods (Zhang et al., 2011), uncertainty expression (Zheng and

Keller, 2007) and the control of uncertainty (Beven et al., 2008). Beck (1987) reported that residual uncertainty exists even with the best model structure and input data. Additionally, measurement uncertainty may stem from errors in flow measurements and water quality sample collection (Harmel and King, 2005; Howden et al., 2011). Given the river discharge data, errors from different sources such as river stage measurement or the interpolation of the rating curve, affect the measured data (Di Baldassare and Montanari, 2009). In a thorough review (Harmel et al., 2006), several potential errors in the H/WQ measured data were compiled, indicating that appreciable inherent errors exist in the measured data even when following strict quality assurance and quality control (QA/QC) guidelines (Beven et al., 2012).

Model evaluation, in terms of calibration and validation, is a critical step in model application (Guinot et al., 2011). Model calibration is the process of estimating model parameters using a pairwise comparison between the predicted and measured data, while the validation process involves running the well-calibrated model to check its performance. In traditional applications, model evaluation is usually conducted by a regression measure, most commonly the point-to-point comparison of predicted and measured data (Westerberg et al., 2011). The multi-objective functions, which usually considered the variety of hydrological events that may occur in a basin, are also used to calibrate models by the

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Appendix 2: First and last page of an article from the most recent issue of the Journal of Hydrology

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The impact of climate change, human interference, scale and modeling uncertainties on the estimation of aquifer properties and river flow components



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SUMMARY

Within the period 1978–2006, climate change and human interference produced noticeable impacts on the hydrology of a small watershed, known as the Beça River basin. Climate change was characterized by a persistent rise in temperature ($+0.78^{\circ}\text{C}/\text{decade}^{-1}$) and a drop in the annual rainfall ($-300\text{ mm}/\text{decade}^{-1}$). Human interferences included the construction of a dam for electric power generation, in 1988, and since then the transference of Beça River flows from the dam lake to the adjacent Tímega River. The impacts on catchment hydrology comprised a decline of aquifer hydraulic conductivity and effective porosity, by approximately one order of magnitude, related to a water table lowering of about 17 m within the bedrock aquifer composed of weathered and fractured Hercynian granites and Paleozoic metasediments and of saprolite layers derived therefrom. Aquifer property estimates were compared across spatial scales, namely the Beça River and the nested sub-basin scale. Sub-basin aquifers are more porous and permeable than the basin aquifer because its responding hydraulic circuits are shallower. Comparisons were also made between aquifer properties derived from measured and simulated stream flows, which revealed effects of modeling uncertainties on the results. River flows also suffered a substantial decrease in the course of climate change and human interference, especially the overland flows (4/5 decrease) and the base flows (2/3 decrease). The interflows were less affected (1/3 decrease) because they were partly fed with water from the aquifer storage, which in turn underwent depletion. The hydrologic changes in the Beça River basin anticipate important impacts on the local use of natural water. In this context, the aforementioned water table lowering may have caused limited access to shallow groundwater for activities such as crop irrigation from dug wells, whereas the severe decline in overland flows and base flows had certainly reduced the availability of surface water for the refilling of dam lakes and of groundwater for the supply of public and private households.

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1. Introduction

The impacts on hydrology caused by climate change in the 20th century have been reported in many watershed studies around the globe, and in some cases were also anticipated for the future. For example, in the St. Lawrence fluvial corridor between Montreal and Quebec City (Canada), Boyer et al. (2010) reported an increase

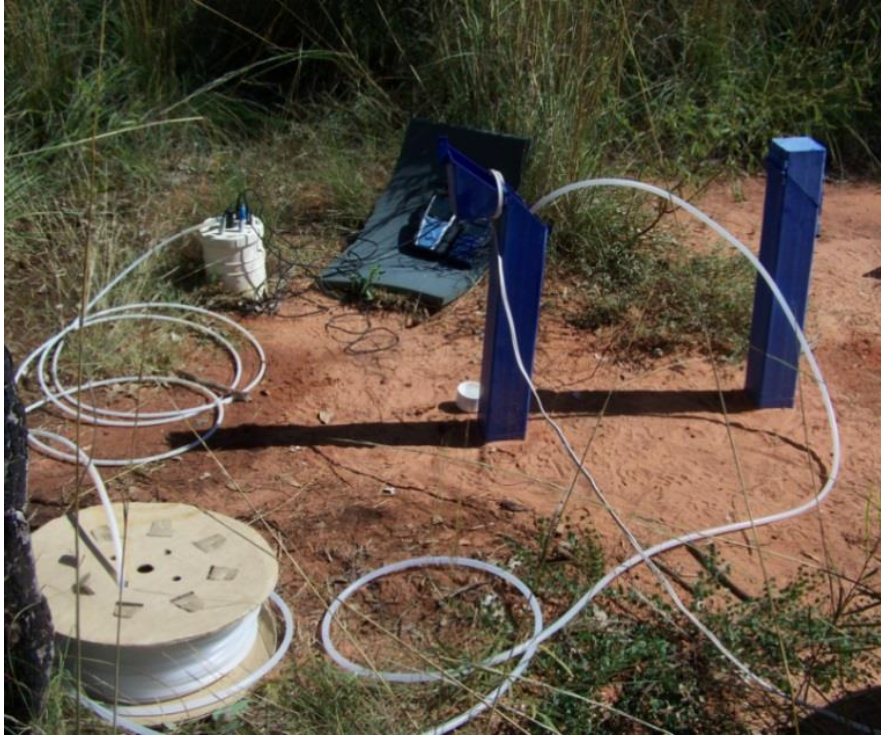
in winter precipitation from snow to rain (early freshet) in the course of a temperature increase occurring within the second half of the 20th century. Based on climate change scenarios set up for the 21st century, which predicted an amplification of winter flows, they also anticipated impacts on the hydrology and ecology of St. Lawrence tributaries, namely an enhancement of river channel erosion and an alteration of stream conditions for winter spawning fish species. Similar studies were carried out in Ireland by Seel-Dunne et al. (2008), in the Loess Plateau of China by Zhang and Liu (2005) and in the Spencer Creek watershed (Southern Ontario,

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Appendix 3: Sampling equipment set up



Sampling equipment set up for bore water sampling



Equipment set up for field parameter measurements



Electronic depth meter used for groundwater level measurements



Apparatus set up for fresh water discharge delineation through the Town Beach intertidal zone

Appendix 4: Calibration and sample analysis methods

Electrode calibration methods

Redox probes were calibrated using Zorbels solutions A and B which were combined at a 1:1 ratio. Dissolved oxygen used an air calibration technique, while electrical conductivity was calibrated using a 1413 $\mu\text{S}/\text{cm}$ solution. pH was calibrated with two buffer solutions (Carroll et al. 2003, Sundaram et al. 2009). For groundwater that was suspected to be alkaline a neutral solution and a pH 10 solution was used, while acidic groundwater was calibrated with both a neutral solution and pH 4 solution. Total alkalinity was measured in the field using the burette titration method to assess the amount of carbonate and bicarbonate in the groundwater (Sundaram et al. 2009). This process involved the titration of 0.016 mol/L sulphuric acid against 100mL aliquots of each groundwater sample, with the addition of the indicator bromocresol green.

Nutrient analysis methods

Ammonium

The QuickChem Method 31-107-06-1-B (USEPA Equivalent Method) was used to analyse samples for Ammonium (Eaton et al. 2012 ; Lachat 2008). Ammonia was mixed with hypochlorite in an alkaline solution, forming monochloramine. Phenate was reacted with monochloramine, producing the complex idophenol blue. To catalyse this reaction nitroferriocyanide was added to the solution. Idophenol blue absorbs light at 630 nm, according to Beers law. Consequently the absorbance at 630 nm is directly proportional to the original concentration of dissolved ammonium within the sample (Eaton et al. 2012).

Nitrate

Nitrate was analysed using the QuickChem Method 31-107-04-1-A (USEPA Equivalent Method). Samples were passed through a copperized cadmium column to quantitatively reduce nitrate to nitrite (Lachat 2008). The concentration of nitrite (reduced nitrate and original nitrite) was assessed by a diazotisation reaction between sulfamylamide and nitrite under acidic conditions, forming diazonium. Diazonium was added to N – (1 – naphthyl) ethylenediamine dihydrochloride to form a magenta azo dye. The resultant dye absorbed light at 520nm. According to Beers Law with linearity the absorbance at 520nm is directly proportional to the concentration of dissolved nitrite within the sample. To determine a value of the original nitrite (no reduced nitrate) within the sample the reduction column was turned

offline and the analysis run again. This value was subtracted from the value for the original nitrite analysis (reduced nitrate and original nitrite) to give the value for nitrate (Eaton et al. 2012). An EDTA buffer was added to the original sample to eliminate metal ions such as iron which can interfere with the analysis (ISO 1996).

Orthophosphate

The QuickChem Method 31-115-01-1-G (USEPA Equivalent Method) was used to assess reactive phosphorus for each bore location (Eaton et al. 2012). Antimony potassium tartrate and ammonium molybdate were reacted in an acidic solution with orthophosphate to form an antimony-phospho-molybdate complex. This was reduced by ascorbic acid, producing a strong blue-coloured complex and absorbing light at 880nm, according to Beers law of linearity. The absorbance of light at this frequency was directly proportional to the concentration of dissolved orthophosphate within the sample (Murphy and Riley 1962).

