Sadat-Noori, Mahmood, Santos, Isaac R., Tait, Douglas R., and Maher, Damien T. (2016) ***Fresh meteoric versus recirculated saline groundwater nutrient inputs into a subtropical estuary.*** **Science of the Total Environment, 566-567 pp. 1440-1453.**

https://doi.org/10.1016/j.scitotenv.2016.06.008

Fresh Meteoric versus Recirculated Saline Groundwater Nutrient Inputs into a Subtropical Estuary

Mahmood Sadat-Noori[1,2*], Isaac Santos[1], Douglas Tait[1,2], Damien Maher[2]

[1]National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, Coffs Harbour, NSW, Australia

[2]School of Environment, Science and Engineering, Southern Cross University, Lismore, NSW, Australia

[*]Corresponding author:

M. Sadat-Noori, School of Environment, Science and Engineering, Southern Cross University, PO Box 157 Lismore, NSW 2480, Australia (mahmood.sadat-noori@scu.edu.au)

Running head: Groundwater discharge as a source of nutrients.

Abstract

The role of groundwater in transporting nutrients to coastal aquatic systems has recently received considerable attention. However, the relative importance of fresh versus saline groundwater-derived nutrient inputs to estuaries and how these groundwater pathways may alter surface water N:P ratios remains poorly constrained. We performed detailed time series measurements of nutrients in a tidal estuary (Hat Head, NSW, Australia) and used radium to quantify the contribution of fresh and saline groundwater to total surface water estuarine exports under contrasting hydrological conditions (wet and dry season). Average nutrient fluxes showed that the estuary was a source of nutrients to the coastal waters. Dissolved inorganic nitrogen (DIN) export was 7-fold higher than the average global areal flux rate for rivers likely due to the small catchment size, surrounding wetlands and high groundwater inputs. Fresh groundwater discharge was dominant in the wet season accounting for up to 45% of total dissolved nitrogen (TDN) and 48% of total dissolved phosphorus (TDP) estuarine exports. In the dry season, fresh and saline groundwater accounted for 21 and 33% of TDN export, respectively. The combined fresh and saline groundwater fluxes of NO_3, PO_4, NH_4, DON, DOP, TDN and TDP were estimated to account for 66, 58, 55, 31, 21, 53 and 47 % of surface water exports, respectively. Groundwater-derived nitrogen inputs to the estuary were responsible for a change in the surface water N:P ratio from typical N-limiting conditions to P-limiting as predicted by previous studies. This shows the importance of both fresh and saline groundwater as a source of nutrients for coastal productivity and nutrient budgets of coastal waters.

Keywords: Submarine groundwater discharge, Groundwater–surface water interaction, radium isotopes, nitrogen, phosphorus.

1. Introduction

Nutrients are key elements for aquatic life but in excess they can be harmful. High inputs of nutrients into aquatic systems can lead to eutrophication (Urquidi-Gaume1 et al., 2016) and potentially toxic algal blooms (Sugimoto et al., 2015). Eutrophication leads to an excess of organic matter and increased oxygen demand, which can create anoxic environments. This can cause losses of aquatic species, environmental stress and threatens the ecosystem health (Seitzinger et al., 2005). Eutrophication can occur naturally as a slow aging process for a water body. However, human activity can greatly speed up eutrophication (Delgado-Baquerizo, 2016).

Coastal estuarine ecosystems are among the most productive biological areas in the world (Borges and Abril, 2011; Maher et al., 2012). While surface water runoff through rivers is often considered the main pathway for delivering nutrients to estuaries, submarine groundwater discharge (SGD) is also proven to be a significant source of nutrient transport from the land to coastal and estuarine waters (Burnett et al. 2006; Santos et al., 2014; Su et al., 2014). Previous studies have shown groundwater can be a major source of nutrients to continental margins (Kim and Swarzenski, 2010), coral reef lagoons (Tait et al., 2014), tropical islands (Erler et al., 2014), estuaries (Wong et al., 2013), mangroves (Gleeson et al., 2013) and coastal lagoons (Bernard et al., 2014).

The modern definition of SGD incorporates both fresh terrestrially-driven groundwater and saline recirculated seawater (Moore, 2010), both of which can deliver high nutrient loads to estuaries. Only the terrestrial source of SGD represents new nutrient loads to surface waters. However, the recirculated saline component may contain high concentrations of nutrients because of biological and chemical reaction between saline groundwater and sediments (Moore et al., 2006; Santos et al., 2015). Saline SGD can buffer seasonal inputs of new nutrients and maintain productivity in coastal waters (Billerbeck et al. 2006). The portion of fresh and saline components of SGD can vary significantly based on hydraulic conditions, tidal forcing and distance of the fresh and saline mixing zone from the shore (Taniguchi et al., 2006). These conditions operate on a seasonal time scale and are significantly regulated by wet and dry seasons (Michael et al., 2005). Santos et al. (2009) reported that fresh SGD accounted for only 5% of total water inputs, but 50% of the total dissolved nitrogen inputs via SGD at a beach site in the Gulf of Mexico. Similarly, in a study in the Mediterranean, fresh groundwater was found to be the main conveyor of inorganic nitrogen to the coastal water while the saline component was nutrient-poor (Weinstein et al., 2011). Kroeger et al., (2008) estimated dissolved inorganic nitrogen from fresh terrestrial SGD was 3.5 times greater than marine source groundwater in Waquoit Bay, Massachusetts, USA. These and similar studies have focussed on defining the contribution of different groundwater sources at a regional scale in open systems (i.e., bays or open ocean), but have not focused on estuarine systems.