Total Nitrogen and Phosphorus

When analysing nitrogenous compounds they must be oxidised in an alkaline medium to convert ammonium to nitrate. Conversely phosphorus bearing compounds must be oxidised in an acidic medium. It is therefore necessary to begin the analysis of these two chemical species in an alkaline solution, finishing with acidic conditions. This allows for the simultaneous oxidation of both nitrogen and phosphorus containing compounds (Patton & Kryskalla 2003). To achieve this potassium persulfate was added to a sodium hydroxide solution. This solution began with a pH of 12, transitioning to a pH of less than 2 during a 30 minute autoclave treatment at 121°C. This allowed for the complete oxidation of both analytes (Eaton et al. 2012). UV digestion was used to supply additional energy, catalysing reactions.

Nitrogenous products were analysed through the passage of the sample through a copperized cadmium column where sulphanilamide was added, forming diazonium ions. The diazonium was added to N-(1-naphthyl)ethylenediamine dihydrochloride to form a pink dye. This dye had an absorbance frequency of 540 nm, which was directly proportional to the total nitrogen present within the sample (Lachat 2008). For the analyses of phosphorus products orthophosphate was added to ammonium molybdate and antimony potassium tartrate, forming a phosphomolybdate complex. This was reduced by ascorbic acid, forming a blue

dye which absorbed light at 880 nm. This frequency was directly proportional to the concentration of reactive phosphorus within the sample (Lachat 2008).

Anions

Anion concentrations were determined by High Performance Ion Chromatography (HPIC) using a Dionex® ICS-1000 ion chromatograph equipped with Dionex AS-14, 4 x250 mm anion column and AG-14 guard column. The isocratic run used an eluent of 3.5 mM NaCO₃ and 1.0 mM NaHCO₃ at a flow rate of 1.5 ml /min. The HPIC method employed electronic suppression and conductivity detection. The instrument was calibrated with anion standards diluted from commercially available 1000 ppm standard solutions (ARC). Sample duplicates were run and reproducibility was better than 3%.

Cations

Cations were determined by High Performance Ion Chromatography (HPIC) using a Dionex® ICS-1000 ion chromatograph equipped with a Dionex IonPac® CS12A medium-capacity, carboxylate-functionalized, 4 x250 mm cation-exchange column, and CS-12 guard column. The isocratic run used an eluent of 33 mM Methasulphonic acid at a flow rate of 1.5 ml /min. Temperature of the column was 30.0°C and the injection volume was 25 µL. The HPIC method employed electronic suppression and conductivity detection. The instrument was calibrated with cation standards made from commercially available 1000 ppm standard solutions (ARC). Sample duplicates were run and reproducibility was better than 3%. Given the high dilutions involved in this analysis a confidence level of 1 ppm is stated.

4 - Nonylphenol Analysis

Each 1L sample was acidified and extracted with dichloromethane. This extract volume was subsequently reduced to 1 mL using rotary evaporation and analysed with the Agilent 7000 Triple Quadrupole Gas Chromatography/Mass Spectrometry (GC/MS) System. 1 µL of the extract was injected into the GC PTV inlet, which was run on splitless mode at 280°C. The GC oven containing a High Performance Mass Spectrometry (HP-MS) column, with the dimensions 30m x 0.25mm x 0.25µm, was run at 35 °C for 1 minute and subsequently heated at 15 °C/min to a heat of 320 °C and held at this temperature for 5 minutes. The total run time was 25 minutes. The MS unit had a solvent delay of 3 minutes. The software package Agilent Masshunter was utilized for data analysis (ChemCentre 2014).

Appendix 5: Interpolation settings

Kriging settings for regional hydraulic head and nutrient interpolation

A simple type Kriging Intepolation with a Normal Score transformation was implemented for this study as demonstrated by Nikroo et al. (2010). The approximation method was set to Gaussian Kernel and a semivariogram optimization implemented to determine the best lag size and number of lags. The K- Bessel model was used and the data found to display anisotropy. The search neighbourhood type was set to smooth. These settings were found to give the lowest Average Standard Error and a Root Mean square closest to 1. The Surfer 11 software package was utilised for the kriging of groundwater nutrients. Default settings were found to give the best interpolated surface.

Appendix 6: Formulas used for SGD and groundwater flow velocity calculations

Dupuit revision of Darcy's Law used to calculated submarine groundwater discharge.

$$q_w = K/2L * (h_i^2 - h_f^2)$$

where

q_w = discharge per unit width of aquifer (m^2/day)

K = hydraulic conductivity (m/day)

L = length of flow (m)

h_i = aquifer thickness where L begins (m)

h_j = aquifer thickness where L begins (m)

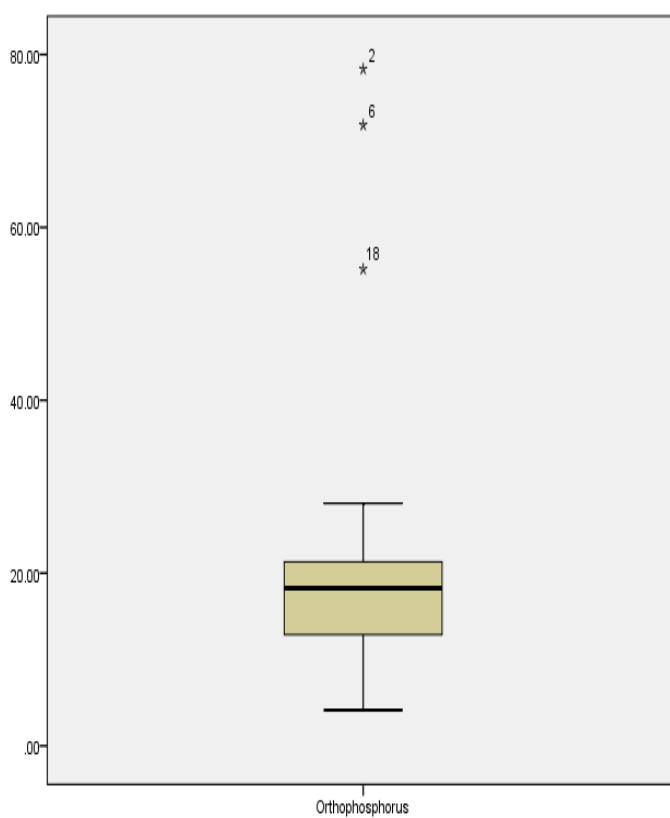
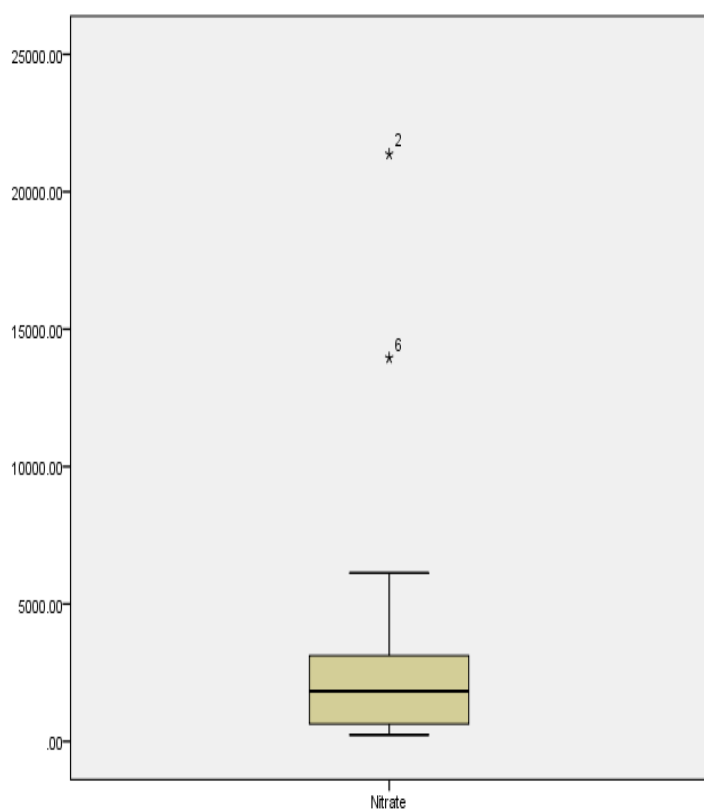
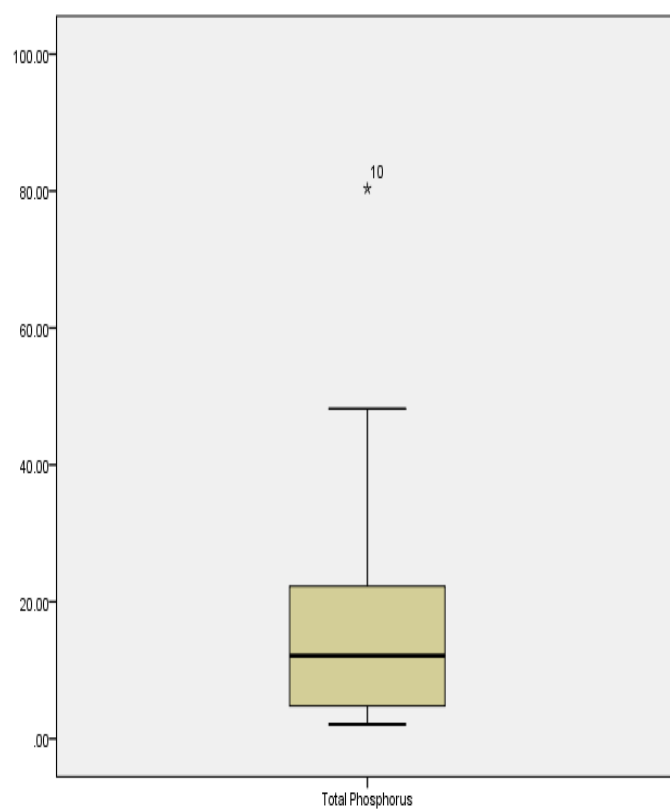
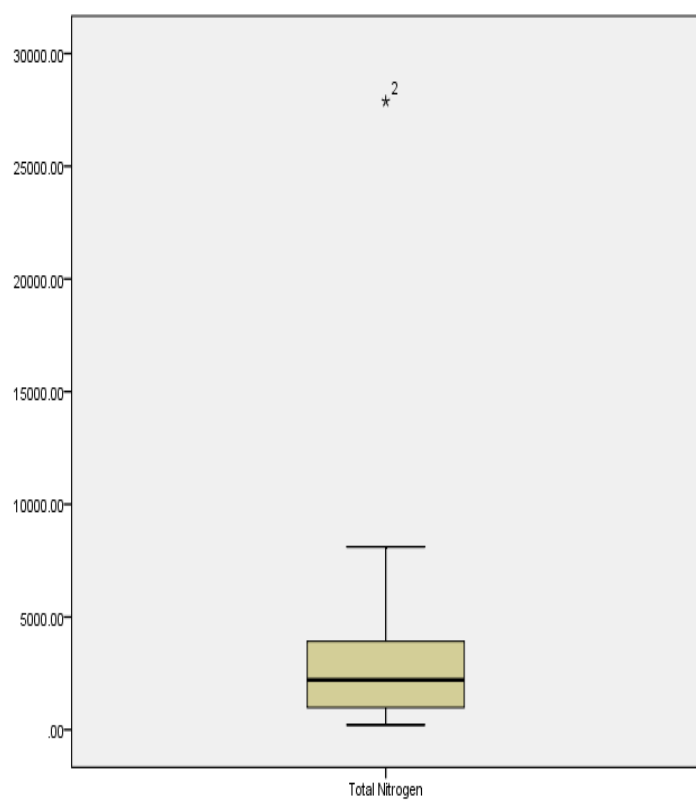
Flow velocity formula