Groundwater can deliver both dissolved organic nutrients and dissolved inorganic nutrients which react differently in the environment. The form of nutrient (i.e. inorganic versus organic or dissolved versus particulate) delivered by groundwater may control the biological effect in the receiving coastal marine ecosystem (Seitzinger et al., 2002a). Inorganic nutrients are bioavailable and therefore consumed rapidly by phytoplankton. While organic nutrients may need to be decomposed by bacteria to become bioavailable (Kroeger et al., 2006), there is increasing evidence that algae and higher plants can directly take up organic nutrients (Bronk et al., 2007; Volkmann et al., 2016). Recent studies showed that groundwater-derived dissolved nutrient inputs have a substantial influence on primary productivity and alter the composition of phytoplankton in coastal areas (Zhang et al., 2016; Rodellas et al. 2015). However, the relative importance of organic nutrient vs. inorganic nutrient is not well understood in a SGD context.

Since coastal groundwater nutrient concentrations can be higher than in surface waters, the supply of nutrients through groundwater may influence nitrogen to phosphorus Redfield ratios (Redfield, 1934) and shift surface water typical N-limiting conditions to P-limiting (Slomp and Van Cappellen, 2004). As coastal wetlands and estuaries are drained for development, they may become more groundwater dominated and shift to P-limiting conditions (Santos et al., 2013). The subterranean estuary also plays an important role in the amount of groundwater nutrient input and N:P ratio in coastal waters. This mixing zone is biogeochemically active and can cause rapid changes in nutrient speciation and transformation (Charette and Sholkovitz, 2002). Moreover, because of chemical and biological processes in the subterranean estuary, SGD may have a different composition than the conventional simple mixing between fresh and saline groundwater (Moore et al., 2003). Additional studies in estuarine environments and subterranean estuaries are required to constrain nutrient transformations and the potential effects of nutrient inputs through groundwater discharge on N:P ratios in estuaries.

In this paper, we hypothesize that both fresh and saline SGD play a major role in delivering nutrient to estuary surface waters. We test this hypothesis by performing detailed measurements of nutrients in a tidal estuary and subterranean estuary. Our objectives were to (1) estimate surface water nutrient export from the mouth of the estuary to coastal waters under contrasting hydrological conditions (wet and dry season), (2) quantify the relative importance of meteoric deep fresh, and shallow saline groundwater-derived nutrient inputs to the estuary, and (3) determine the relative importance of groundwater in the total nutrient exports from the estuary to the coastal ocean. This paper builds on the literature by investigating the contribution of deep fresh groundwater discharge versus shallow saline groundwater discharge in the transport and transformation of nutrients in estuaries as well as investigating how groundwater may alter N:P ratios and the release of organic nutrients in surface waters. We rely on a radium mass balance reported in a companion paper to separate the fluxes of fresh and saline groundwater (Sadat-Noori et al., 2015).

2. Material and methods

2.1. Study site

Field measurements were conducted at Korogoro Creek (latitude 31.04781°, longitude 153.06492°), a small subtropical tidal estuary in New South Wales, Australia (Fig. 1A). The estuary is ~5 km long, ~20–25 m wide, has an average depth 0.9 m, and a high tide surface area of ~116×10^3 m^2. The estuary catchment size is 18 km^2 and is characterized by a low topography which is subject to flooding by seawater during spring tides. The estuary has a residence time of around 1 day and is normally flushed during each tidal cycle, with ocean water penetrating the lower 4 km of the estuary at high tide (Ruprecht and Timms 2010). The region has a mild subtropical climate with an average annual rainfall of 1490 mm. The highest (26.9 °C) and lowest (11.2 °C) mean air temperatures are experienced in January and July, respectively, whilst rainfall is highest from February to March (175.2 mm $month^{-1}$) and lowest from July to September (71 mm $month^{-1}$) (http://www.bom.gov.au). This estuary has been well studied from a hydrological (Acworth et al., 2007; Sadat-Noori et al., 2015) and biogeochemical perspective (Sanders et al., 2015; Sadat-Noori et al., 2016), but nutrient observations have not been reported before.

Two field campaigns were carried out under different hydrological conditions. In the first field campaign there was 375 mm of rain over the preceding month while in the second field campaigns there was 103 mm (Fig. 1C). Based on the rainfall events in the area, and for simplicity, the first field campaign was termed the wet season and the second the dry season. The wet season field campaign was conducted from 25-27 March, 2013, while the dry season field campaign was carried out from 6-10 June 2013 with both field campaigns being conducted around spring tide.

2.2. Surface water time series sampling

During both field campaigns, we deployed an automatic high frequency time series monitoring station at the mouth of the estuary. A calibrated Hydrolab automatic logger was used to measure pH (±0.02), salinity (±0.02), dissolved oxygen (±0.2 mg L^{-1}) and water temperature (±0.10 °C), at 15 min intervals during both sampling campaigns. An acoustic Doppler current profiler (ADCP; Sontek Argonaut) was installed in the middle of the estuary to measure current velocity and direction of flow averaged over 10 min intervals whilst depth loggers (CTD divers; Schlumberger Water Services) measured estuary depth (±0.01 m), at 10 min intervals. These ancillary data as well as radium isotope observations are reported in our companion paper (Sadat-Noori et al. 2015).

Discrete nutrient samples were collected using a sample-rinsed 60 ml polyethylene syringe every hour for about 25 h in both seasons. Samples were filtered through 0.45 µm cellulose acetate filters for later analysis of nitrate + nitrite (hereafter referred to as NO_3), ammonium (NH_4), total dissolved nitrogen (TDN), ortho-phosphate (PO_4) and total dissolved phosphorus (TDP). Samples were stored on ice immediately after sampling until returned to the laboratory where they were stored frozen until analysis.

2.3. Groundwater Sampling

During both field campaigns groundwater samples were collected at the same time as surface water sampling was under way. Shallow samples were collected using a push point piezometer system (Charette and Allen 2006) or by digging wells ranging between 0.5 and 2 m deep adjacent to the estuary near the time series station. A 2D-groundwater transect was sampled with bores up to two meters deep and at half a meter increments at low tide (Fig. 1B). The sampling started at the high tide mark and moved towards the low tide mark. The tubing for sampling was thoroughly flushed with the sample water prior to collecting each sample. A calibrated handheld YSI multiprobe was used to measure pH, temperature, DO, and salinity for each groundwater sample. Nutrient samples were collected as per surface water methods described earlier. Deep (5 to 21

m) monitoring wells installed by the NSW Office of Water located across the catchment were also sampled (Fig. 1A). A peristaltic pump was used to collect samples after the well volume was purged at least 3 times.

Groundwater discharge into the estuary surface water was divided into shallow saline and deep fresh groundwater components. We used the depth at which the sample was collected as the separating factor rather than salinity as the tidal estuary has a short resident time and therefore salinity may not truly represent the spatial groundwater distribution along the estuary. Additionally, because average radium concentrations were >70-fold higher in samples collected bellow 5 m, the 5 m mark was used as the division point. The average ^{224}Ra concentration in groundwater at each depth (above and below 5m) was used as the end-member and to estimate separate discharge rates for fresh and saline groundwater discharging in each season. We refer to estuarine surface water that recirculates through the sediments as saline groundwater.

2.4. Analytical Techniques

Dissolved nutrient analysis (NO_3, NH_4 and PO_4) was carried out colourimetrically using a Lachat Flow Injection Analyser. Total dissolved nitrogen and total dissolved phosphorus were determined using the same analysis after digestion with a di-potassium eroxodisulphate solution and the sample was autoclaved. Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were determined as the difference between the total dissolved nutrient concentration and the dissolved inorganic concentrations. Analytical errors better than 5% were determined as the average percentage coefficient of variation of triplicate samples. Additional details on method and detection limits can be found in Eyre and Ferguson (2005).

2.5. Calculations

The estuarine export (ebb tide) and import (flood tide) of nutrients were estimated by multiplying hourly surface water discharge rates by nutrient concentrations in surface waters, and then integrating hourly fluxes from high to low tide (or low to high tide). Hourly surface water discharge rates were calculated based on specific cross sectional area (adjusted for tidal height) and measured current velocity assuming homogenous currents across the channel. Fresh and saline groundwater-derived nutrient fluxes were calculated by multiplying groundwater fluxes estimated from a radium mass balance

(Sadat-Noori et al. 2015) and the median groundwater nutrient concentration. ^{224}Ra was used due to the largest concentration difference in fresh and saline groundwater samples which significantly assists in distinguishing the two sources. ^{224}Ra also has a half-life of 3.6 days which is on the same temporal scale as physical processes that drive estuarine mixing and tidally-driven groundwater discharge. Briefly, the non-steady state radium mass balance model accounted for all known sources and sinks of radium entering and leaving the system over a 24 h diel cycle. Inputs to the radium model were groundwater, upstream ^{224}Ra input flux during flood tide, diffusion from sediments, and desorption from suspended sediments while outputs consisted of ^{224}Ra downstream flux during ebb tides and the decay. Daily averages where calculated by integrating export and import rates over two tidal cycles then dividing by total time for the two tidal cycles (~25 h) to get an hourly rate, and multiplying by 24 (hours in 1 day) to estimate a daily rate. The median groundwater nutrient concentration was used due to the non-normal distribution of the groundwater endmember concentrations. Uncertainty for export rates were calculated based on the basic rules of error propagation. Standard errors are reported for concentration uncertainties.

3. Results

3.1. Surface water

Salinity followed a similar tidal trend in both seasons and ranged from 7.4 to 34.7 in the wet season and from 3.9 to 35.8 in the dry season over the 24 h time series sampling at the mouth of the estuary (Fig. 2). Radium-224 also followed a tidal trend in both seasons with the lowest concentrations being recorded at high tide. The average radium-224 concentration was 46.0 ± 6.1 and 39.3 ± 3.9 dpm $100L^{-1}$ (±SE) in the wet and dry seasons respectively (Fig. 2; Table 1). Surface water nutrient concentrations followed a distinct tidal pattern with the highest concentrations observed at low tide. The median surface water NO_3 concentrations were 0.42 and 0.62 μmol L^{-1} in the wet and dry seasons, respectively. The range of NH_4 concentrations was larger in the wet (0.68 – 6.50 μmol L^{-1}) than the dry season (0 – 4.94 μmol L^{-1}). Median DON concentrations were 17.93 and 30.62 μmol L^{-1} in wet and dry season, respectively. PO_4 concentrations ranged from 0.15 to 0.81 μmol L^{-1} in the wet season and 0.17 to 0.43 μmol L^{-1} in the dry season. DOP concentrations were similar in wet and dry season (0.35 and 0.32 μmol L^{-1}, respectively). TDN and TDP median concentrations were 1.8 and 1 fold higher in the dry season than the wet, respectively (Table 2).