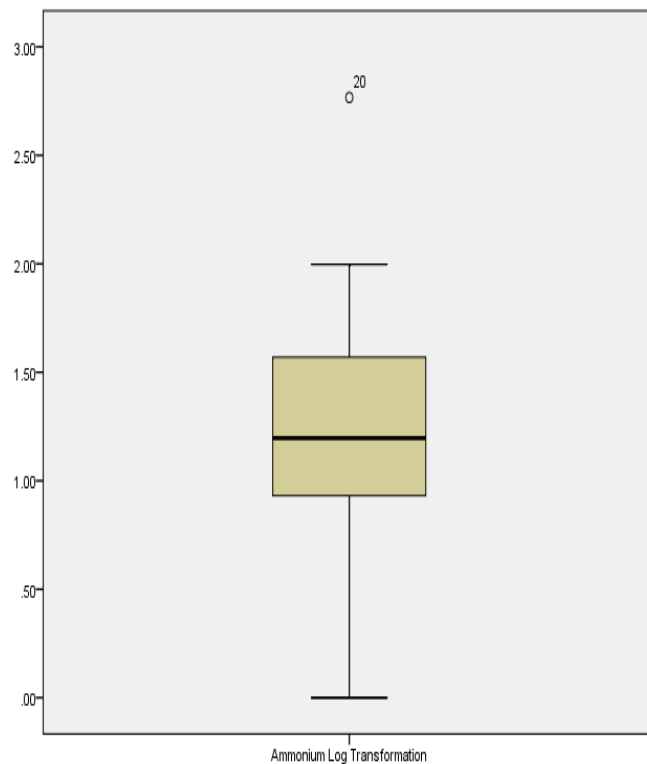
Average linear velocity was calculated as follows (Fetter 1999):

$$v_x = Ki/n_e * dh/dl$$

where v_x = average linear velocity (L/T); K = hydraulic conductivity (L/T); n_e = effective porosity; i = hydraulic gradient (L/L)

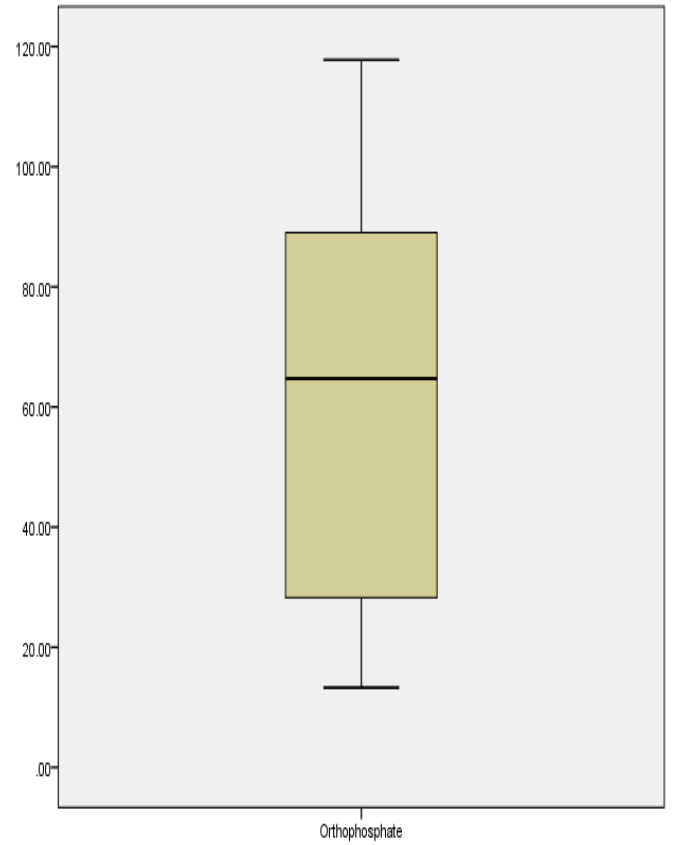
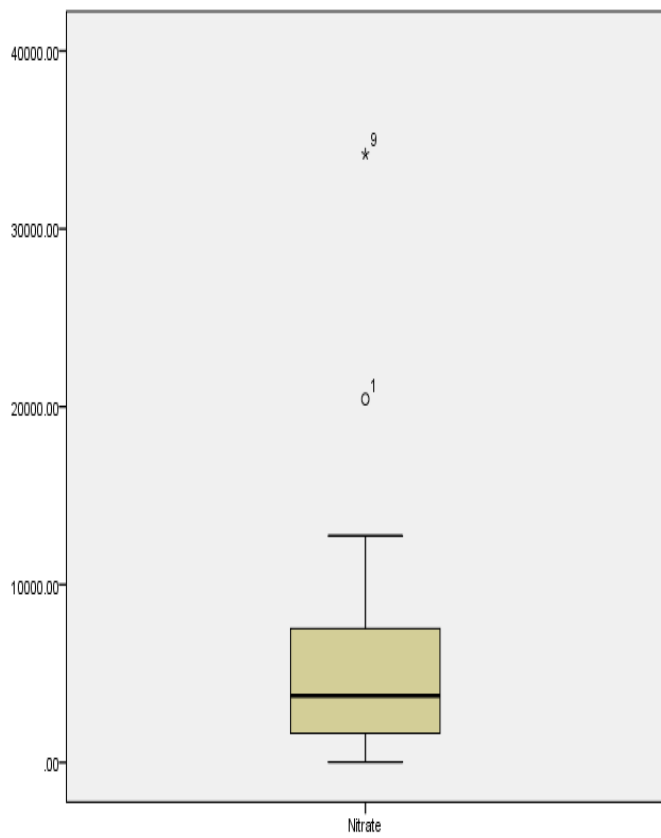
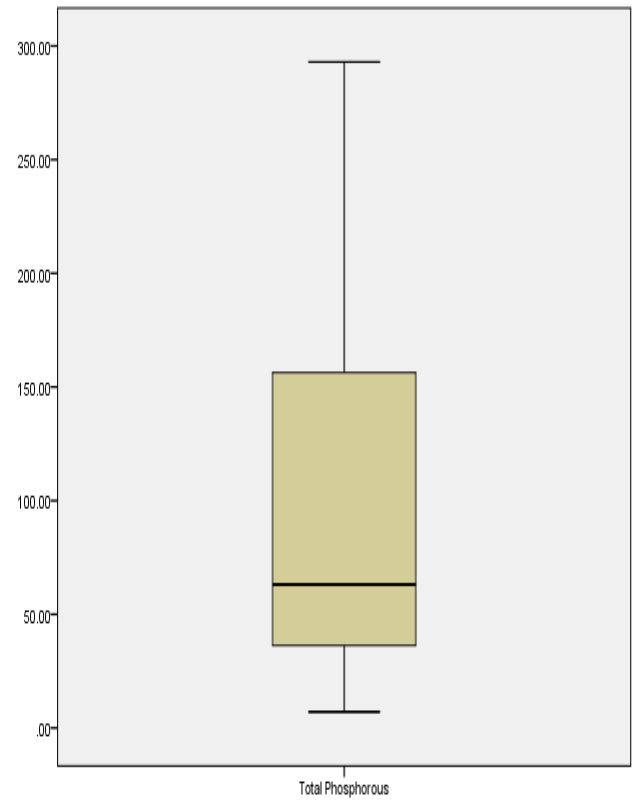
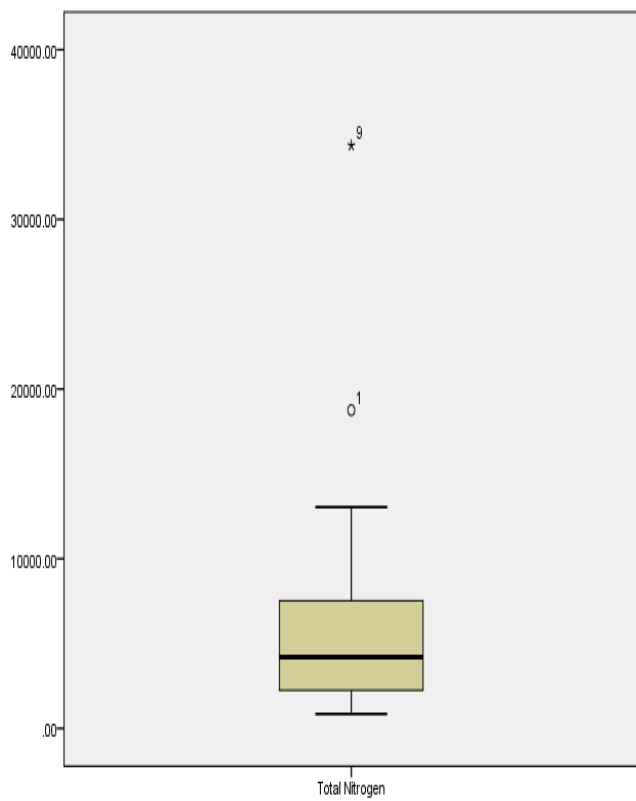
Appendix 7: Statistical analysis – diagrams, figures, and tables

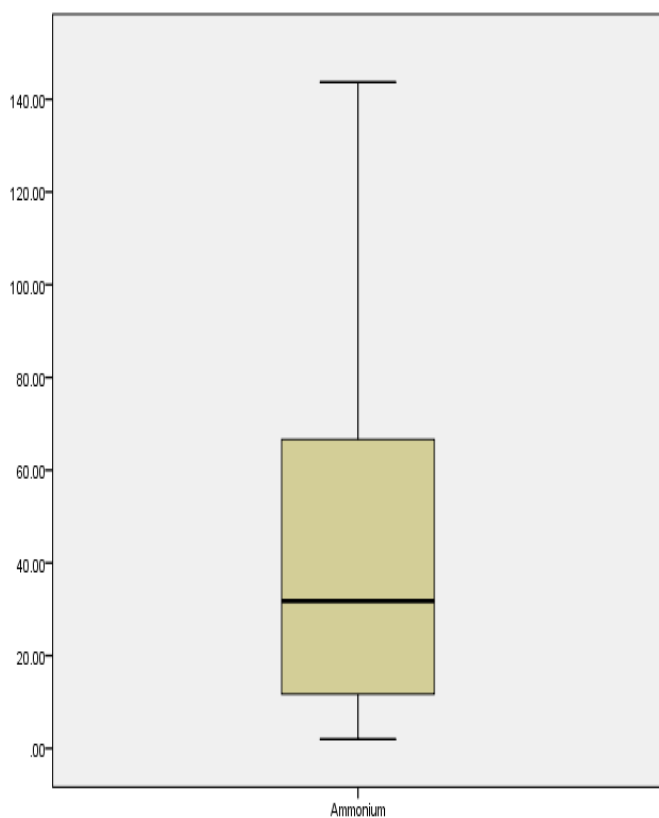




Box Plots showing median concentrations of nutrients and extreme outliers ($\mu\text{g/L}$) for groundwater samples taken at the end of the 2014 wet season.

Nutrient Type	Extreme Outliers; Corresponding Bore location	Nutrient concentration ($\mu\text{g/L}$)
Total Nitrogen	2 = AS	27884.86
Total Phosphorus	10 = ES	80.37
Ammonium	20 = BP	584.17
Nitrate	2 = AS; 6 = CS	AS = 21368.45; CS = 13952.28
Orthophosphorus	2= AS; 6 = CS; 18 = TO	AS = 78.325; CS = 71.85; TO = 55.17





Box Plots showing median concentrations of nutrients and extreme outliers (µg/L) for groundwater samples taken at the end of the 2013 dry season.

Nutrient Type	Extreme Outliers; Corresponding Bore location	Nutrient concentration (µg/L)
Total Nitrogen	1 = AD; 9 = CD	AD = 20429.2; CD = 34359.54
Total Phosphorus	-	-
Ammonium	-	-
Nitrate	1 = AD; 9 = CD	AD = 18751.59; CD = 34200
Orthophosphorus	-	-

Test for the normality of nutrients data in shallow and deep bores in both the wet and dry season

Tests of Normality

	Kolmogorov-Smirnov ^a			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Total Nitrogen ug/L	.271	12	.015	.784	12	.006
Total Phosphorous ug/L	.283	12	.009	.659	12	.000
Ammonium (N-NH4+) ug/L	.185	12	.200 [*]	.884	12	.098
Nitrate (N-NOx) ug/L	.299	12	.004	.793	12	.008
Phosphorous (P-PO43-) ug/L	.154	12	.200 [*]	.938	12	.476

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

Test for the normality of nutrients data after log transformation in shallow and deep bores in both the wet and dry season

Tests of Normality

	Kolmogorov-Smirnov ^a			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
TotalNitrogenlog	.187	15	.169	.952	15	.564
TotalPhosphorouslog	.137	15	.200 [*]	.967	15	.816
Nitratelog	.183	15	.190	.937	15	.349

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

SPSS output for One-Way ANOVA analysing differences in the means of shallow and deep bores in both the wet and dry season

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Ammonium (N-NH4+) ug/L	Between Groups	12682.324	3	4227.441	7.588	.002
	Within Groups	10028.010	18	557.112		
	Total	22710.334	21			
Phosphorous (P-PO43-) ug/L	Between Groups	29005.297	3	9668.432	19.985	.000
	Within Groups	13546.047	28	483.787		
	Total	42551.344	31			
TotalNitrogenlog	Between Groups	1.482	3	.494	1.877	.156
	Within Groups	7.369	28	.263		
	Total	8.851	31			
TotalPhosphorouslog	Between Groups	9.169	3	3.056	20.893	.000
	Within Groups	3.950	27	.146		
	Total	13.118	30			
Nitratelog	Between Groups	1.396	3	.465	.866	.470
	Within Groups	15.045	28	.537		
	Total	16.441	31			

Tukey HSD post hoc test for One-Way ANOVA analysis of differences in the means of shallow and deep bores in both the wet and dry season.

TotalNitrogenlog

Tukey HSD^a

SeasonandDepth	N	Subset for alpha = 0.05
		1
Wet Season Deep Bore	8	3.1971
Wet Season Shallow Bore	8	3.4249
Dry Season Shallow Bore	8	3.4789
Dry Season Deep Bore	8	3.7998
Sig.		.111

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 8.000.

Ammonium (N-NH4+) ug/L

Tukey HSD^{a,b}

SeasonandDepth	N	Subset for alpha = 0.05	
		1	2
Wet Season Deep Bore	7	17.771714	78.526200
Wet Season Shallow Bore	6	23.016167	
Dry Season Shallow Bore	4	26.736250	
Dry Season Deep Bore	5		
Sig.		.926	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 5.266.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Nitratelog

Tukey HSD^a

SeasonandDepth	N	Subset for alpha = 0.05
		1
Wet Season Deep Bore	8	3.1114
Dry Season Shallow Bore	8	3.1417
Wet Season Shallow Bore	8	3.2731
Dry Season Deep Bore	8	3.6368
Sig.		.490

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 8.000.

TotalPhosphorouslog

Tukey HSD^{a,b}

SeasonandDepth	N	Subset for alpha = 0.05	
		1	2
Wet Season Shallow Bore	7	.9974	1.9434
Wet Season Deep Bore	8	1.0245	
Dry Season Deep Bore	8		
Dry Season Shallow Bore	8		
Sig.		.999	.498

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 7.724.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Phosphorous (P-PO43-) ug/L

Tukey HSD^a

SeasonandDepth	N	Subset for alpha = 0.05	
		1	2
Wet Season Deep Bore	8	14.130375	75.425500
Wet Season Shallow Bore	8	30.144500	
Dry Season Shallow Bore	8		
Dry Season Deep Bore	8		
Sig.		.476	.764

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 8.000.

Test for the normality of nutrients data in wastewater irrigated and non-wastewater irrigated sites in both the wet and dry season

Tests of Normality

	Kolmogorov-Smirnov ^a			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
TotalNitrogen	.326	19	.000	.575	19	.000
TotalPhosphorus	.517	19	.000	.372	19	.000
Ammonium	.494	19	.000	.378	19	.000
Nitrate	.222	19	.014	.872	19	.016
Phosphorous	.516	19	.000	.375	19	.000

a. Lilliefors Significance Correction

Test for the normality of nutrients data after log transformation in wastewater irrigated and non-wastewater irrigated sites in both the wet and dry season

Tests of Normality

	Kolmogorov-Smirnov ^a			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
TotalNitrogenlog	.103	19	.200 [*]	.967	19	.716
TotalPhosphorouslog	.296	19	.000	.739	19	.000
Ammoniumlog	.251	19	.003	.717	19	.000
Nitratelog	.140	19	.200 [*]	.916	19	.097
Phosphorouslog	.343	19	.000	.664	19	.000

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

SPSS output for One-Way ANOVA analysing differences in the means of wastewater irrigated and non-wastewater irrigated sites in both the wet and dry seasons

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
TotalNitrogenlog	Between Groups	4.024	2	2.012	14.646	.000
	Within Groups	2.748	20	.137		
	Total	6.772	22			
Nitratelog	Between Groups	3.231	2	1.616	6.627	.006
	Within Groups	4.876	20	.244		
	Total	8.107	22			

Tukey HSD post hoc test for One-Way ANOVA analysis of wastewater irrigated and non-wastewater irrigated sites in both the wet and dry seasons

TotalNitrogenlog

Tukey HSD^{a,b}

Samplegroups	N	Subset for alpha = 0.05	
		1	2
Sites not irrigated with waste water	17	3.2094	
Waste water irrigated sites	4		3.9471
Waste water effluent	2		4.4630
Sig.		1.000	.166

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.709.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Nitratelog

Tukey HSD^{a,b}

Samplegroups	N	Subset for alpha = 0.05	
		1	2
Waste water effluent	2	1.9846	
Sites not irrigated with waste water	17		3.1653
Waste water irrigated sites	4		3.5131
Sig.		1.000	.610

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.709.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Kruskal Wallis test assessing differences in the means of wastewater irrigated and non-wastewater irrigated sites in both the wet and dry seasons

Ranks

	Samplegroups	N	Mean Rank
TotalPhosphorus	Waste water effluent	2	21.50
	Waste water irrigated sites	4	8.75
	Sites not irrigated with waste water	16	10.94
	Total	22	
Ammonium	Waste water effluent	2	19.50
	Waste water irrigated sites	2	8.00
	Sites not irrigated with waste water	16	9.69
	Total	20	
Phosphorous	Waste water effluent	2	22.50
	Waste water irrigated sites	4	14.75
	Sites not irrigated with waste water	17	10.12
	Total	23	

Chi-square statistics for data assessed under the Kruskal Wallis regime.