NO_3 export rates in the wet season were 7 ± 2 μmol m^{-2} catchment d^{-1} and 5 ± 1 μmol m^{-2} catchment d^{-1} in the dry season. NH_4 export from estuary in the wet season (54 ± 11 μmol catchment m^{-2} d^{-1}) was 3 fold higher than in dry season (18 ± 4 μmol catchment m^{-2} d^{-1}). PO_4 export rates (3 ± 1 μmol m^{-2} catchment d^{-1}) were similar in the both season. DON, DOP, TDN and TDP exports were 120%, 45%, 56% and 36% higher in the wet season compared to the dry season (Table 2).

For both flood and ebb tides, DON was the dominant form of nitrogen (~88% flood and ~86% ebb), however during the wet season, the total TDN pool was 2 fold higher than the dry (Fig. 3). Ebb tide TDN export in the wet season (486 μmol m^{-2} catchment d^{-1}) was 1.6-fold higher than ebb tide TDN export in the dry season (293 μmol m^{-2} catchment d^{-1}) while TDN import from flood tides were higher in the dry season. The major form of nitrogen in groundwater and surface water in both seasons was DON. In the wet season fresh groundwater NO_3 inputs to estuary exceed estuary export rates indicating a loss possibly due to denitrification along the estuary mixing gradient.

3.2. Groundwater

In the wet season, the input of fresh deep groundwater-derived NO_3 (3001.4 ± 3001.4 μmol m^{-2} of estuary d^{-1}) and NH_4 (3687.1 ± 3687.1 μmol m^{-2} estuary d^{-1}) was 70 and ~3 times higher than saline shallow groundwater-derived NO_3 (43.7 ± 9.7 μmol m^{-2} estuary d^{-1}) and NH_4 (1360.4 ± 316.5 μmol m^{-2} estuary d^{-1}) (Table 2). DON derived from fresh deep groundwater was ~25 fold higher than saline shallow groundwater. The flux of fresh and saline groundwater-derived PO_4 was 180.0 ± 180.0 and 271.0 ± 56.1 μmol m^{-2} estuary d^{-1}, respectively. Groundwater-derived DOP flux from fresh groundwater was ~7 fold higher than saline groundwater-derived DOP.

In the dry season, groundwater-derived NO_3 flux from fresh and saline groundwater sources were similar (148.0 ± 328.0 and 100.5 ± 123.8 μmol m^{-2} estuary d^{-1}, respectively) while the flux of NH_4, DON, PO_4 and DOP from saline groundwater was approximately 7, 14, 10, and 2 fold higher than the fresh groundwater fluxes. In general nutrient fluxes from fresh groundwater were higher in wet season while in the dry season groundwater-derived nutrients fluxes from saline groundwater were dominant (Table 3).

Within the subterranean estuary deeper anoxic and brackish groundwater contained the highest ammonium concentrations (Fig. 4). Surface nitrate was higher than deeper samples, and higher nitrate concentrations corresponded to a small oxic area irrespective of whether these samples were saline or fresh. A high concentration DON plume was observed a meter beneath the surface directly on top of the ammonium plume. DOP concentrations were slightly higher in the samples close to surface (Fig. 4).

3.3 Nitrogen to phosphorus ratios

The ratio of nitrogen to phosphorus is an important factor controlling phytoplankton production and community composition in estuarine environments. Phytoplankton typically utilise N:P in the ratio of 16:1(Redfield, 1934). In the wet season, groundwater DIN:DIP was below the Redfield ratio. However, when both inorganic and organic forms are taken into account, the ratio falls largely around the Redfield ratio (Fig. 5). In the dry season groundwater is above Redfield ratio, calculated with both DIN:DIP and TDN:TDP. Surface water samples show clear P-limiting conditions in both seasons using either inorganic or total forms of nutrients. The average TDN:TDP ratio in Hat Head estuary surface and groundwater was 47.5 and 50.1, respectively showing P-limiting conditions. However, if only the inorganic form of nitrogen is considered, the DIN:DIP ratio would change significantly, reducing to 14.8 and 18.7 for surface and groundwater.

4. Discussion

4.1. Surface water nutrient exports

Surface water nutrient fluxes indicated that the estuary was a source of nutrients to the coastal waters in both wet and dry study periods. Higher exports rates of total dissolved nitrogen and phosphorus were observed in the wet season despite higher surface water concentrations in the dry season (Table 2). Averaged over the entire year, DIN export from the catchment was 15.3 mmol m^{-2} catchment yr^{-1}. Modelled global DIN export to the coastal ocean by rivers is reported to be 236×10^{9} mol yr^{-1} (Mayorga et al., 2010). Using the total land drainage area of all continents of 114×10^{6} km^{2} (Beusen et al. 2005; Seitzinger et al., 2002b), global riverine DIN exports per unit area to coastal waters would be 2.0 mmol m^{-2} yr^{-1} which is 7-fold lower than the DIN export observed during this study. On the continental scale, Australia DIN export from rivers to the coastal waters is estimated to be 25×10^{8} mol yr^{-1}

(Seitzinger et al., 2002b). Considering Australia's exoreic surface area (5.5 million km^{-2}; Harrison et al., 2005), Australian DIN exports rates would be 0.45 mmol m^{-2} yr^{-1} or 30 times less than the DIN export seen in this study. The reason for this high DIN export is likely due to the combination of the fertile coastal floodplain, surrounding agriculture lands, wetlands, porous sediments that could allow for significant volumes of high nutrient groundwater into the estuary, and short estuarine residence time preventing significant nutrient consumption. Wetlands are natural ecosystems that gather, transform and export inflowing nutrient-rich waters (Sánchez-Carrillo et al., 2009). Previous studies have shown wetlands to have DIN export rates of 21 mmol m^{-2} yr^{-1} (Santos et al., 2013) and 165 mmol m^{-2} yr^{-1} (Kovacic et al., 2000). As more than 70% of the Hat Head estuary catchment is wetlands, this could likely be a significant source of the high DIN export.

Hat Head estuary surface water DIP export (1.09 mmol m^{-2} catchment yr^{-1}) was >2-fold higher than the global exoreic DIP export per unit area to coastal waters delivered by rivers which is reported to be 0.46 mmol m^{-2} yr^{-1} (Mayorga et al., 2010). Surface water DIP exports from this study were approximately 21-fold greater than the DIP export rates from the Australian continent (0.05 mmol m^{-2} yr^{-1}) (Mayorga et al., 2010, Seitzinger et al., 2005). Therefore, our observations indicate the Hat Head's small catchment disproportionally contribute, to nutrient exports to the nearby ocean.

4.2. Groundwater-derived nutrient inputs: Fresh vs Saline

Groundwater was shown to be an import pathway for nitrogen and phosphorous to surface waters in Hat Heat estuary. Groundwater-derived DIN from Hat Head estuary ranged from 1.6 to 8.1 mmol m^{-2} estuary d^{-1} in dry and wet season, respectively. To put the results in perspective, we compare Hat Head with a number of studies conducted over a range of scales. Santos et al., (2008) reported similar GW-derived DIN fluxes of 6 mmol m^{-2} d^{-1} from a non-contaminated coastal plain in the Gulf of Mexico. Boehm et al. (2004) estimated GW-derived DIN fluxes of 0.7 to 12 mmol m^{-2} d^{-1} in coastal open waters located at Huntington Beach, USA. Hwang et al. (2005) reported higher fluxes of 21.4 mmol m^{-2} d^{-1} driven by high SGD rates from Bangdu Bay on Jeju Island, Korea. In smaller estuarine systems, lower GW-derived DIN fluxes of 0.33 mmol m^{-2} d^{-1} were estimated from Pettaquamscutt Estuary, USA, likely due to a smaller groundwater nutrient reservoir in the region (Kelly and Moran, 2002) while average SGD-derived NO_3 flux from Werribee Estuary, Australia was reported to be 166 mmol m^{-2} d^{-1}, 35 fold higher than our average observations (Wong, et al. 2013).

In the Hat Head estuary, the dominant form of nitrogen exported via groundwater was DON, followed by NH_4 and NO_3 from fresh groundwater, in the wet season (Table 3). Average total groundwater fluxes of NO_3, PO_4, NH_4, DON, DOP, TDN and TDP were estimated to account for 66, 58, 55, 31, 21, 53 and 47 % of surface water exports, respectively (Fig. 6). This demonstrates that groundwater can be a major source of nutrients from small estuaries to the coastal waters. The positive relationship observed between radium and nutrient species provides evidence that is consistent with the mass balance in indicating a major contribution of groundwater in delivering nutrients to the estuary (Fig. 7). Previous studies have also indicated that groundwater discharge plays an important role in delivering DIN to estuaries (Moore, 2006; Wong, et al. 2013; Porubsky et al., 2014). In a study in the upper Gulf of Thailand, groundwater-derived DIN, DIP, DON and DOP were reported to be 40-50%, 60-70%, 30-40% and 30-130% of the fluxes delivered by the Chao Phraya River into the ocean (Burnett et al., 2007). The contribution of groundwater to surface water exports increased from 4% in the wet season to 20% in the dry season (Dulaiova et al., 2006).

The relative contribution of fresh groundwater-driven nutrient export to estuary waters was highest in the wet season. This was largely due to the higher proportion of groundwater discharge from deep fresh sources in the wet season (Table 1). The higher groundwater levels during the wet season increased hydraulic head, and consequently the hydraulic gradient, which in turn would drive higher SGD fluxes (Sadat-Noori et al., 2015). In the wet season, TDN from fresh terrestrial groundwater was the main contributor (~45% of the total 52% groundwater contribution) to total TDN export from the estuary. This however changed in the dry season and saline groundwater became the dominant source of TDN (33% of the total 54% groundwater contribution) (Fig. 6). This significant contribution of saline groundwater is in contrast with findings from Weinstein et al. (2011) which indicated that the recirculated seawater component of SGD can often be relatively nutrient-poor. However, a study conducted in a Florida coastal bay, suggested significant loads of nitrogen were delivered via recirculated saline groundwater (Kroeger et al., 2007). Similarly, in a study from the north-eastern Gulf of Mexico, saline porewater was reported to contain high loads of nutrients, with the source being mineralization of marine organic matter within the subterranean estuary (Santos et al., 2009). Here, the major driver of fresh groundwater nutrient in the wet season was likely increased flux rates of SGD from increased hydraulic gradient which has the capacity to deliver deep, nutrient rich groundwaters into the estuary. In the dry season where the hydraulic head was lower, tidal pumping of recirculated seawater was the dominant groundwater nutrient source.