Test Statistics^{a,b}

	TotalPhosphorus	Ammonium	Phosphorous
Chi-Square	5.581	5.288	6.761
df	2	2	2
Asymp. Sig.	.061	.071	.034

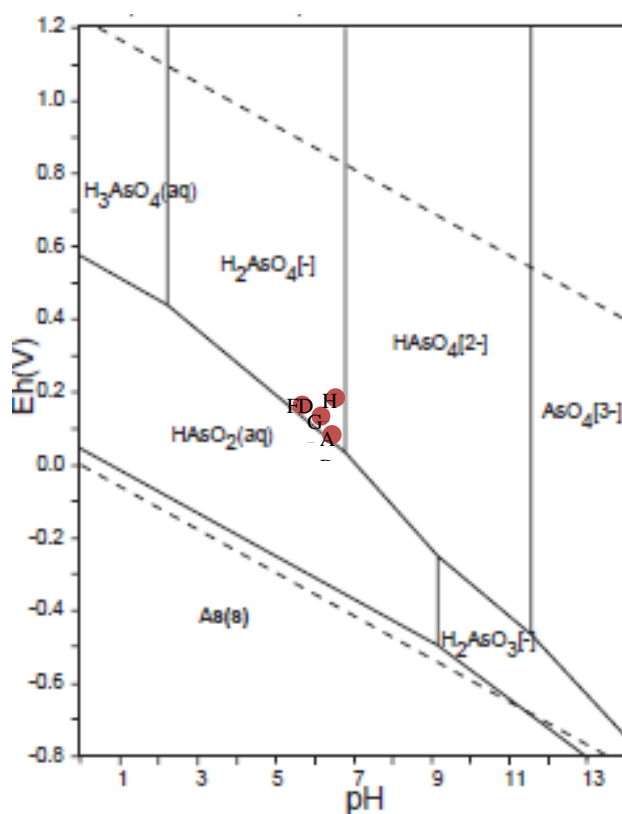
a. Kruskal Wallis Test

b. Grouping Variable: Samplegroups

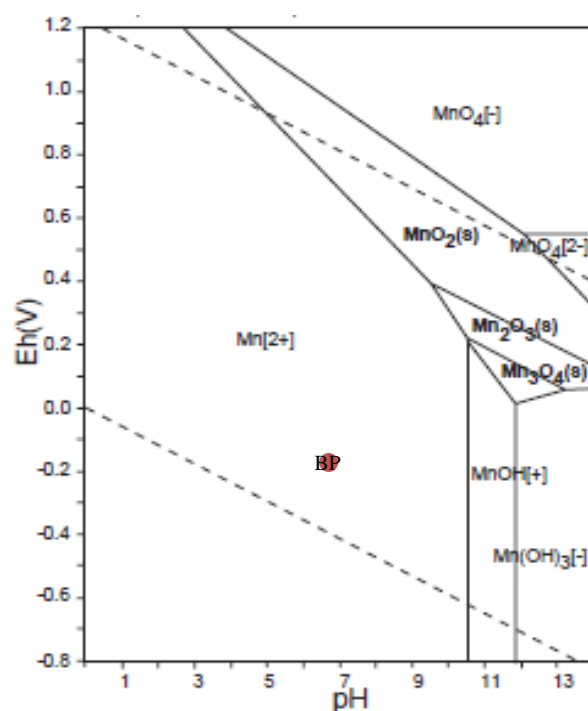
Appendix 8: Total concentrations of metal contaminants of environmental significance (mg/L).

Element	Lithium mg	Barium mg	Scandium mg	Titanium mg	Vanadium mg	Manganese mg	Cobalt	Nickel	Copper	Zinc	Arsenic mg	Selenium mg	Rubidium mg	Strontium mg	Molybdenum mg	Antimony mg	Bismuth mg	Tungsten mg	Uranium mg
AD1	0.0037 6	0.285	0.00234	0.0296	0.002	0.001	0.001	0.001	0.001	0.001	0.0156	0.055	0.0537	3.34	0.001	0.001	0.0378	0.001	0.0141
AB1	0.0136 0.0065	0.0157 6	0.0194	0.001	0.00564	0.0108	0.001	0.001	0.0118	5	0.001	0.00126	0.00438	0.0578	0.001	0.001	0.0194	0.001	0.001
BD1	0.0070	0.177	0.00667	0.00663	0.00691	0.00188	0.001	0.001	0.0017	0.001	0.0037	0.014	0.0156	0.373	0.001	0.001	0.0195	0.0143	0.00153
Bedford Park	9	0.0103	0.00993	0.00641	0.00233	0.446	0.0185	0.0247	0.001	0.001	0.0051	0.00398	0.0149	0.725	0.00185	0.001	0.0938	0.001	0.00237
Black Oval	0.0108	0.0216	0.0132	0.001	0.001	0.0174	0.001	0.001	0.0021	0.0005	0.0012	0.00226	0.0329	0.266	0.001	0.002	0.104	0.001	0.001
BB1	0.0147	0.0119	0.0131	0.001	0.00395	0.00331	0.001	0.001	0.0029	3	0.0028	0.00278	0.00681	0.0981	0.001	0.001	0.0402	0.00137	0.001
Cable Beach	0.0128	0.0102	0.0117	0.001	0.0026	0.001	0.001	0.001	0.0032	0.0097	0.00162	0.00502	0.0113	0.251	0.001	0.001	0.154	0.001	0.001
Cable Beach	0.0051	0.0185	0.0097	0.001	0.00298	0.001	0.001	0.001	0.001	1	0.001	0.00581	0.0105	1.51	0.001	0.001	0.171	0.001	0.00437
B	5	0.0088	0.00749	0.00249	0.00271	0.001	0.001	0.001	0.001	6	0.0042	0.0121	0.0185	1.33	0.001	0.001	0.0496	0.001	0.00556
CD2	0.0118	9	0.00749	0.00249	0.00271	0.001	0.001	0.001	0.001	1	0.0042	0.0121	0.0185	1.33	0.001	0.001	0.0496	0.001	0.00556
CS2	0.0039	0.0048	0.00749	0.00249	0.00271	0.001	0.001	0.001	0.001	1	0.0042	0.0121	0.0185	1.33	0.001	0.001	0.0496	0.001	0.00556
CS2	0.0087	5	0.0035	0.00439	0.00299	0.001	0.001	0.001	0.0018	0.0058	0.0022	0.00157	0.0121	0.535	0.00135	0.001	0.0759	0.001	0.00559
DD2	0.0037	5	0.0035	0.00439	0.00299	0.001	0.001	0.001	0.0018	0.0058	0.0022	0.00157	0.0121	0.535	0.00135	0.001	0.0759	0.001	0.00559
DS2	0.0070	1	0.0035	0.00439	0.00299	0.001	0.001	0.001	0.0018	0.0058	0.0022	0.00157	0.0121	0.535	0.00135	0.001	0.0759	0.001	0.00559
ED2	0.0070	1	0.0035	0.00439	0.00299	0.001	0.001	0.001	0.0018	0.0058	0.0022	0.00157	0.0121	0.535	0.00135	0.001	0.0759	0.001	0.00559
ES3	0.0127	0.0433	0.0033	0.001	0.001	0.001	0.001	0.001	0.0019	3	0.00587	0.0121	0.0185	1.94	0.001	0.001	0.231	0.00305	0.001
FD3	0.0032	9	0.00354	0.038	0.00135	0.001	0.0026	0.0047	0.001	0.001	0.0054	0.014	0.0157	2.38	0.00191	0.001	0.0873	0.00146	0.00204
FS3	0.0031	7	0.0119	0.015	0.00418	0.0166	0.0013	0.001	0.0037	5	0.0026	0.0163	0.0157	0.807	0.001	0.001	0.0418	0.00201	0.00352
GS4	0.0014	6	0.0062	0.00288	0.001	0.001	0.0019	0.0058	0.0019	8	0.0075	0.0639	0.0575	6.14	0.001	0.001	0.0382	0.00167	0.00484
GS4	0.0119	0.0555	0.0146	0.00313	0.0136	0.001	0.001	0.001	0.0028	0.0093	0.0017	0.00524	0.0157	0.124	0.001	0.001	0.0039	0.001	0.001
Haynes Park	0.0069	1	0.0161	0.0123	0.001	0.0172	0.001	0.001	0.0102	0.0064	0.0011	0.00267	0.0305	0.257	0.001	0.00117	0.106	0.001	0.001
HC4	0.0062	3	0.245	0.00912	0.0098	0.0122	0.001	0.001	0.0035	3	0.0302	0.0736	0.106	7.29	0.00124	0.001	0.068	0.0112	0.0164
HB4	0.0090	1	0.0078	0.001	0.00329	0.001	0.001	0.001	0.0027	5	0.0021	0.0014	0.00931	0.07	0.001	0.001	0.0352	0.001	0.001
KBO	0.0037	9	0.144	0.00733	0.00759	0.001	0.001	0.001	0.0187	0.001	0.0021	0.0086	0.0114	0.382	0.00345	0.001	0.0556	0.001	0.00275
Town Oval	0.0138	0.058	0.001	0.001	0.001	0.001	0.001	0.001	0.0018	8	0.00736	0.00879	0.0372	0.00614	0.001	0.001	0.0629	0.001	0.001

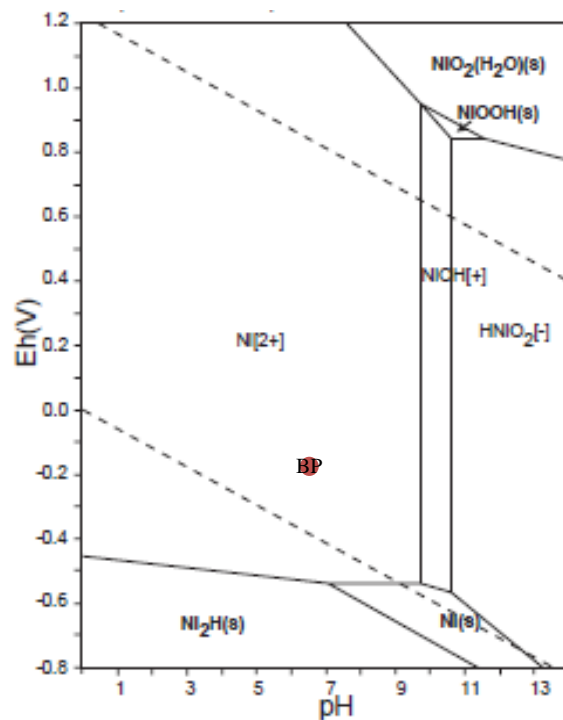
Appendix 9: Eh – pH diagram showing speciation for metals of environmental significance



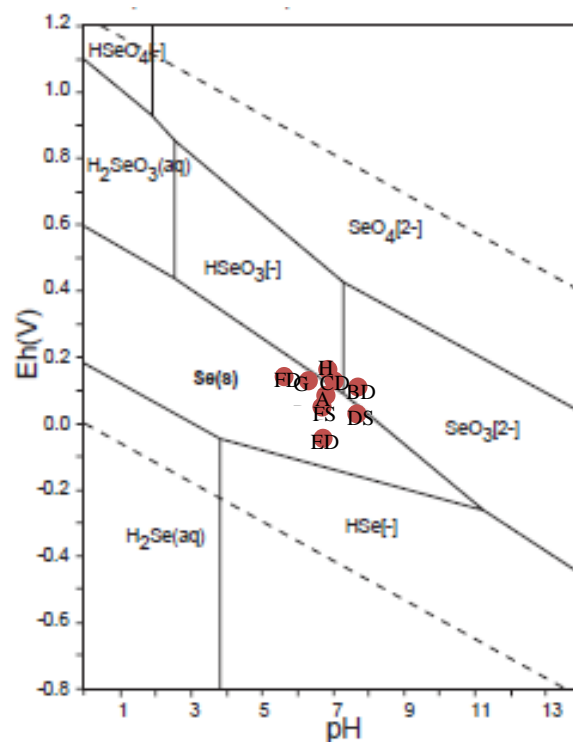
Eh – pH diagram for Arsenic showing chemical speciation of sites violating guideline levels (Brookins 1986; NIAIST 2005)



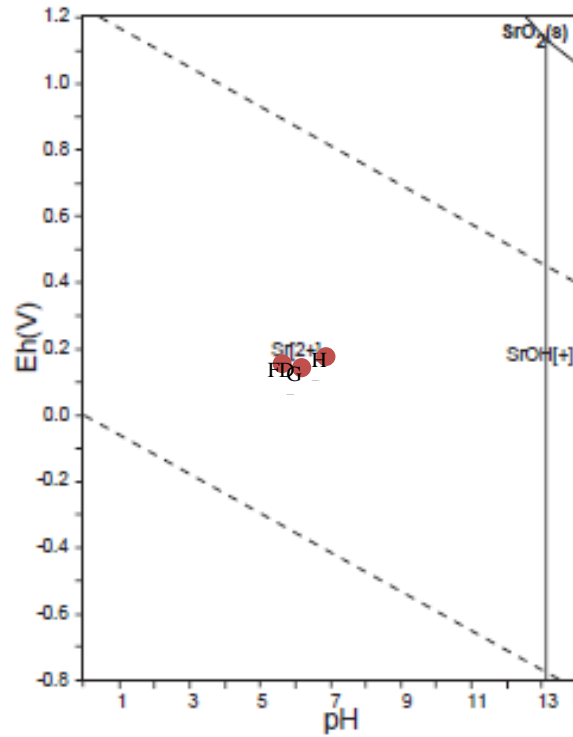
Eh – pH diagram for Manganese showing chemical speciation of sites violating guideline levels (NIAIST 2005)



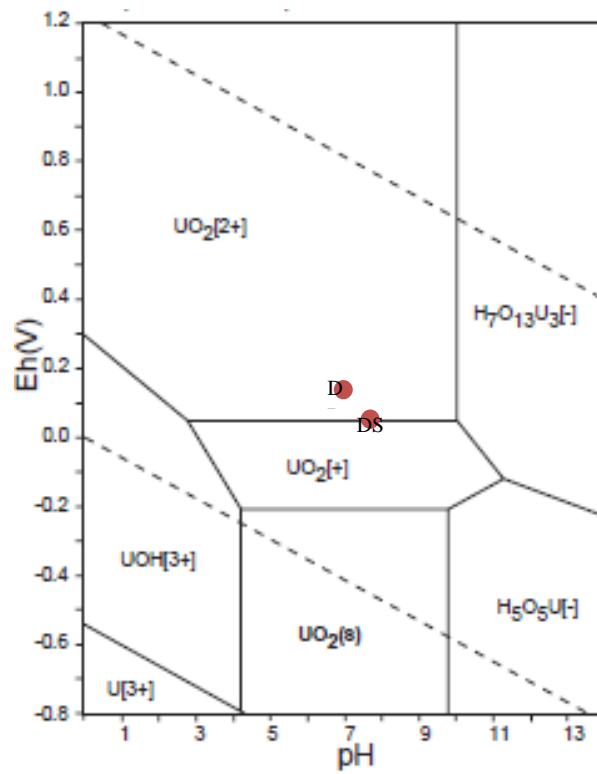
Eh – pH diagram for Nickel showing chemical speciation of sites violating guideline levels (NIAIST 2005).



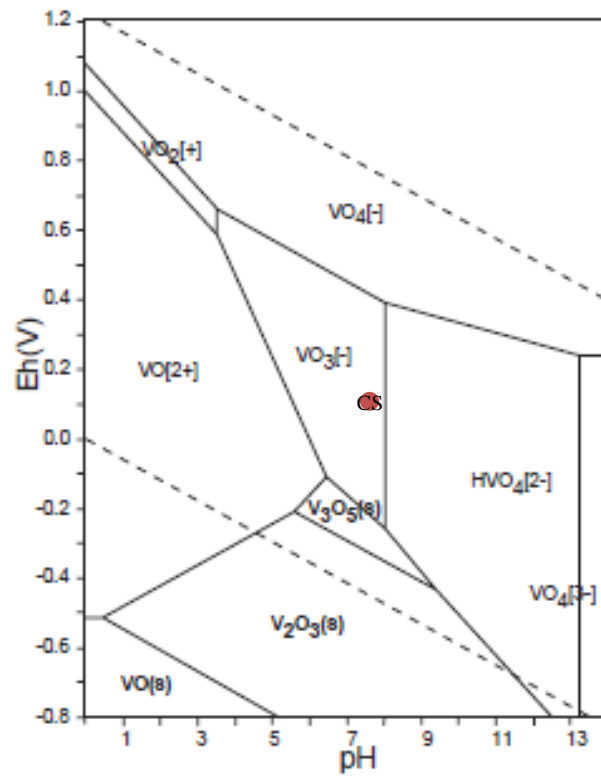
Eh – pH diagram for Selenium showing chemical speciation of sites violating guideline levels (NIAIST 2005)