There are some limitations regarding our sampling strategy. We were not able to collect deep groundwater samples during the wet season, due to flooding of the overlying catchment. However, previous studies have indicated that deep groundwater has relatively stable temporal composition (Dhar et al. 2008; Santos et al., 2009; Chapagain et al. 2010), and therefore we assumed that the dry season deep groundwater concentrations were representative of wet season concentrations. In order to account for this, we have assigned a 100% uncertainty to the estimated deep GW fluxes in the wet season when propagating errors in fluxes (Table 3). Another limitation regarding our GW-derived nutrient fluxes is that we only have data from two field campaigns. Additional sampling incorporating seasonal and annual temperature differences, different terrestrially nutrient loading, and the impacts of floods on local hydrology and nutrient dynamics could also influence exports rates (Constantz et al., 1994; de Sieyes et al., 2008).

4.3. Nutrient dynamics in surface and groundwater

Nutrient speciation may change as deeper groundwater moves to surface waters (Knee et al., 2008). Surface water salinity mixing plots showed that in the wet season, NH_4 had a convex trend indicating production while NO_3 illustrated a concave trend relative to the theoretical conservative mixing line indicating consumption occurring as mixing of seawater and fresh water takes place (Fig. 7). In the dry season, conservative mixing was observed for NH_4 and NO_3 possibly due to cooler temperatures which reduce primary productivity and microbial respiration rates (Maher and Eyre 2011). The nitrate-consumption process may be caused by denitrification or dissimilatory nitrate reduction to ammonium (DNRA) (Gardner et al., 2006; Tait et al., 2014). Denitrification seems more likely due to the high nitrate and organic matter supply in Hat Head estuary. Other sources of nutrient that could account for the remaining extra nitrogen export from the estuary (difference between import at high tide and export at low tide) may be surface water runoff, nitrogen fixation or resuspension. Phosphate showed conservative mixing in the wet season while production was seen in the dry season similar to DOP (Fig. 7).

Groundwater nutrient salinity mixing plots did not show simple trends which may be masked by the spatial variability in GW nutrient concentration (Fig. 8) as observed before (Santos et al., 2009). However, the 2D transect observations shows much clearer trends (Fig. 4). As deep NH_4 laden groundwater, moves through the subterranean estuary (the brackish zone) to the surface, it undergoes nitrification to NO_3 when sufficient dissolved oxygen is available. At this point of nitrification, there is also significant DON production arising from the breakdown of microbial matter. This may partially explain the large DON exports from the estuary. As estuarine waters are recirculated through sediments, the produced NO_3 and DON would be discharged into the surface waters. Similar subterranean estuary dynamics were observed by Kroeger et al., (2008) and Erler et al., (2014) where local organic matter produced NH_4 in the deeper anoxic groundwater and a NO_3 rich brackish water plume was located in shallow groundwaters a meter below the surface. Erler et al. (2014) also used N isotopes to show that the loss of NH_4 through nitrification increased towards the surface and reduced NH_4 concentrations by up to 80%.

Previous studies have suggested that DON may be enriched in groundwater relative to surface waters (Kim et al., 2013; Santos et al., 2013; Santos et al., 2014). Here, groundwater nitrogen was dominated by DON, accounting for 66 and 85% of TDN in groundwater in the wet and dry season, respectively. The fraction of DON in surface water was ~88% of TDN in both the wet and dry seasons. The reason for the high DON concentrations observed in surface waters is likely due to DON-rich groundwater inputs as supported by the positive correlation between radium-224 and DON concentrations (Fig 7). Additionally, the production of DON in the mid subterranean estuary delivered by both fresh and recirculated groundwater sources contributes to high DON concentrations.

4.4. N:P ratios

Average TDN:TDP ratio in the dry season was 144 ± 35 (SE) in saline groundwaters indicating P-limited conditions while it was 16 ± 1 (SE) in the fresh groundwaters. This shows the potential role saline groundwater can play in shifting N:P ratios. Surface water N:P ratios indicated that when organic nutrients are included, the estuary is P-limited on both ebb and flood tide however not at low tide (Fig. 9). Alternatively, when ratios are calculated using only inorganic nutrients, the estuary was P-limited during flood tides and N-limited on ebb tides during the wet season. In the dry season, surface water was N-limited on both ebb and flood tides but not at direct low tide. This suggests that groundwater discharge of inorganic nitrogen in the wet season (as illustrated in Fig. 6) may change the estuary to P limitation. The significant correlations between the groundwater tracer ^{224}Ra and N:P ratios (Fig. 7) further supports the notion that groundwater discharge can increase the N:P ratios of estuary surface waters providing multiple lines of evidence that groundwater exerts a strong control over surface water nutrient ratios as also observed in a mangrove creek (Gleeson et al., 2013).

Hwang et al., (2005) reported high DIN:DIP ratios (96–193) in groundwater and suggested a large DIN:DIP imbalance can affect the ecosystem of coastal seawater. Santos et al., (2013) showed that a post-flood groundwater seepage in a coastal floodplain can shift the system from a DON to a DIN-dominated system and groundwater inputs doubled the N:P ratio in surface waters. Groundwater discharge was also reported to drive high N:P ratios in two estuaries in New Zealand (Santos et al., 2014). The common conception that TDN loads which have high DIN:DON ratios can create favourable conditions for eutrophication rather than TDN loads with less DIN may not be the case in estuaries. Previous studies have showed that DON uptake can rival DIN in some cases and that DON can play a major role in eutrophication (Bronk et al., 1998; Antia et al., 1991). Some recent studies have suggested that DON provides an alternative to DIN as a nitrogen source that allows the successful growth of macrophytes (Mozdzer et al., 2010; Volkmann et al., 2016).

Previous studies have used either inorganic or total dissolved forms of nutrient to calculate N:P ratios (Santos et al., 2014, Slomp and Van Cappellen, 2004) with little discussion on whether N:P ratios should be based on inorganic or total nutrients. For example TDN:TDP may be preferred over DIN:DIP for calculating N:P ratios as total concentrations provide analytically robust estimates of bioavailable N and P, and TDN is considered the analogue of TDP and its use (Zirino et al., 2016; Lomas et al., 2009). Other studies have used DIN:DIP ratios (Kim et al., 2003; Murrel et al., 2007; Wang et al., 2015). Here significantly lower N:P ratios were observed when only inorganic nutrients were used to calculate N:P ratios. Therefore, not including organic nutrient in N:P ratios may lead to an underestimation in the potential limitation of primary production by nitrogen. Moreover, the groundwater-derived DON dominates the estuaries surface water at ebb tide in both wet and dry conditions (Fig. 3), and some portion of particulate phosphorus in the estuary can become bioavailable. Both processes drive high productivity, suggesting TDN:TDP is a more useful index for calculating N:P ratios in the estuary investigated.

5. Conclusion

We estimated both fresh terrestrial groundwater and saline groundwater nutrient fluxes into a tidal estuary and the relative contribution of groundwater to surface water exports to the coastal ocean. Average nutrient fluxes over the study period showed that the estuary was a source of nutrient to the coastal waters. DIN exports were 7-fold higher than the global flux rate estimate for rivers and 30 times more than Australian surface water averages.

Groundwater discharge accounted for up to 53% of TDN and 47% of TDP export from the estuary to the coastal waters. Fresh groundwater accounted for 45% of the TDN and 48% of the TDP export and was the dominant source of nutrient in the wet season while saline groundwater accounted for 32% of TDN export in the dry season. High fluxes of groundwater nitrogen were found to be a major regulator of the observed N:P ratios.

Groundwater entering estuarine surface waters can significantly affect the chemistry and biology of the surface water over short time scales creating a highly dynamic aquatic system. Phytoplankton's are important primary producers in coastal waters that can respond rapidly to changes in the environment. Here we show groundwater has the ability to deliver large amount of both inorganic and organic nutrients to estuarine waters. Since coastal phytoplankton community composition is often moderated by DIN availability, groundwater can play a key role in potential shifts in phytoplankton community in estuaries and the nearby coastal ocean. Our observations imply that strategies to manage eutrophication on coastal waters scale should address both groundwater and surface water sources. Small groundwater dominated estuaries can export significantly more nutrients per unit area than larger river systems.

Acknowledgements

We would like to thank Christian Sanders, Luciana Sanders, Paul Macklin, Ashley McMahon, Jennifer Taylor and Benjamin Stewart for their support during field campaigns. IRS and DTM are funded through Australian Research Council DECRA Fellowships (DE140101733 and DE150100581). We acknowledge support from the Australian Research Council (DP120101645 and LE120100156).

References

Acworth, R.I., Hughes, C.E. and Turner, I.L., 2007. A radioisotope tracer investigation to determine the direction of groundwater movement adjacent to a tidal creek during spring and neap tides. Hydrogeology Journal, 15(2), 281-296.

Antia, N.J., Harrison, P.J. and Oliveira, L., 1991. The role of dissolved organic nitrogen in phytoplankton nutrition cell biology and ecology. Phycologia, 30(1), 1-89.

Bernard, R.J., Mortazavi, B., Wang, L., Ortmann, A.C., MacIntyre, H. and Burnett, W.C., 2014. Benthic nutrient fluxes and limited denitrification in a sub-tropical groundwater-influenced coastal lagoon. Marine Ecology Progress Series, 504,13-26.

Beusen, A. H. W., Dekkers, A. L. M., Bouwman, A. F., Ludwig, W., Harrison, J. 2005. Estimation of global river transport of sediments and associated particulate C, N, and P, Global Biogeochemical Cycles, 19, GB4S05, doi:10.1029/2005GB002453.