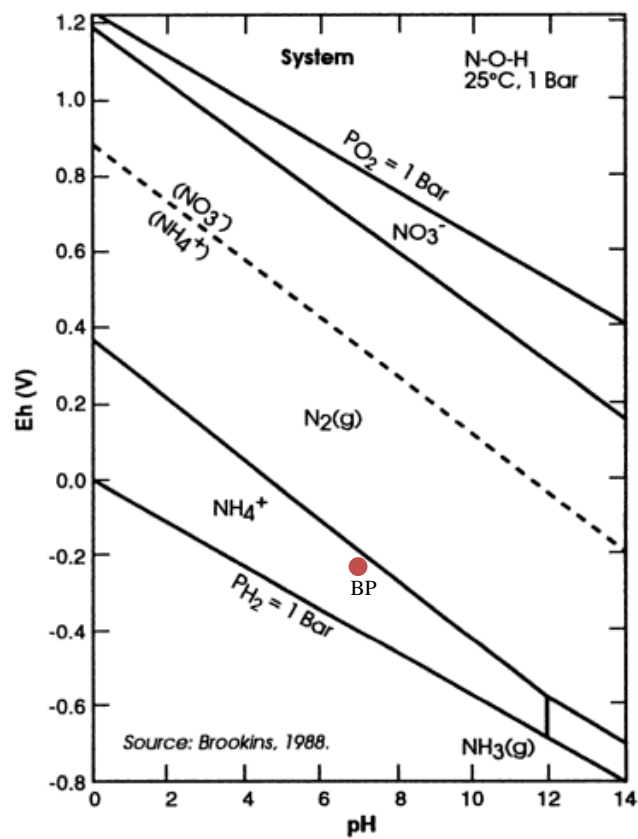
Eh – pH diagram for Strontium showing chemical speciation of sites violating guideline levels (NIAIST 2005)



Eh – pH diagrams for Uranium showing chemical speciation of sites violating guideline levels (NIAIST 2005)



Eh - pH diagram for Vanadium showing chemical speciation of sites violating guideline levels (NIAIST 2005)



Eh - pH diagram for nitrogen species at Bedford Park (Pyne 1995)

Regional Recharge

412446.5 mE
8018067.1 mS



Legend

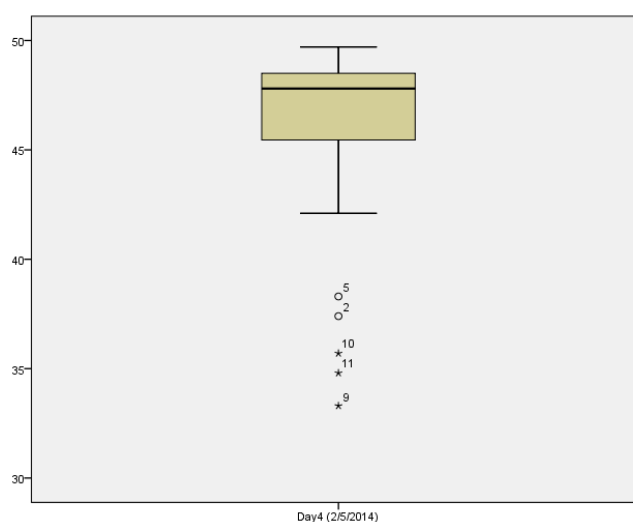
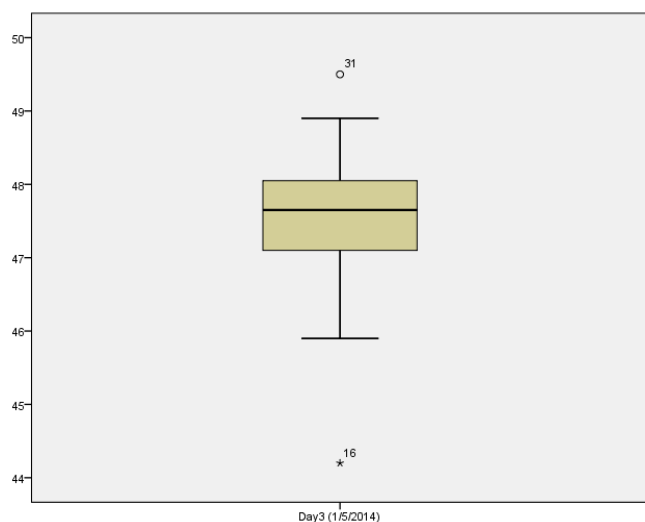
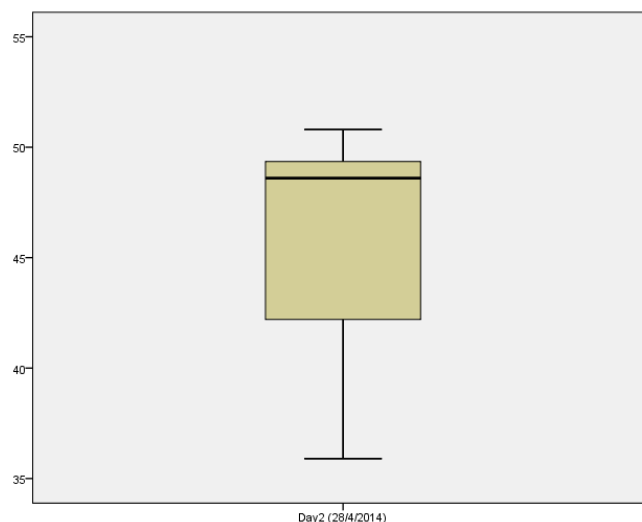
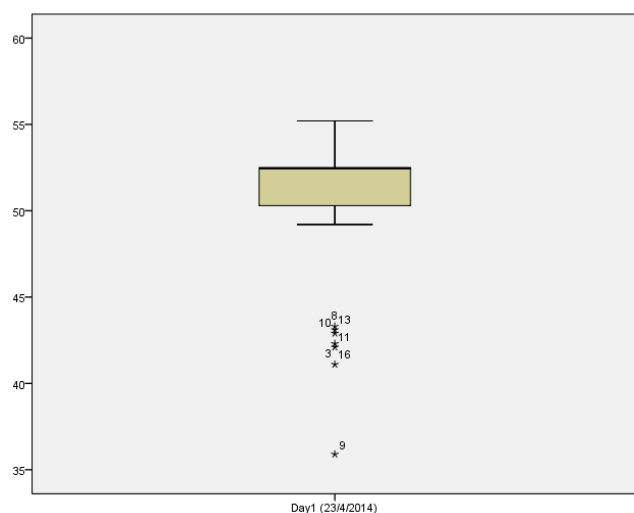
- ◆ Broome Bore Locations
- Recharge Extent - North West
- Recharge Extent - South East
- Recharge Extent - North
- Recharge Extent - Middle
- Recharge Extent - South West

420941.9 mE
8007851.4 mS

WGS 84 51 S

0 0.5 1 2 3 4 Kilometers

Appendix 10: Regional recharge areas (Km^2) throughout the Broome peninsula.



Outlier Number	E	N	EC (mS/cm)	Date Sampled
Day 1 - 3	418334	8012405	42.3	23/04/2014
Day 1 - 8	417391	8011683	43.3	23/04/2014
Day 1 - 9	417374	8011688	35.9	23/04/2014
Day 1 - 10	417384	8011677	42.9	23/04/2014
Day 1 - 11	417371	8011665	42.1	23/04/2014
Day 1 - 13	417393	8011683	43.1	23/04/2014
Day 1 - 16	417391	8011684	41.1	23/04/2014
Day 3 - 16	417510	8011718	44.2	01/05/2014
Day 4 - 9	417384	8011680	33.3	02/05/2014
Day 4 - 10	417375	8011673	35.7	02/05/2014
Day 4 - 11	417368	8011665	34.8	02/05/2014

Appendix 11: Box and whisker plots showing extreme outliers () for EC measurements. The outlier locations and EC readings are displayed in the table.*

Appendix 12: Town Beach near shore groundwater discharge zone



Predominant site of groundwater discharge along Town Beach



Shoreline wetting gradient, due to the groundwater discharge

Wednesday 23		Thursday 24		Friday 25		Saturday 26		Sunday 27		Monday 28		● Tuesday 29	
Time	Height	Time	Height	Time	Height	Time	Height	Time	Height	Time	Height	Time	Height
0324	7.19	0451	6.71	0034	4.15	0213	3.64	0315	2.92	0402	2.27	0442	1.79
0928	4.10	1125	4.56	0700	6.87	0829	7.62	0919	8.44	0958	9.11	1033	9.56
1550	7.16	1747	6.80	1333	4.16	1454	3.29	1545	2.41	1627	1.71	1706	1.25
2230	4.07			1944	7.16	2054	7.88	2141	8.55	2221	9.04	2257	9.32

Wednesday 30		Thursday 1		Friday 2		Saturday 3		Sunday 4		Monday 5		Tuesday 6	
Time	Height	Time	Height	Time	Height	Time	Height	Time	Height	Time	Height	Time	Height
0519	1.53	0552	1.46	0004	9.32	0036	9.08	0109	8.72	0141	8.25	0215	7.72
1106	9.79	1138	9.82	0623	1.59	0652	1.87	0720	2.30	0747	2.83	0815	3.42
1741	1.06	1812	1.10	1209	9.66	1240	9.34	1311	8.88	1342	8.33	1415	7.71
2331	9.41			1843	1.34	1911	1.74	1939	2.25	2006	2.84	2036	3.46

Broome tidal regime during field work period (Bureau of Meteorology 2014 (b))

Appendix 13: Ion Balance (meq/L) for anions and cations analysed at each bore

Location	Ca	Mg	Na	K	HCO ₃	F	Br	NO ₃	Cl	SO ₄	Total cations	Total anions	CBE
AD	11.81801	19.59383	135.8613	1.883632	0.832787	0.037441	0.233955	3.055093	146.7215	11.935	169.1568	162.8157	1.91011
AS	0.350599	0.19926	2.538522	0.067187	0.157377	0.000632	0.000613	0.3014	0.397944	0.6215	3.155567	1.479466	36.16158
BD	1.311727	2.53081	38.27078	0.801253	5.87541	0.063138	0.033029	1.246016	23.49992	3.670896	42.91457	34.3884	11.02955
BS	0.23513	0.500864	2.620261	0.121662	0.931148	0.001948	0.001101	0.542223	0.67307	0.479688	3.477917	2.629178	13.89758
CD	4.352395	2.341012	19.77652	0.392685	4.859016	0.050448	0.0299	1.883008	12.68166	2.50475	26.86261	22.00878	9.931844
CS	2.117166	0.347594	18.34243	0.107519	6.990164	0.030174	0.005407	0.099252	7.427127	0.966813	20.91471	15.51894	14.80988
DD	4.242465	5.467873	22.70196	0.219591	6.740984	0.04871	0.022003	0.073366	17.53369	3.037646	32.63189	27.4564	8.613139
DS	2.456687	5.241876	47.16161	0.324015	10.95082	0.095313	0.061552	0.025498	30.09969	4.671	55.18419	45.90387	9.180424
ED	1.968214	3.071822	35.17709	0.320512	0.636066	0.012954	0.062691	0.087462	25.90206	3.0295	40.53763	29.73073	15.37947
ES	1.412226	1.971205	6.542913	0.548568	0.263934	0.022064	0.007222	0.123524	3.92262	0.563292	10.47491	4.902656	36.23626
FD	19.39142	34.43982	158.2645	7.99312	2.655738	0.44139	0	0.222099	159.5912	13.80888	220.0888	176.7193	10.92959
FS	7.167914	12.81752	73.93483	7.663836	4.708197	0	0.091264	0.415844	67.74896	6.044125	101.5841	79.00839	12.50091
GD	20.7015	42.28392	187.657	8.665524	0.55082	0.554871	0.256809	0.185359	186.3006	16.04685	259.3079	203.8954	11.9629
GS	0.428543	0.842123	8.996217	0.59046	0.378689	0.026962	0.004931	0.196245	2.076901	1.513208	10.85734	4.196936	44.24261
HD	14.92984	29.77968	153.9444	12.63744	0.988525	0.025856	0.222753	1.541304	161.7451	15.25348	211.2914	179.777	8.058542
HS	0.092764	0.177376	0.805217	0.117315	0.07377	0.006056	0.001076	0.07056	0.381014	0.079896	1.192672	0.612373	32.14876
KRO	2.12984	3.947511	22.14009	1.667775	0.478689	0.037441	0.033267	0.374121	19.25025	2.726625	29.88521	22.9004	13.23243
TO	2.132086	4.78659	16.12565	1.4311	0.465574	0.02812	0.022453	0.325785	16.59014	2.098667	24.47543	19.53074	11.23635
CB	2.511178	2.405183	7.807696	1.228849	0.531148	0.038915	0.020138	0.321866	15.78789	1.459542	13.95291	18.1595	-13.0996
BP	4.122655	5.346442	25.11143	1.858721	0.419672	0.037599	0.032253	0.090188	25.67093	3.484604	36.43925	29.73525	10.1308

412534.2 mE
8017777.4 mS



422385.3 mE
8008749.7 mS

Legend

- Broome Bore Locations

Discharge Boundaries

- F
- G
- H
- C
- BP

WGS84 51S



Appendix 14: Boundaries used to quantify SGD throughout Roebuck Bay

Appendix 15: Natural attenuation and submarine groundwater discharge of nutrients from the Broome peninsula to Roebuck Bay

Submarine groundwater discharge rate throughout Roebuck Bay, proximal to the Broome town site, during the wet season (L/day)

L/day	K=1	K=7.5	K=15	K=25
30m	1012976	7597320	15194641	25324402
40m	1340686	10055145	20110291	33517152
50m	1668396	12512970	25025941	41690608

Submarine groundwater discharge rate throughout Roebuck Bay, proximal to the Broome town site during the dry season (L/day)

L/day	K=1	K=7.5	K=15	K=25
30m	923394	6542938	13085877	21809794
40m	1155786	8668392	17336784	28894640
50m	1439179	10793846	21587692	35967988

Submarine groundwater discharge rate from the WWTP into Roebuck Bay (L/day)

L/day	K=1	K=7.5	K=15	K=25
30m	652800	4896000	9792000	16320000
40m	844800	6336000	12672000	21120000
50m	1036800	7776000	15552000	25920000

Submarine groundwater discharge from the Broome Golf Course into Roebuck Bay (L/day)

L/day	K=1	K=7.5	K=15	K=25
30m	161200	1209000	2418000	4030000
40m	213200	1599000	3198000	5330000
50m	265200	1989000	3978000	6630000

Groundwater nutrient discharge rate for Roebuck Bay, proximal to the Broome town site, during the wet season (kg/day)

Total Nitrogen				
kg/day	K=1	K=7.5	K=15	K=25
30m	5.037257	37.77943	75.55886	125.9314
40m	6.669826	50.0237	100.0474	166.7457
50m	8.302395	62.26797	124.5359	207.53
Nitrate				
kg/day	K=1	K=7.5	K=15	K=25
30m	4.68196	35.1147	70.22939	117.049
40m	6.199647	46.49736	92.99471	154.9912
50m	1.86537	57.88001	115.76	192.9139
Total Phosphorus				
kg/day	K=1	K=7.5	K=15	K=25
30m	0.025782	0.193363	0.386725	0.644542
40m	0.034124	0.255933	0.511866	0.85311
50m	0.042467	0.318503	0.637006	1.06116

Groundwater nutrient discharge rate for Roebuck Bay, proximal to the Broome town site, during the dry season (kg/day)

Total Nitrogen				
kg/day	K=1	K=7.5	K=15	K=25
30m	11.72859	81.22935	162.4587	270.7645
40m	14.34463	107.5847	215.1694	358.6157
50m	17.85868	133.9401	267.8802	446.44
Nitrate				
kg/day	K=1	K=7.5	K=15	K=25
30m	11.40433	78.91086	157.8217	263.0362
40m	13.93502	104.5126	209.0253	348.3754
50m	17.34859	130.1144	260.2288	433.6937
Total Phosphorus				
kg/day	K=1	K=7.5	K=15	K=25
30m	0.069515	0.489551	0.979103	1.631838
40m	0.086464	0.648478	1.296957	2.161594
50m	0.107654	0.807405	1.614811	2.690995

Groundwater nutrient discharge rate from the WWTP into Roebuck Bay (kg/day)

Total Nitrogen				
kg/day	K=1	K=7.5	K=15	K=25
30m	4.597886	34.48414	68.96829	114.9471
40m	5.950205	44.62654	89.25308	148.7551
50m	7.302525	54.76893	109.5379	182.5631
Nitrate				
kg/day	K=1	K=7.5	K=15	K=25
30m	3.490306	26.1773	52.35459	87.25765
40m	4.516867	33.8765	67.753	112.9217
50m	5.543427	41.57571	83.15141	138.5857
Total Phosphorus				
kg/day	K=1	K=7.5	K=15	K=25
30m	0.075072	0.56304	1.12608	1.8768
40m	0.097152	0.72864	1.45728	2.4288
50m	0.119232	0.89424	1.78848	2.9808

Groundwater nutrient discharge rate from the Broome Golf Course into Roebuck Bay (kg/day)

Total Nitrogen				
kg/day	K=1	K=7.5	K=15	K=25
30m	4.40076	33.0057	66.0114	110.019
40m	5.82036	43.6527	87.3054	145.509
50m	7.23996	54.2997	108.5994	180.999
Nitrate				
kg/day	K=1	K=7.5	K=15	K=25
30m	4.310488	32.32866	64.65732	107.7622
40m	5.700968	42.75726	85.51452	142.5242
50m	7.091448	53.18586	106.3717	177.2862
Total Phosphorus				
kg/day	K=1	K=7.5	K=15	K=25
30m	0.007523	0.05642	0.11284	0.188067
40m	0.009949	0.07462	0.14924	0.248734
50m	0.012376	0.09282	0.18564	0.3094

Estimated nitrate discharge into Roebuck Bay from Bore C considering the best discharge concentration under natural attenuation processes (kg/day).

K (m/day)	Depth (m)	Nitrate Discharge (kg/day) Wet Season	Nitrate Discharge (kg/day) Dry Season
1	30	2.09	8.22
7.5	30	15.71	56.38
15	30	31.42	112.76
25	30	52.37	187.94
1	40	2.77	9.96
7.5	40	20.81	74.67
15	40	41.61	149.34
25	40	69.35	248.90
1	50	3.45	12.39
7.5	50	25.90	92.96
15	50	51.80	185.92
25	50	86.34	309.86

Estimated total nitrate discharge into Roebuck Bay from WWTP considering the best discharge concentration under natural attenuation processes (kg/day).

K (m/day)	Depth (m)	Nitrate Discharge (kg/day)
1	30	2.043264
7.5	30	15.32448
15	30	30.64896
25	30	51.0816
1	40	2.644224
7.5	40	19.83168
15	40	39.66336
25	40	66.1056
1	50	3.245184
7.5	50	24.33888
15	50	48.67776
25	50	81.1296

Estimated total nitrate discharge into Roebuck Bay from Golf Course considering the best discharge concentration under natural attenuation processes (kg/day).

K (m/day)	Depth (m)	Nitrate Discharge (kg/day)
1	30	2.255188
7.5	30	16.91391
15	30	33.82782
25	30	56.3797
1	40	2.982668
7.5	40	22.37001
15	40	44.74002
25	40	74.5667
1	50	3.710148
7.5	50	27.82611
15	50	55.65222
25	50	92.7537

412757.6 mE
8017255.9 mS



420700.7 mE
8009505.6 mS

Legend

- ◆ Broome Bore Locations

Type

- Wastewater Treatment Plant
- Wastewater Irrigated Ovals

WGS84 51S

0 0.3 0.6 1.2 1.8 2.4 Kilometers

Appendix 16: Location of wastewater treatment plant and ovals irrigated with wastewater effluent