Billerbeck, M., Werner, U., Bosselmann, K., Walpersdorf, E., Huettel, M., 2006. Nutrient release from an exposed intertidal sand flat. Marine Ecology Progress Series, 316, 35-51.
Boehm, A. B, Shellenbarger G. G, Paytan, A. 2004. Groundwater discharge: potential association with fecal indicator bacteria in the surf zone. Environmental Science and Technology, 38, 3558–3566.
Borges, A. V. & Abril, G. in Treatise on estuarine and coastal science. Vol. 5 (eds E. Wolanski & D. S. McLusky) 119-161 (Academic Press, 2011).
Bronk, D.A., Glibert, P.M., Malone, T.C., Banahan, S. and Sahlsten, E., 1998. Inorganic and organic nitrogen cycling in Chesapeake Bay: autotrophic versus heterotrophic processes and relationships to carbon flux. Aquatic Microbial Ecology, 15(2), 177-189.
Bronk, D.A., See, J.H., Bradley, P. and Killberg, L., 2007. DON as a source of bioavailable nitrogen for phytoplankton. Biogeosciences, 4(3), 283-296.
Burnett, W. C., et al. 2006. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. The Science of the Total Environment, 367: 498-543.
Burnett, W.C., Dulaiova, H., 2003. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. Journal of Environmental Radioactivity, 69, 21-35.
Burnett, W.C., Wattayakorn, G., Taniguchi, M., Dulaiova, H., Sojisuporn, P., Rungsupa, S. and Ishitobi, T., 2007. Groundwater-derived nutrient inputs to the Upper Gulf of Thailand. Continental Shelf Research, 27(2), 176-190.
Chapagain, S.K., V.P. Pandey, S. Shrestha, T. Nakamura, and F. Kazama. 2010. Assessment of deep groundwater quality in Kathmandu valley using multivariate statistical techniques. Water, Air, and Soil Pollution, 210: 277-288.
Charette, M.A., and M.C. Allen. 2006. Precision ground water sampling in coastal aquifers using a direct - push, Shielded - Screen Well - Point System. Groundwater Monitoring & Remediation, 26: 87-93.
Charette, M.A., Sholkovitz, E.R., 2002. Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. Geophysical Research Letters, 29 (10).
Constantz, J., C.L. Thomas, and G. Zellweger. 1994. Influence of diurnal variations in stream temperature on streamflow loss and groundwater recharge. Water Resources Research, 30: 3253-3264.
de Sieyes, N.R., K.M. Yamahara, B.A. Layton, E.H. Joyce, and A.B. Boehm. 2008. Submarine discharge of nutrient-enriched fresh groundwater at Stinson Beach, California is enhanced during neap tides. Limnology and Oceanography, 53: 1434-1445.
Delgado-Baquerizo, M., Maestre, F. T., Gallardo, A., Eldridge, D. J., Soliveres, S., Bowker, M. A., Prado-Comesaña, A., Gaitán, J., Quero, J. L., et al. 2016. Human impacts and aridity differentially alter soil N availability in drylands worldwide. Global Ecology and Biogeography, 25, 36–45.
Dhar, R.K., Y. Zhenga, A. van Geen, Z. Cheng, M. Shanewaz, M. Shamsudduha, M.A. Hoque, M.W. Rahman, and K.M. Ahmed. 2008. Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihazar, Bangladesh. Journal of Contaminant Hydrology, 99: 97-111.
Dulaiova, H., Burnett, W.C., Wattayakorn, G., Sojisuporn, P., 2006. Are groundwater inputs into river-dominated areas important? The Chao Phraya River-Gulf of Thailand. Limnology and Oceanography 51, 2232-2247.
Dumont, E., Harrison, J. A., Kroeze, C., Bakker, E. J., Seitzinger, S. P. 2005. Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: Results from a spatially

explicit, global model, Global Biogeochemical Cycles, 19, GB4S02, doi:10.1029/2005GB002488.

Erler, D.V., Santos, I.R., Zhang, Y., Tait, D.R., Befus, K.M., Hidden, A., Li, L. and Eyre, B.D., 2014. Nitrogen transformations within a tropical subterranean estuary. Marine Chemistry, 164, 38-47.

Eyre, B.D. and Ferguson, A.J., 2005. Benthic metabolism and nitrogen cycling in a subtropical east Australian estuary(Brunswick): Temporal variability and controlling factors. Limnology and Oceanography, 50(1), 81-96.

Gardner, W.S., McCarthy, M.J., An, S., Sobolev, D., Sell, K.S. and Brock, D., 2006. Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries. Limnology and Oceanography, 51, 558-568.

Gleeson, J., Santos, I. R., Maher, D. T. & Golsby-Smith, L. 2013. Groundwater-surface water exchange in a mangrove tidal creek: Evidence from natural geochemical tracers and implications for nutrient budgets. Marine Chemistry, 156, 27-37, doi:dx.doi.org/10.1016/j.marchem.2013.02.001.

Harrison, J. A., Caraco, N. F., Seitzinger, S. P. 2005. Global patterns and sources of dissolved organic matter export to the coastal zone: Results from a spatially explicit, global model, Global Biogeochemical Cycles, 19, GB4S04, doi:10.1029/2005GB002480.

Hwang, D. W, Lee, Y. W, Kim, G., 2005. Large submarine groundwater discharge and benthic eutrophication in Bangdu Bay on volcanic Jeju Island, Korea. Limnology and Oceanography, 50, 1393–1403.

Kelly, R. P., and Moran, S. B. 2002. Seasonal changes in groundwater input to a well-mixed estuary estimated using radium isotopes and implications for coastal nutrient budgets. Limnology and Oceanography, 47, 1796–1807

Kim, G. and Swarzenski, P.W., 2010. Submarine groundwater discharge (SGD) and associated nutrient fluxes to the coastal ocean. In carbon and nutrient fluxes in continental margins, 529-538. Springer Berlin Heidelberg.

Kim, T. H., Kwon, E., Kim, I., Lee, S.-A., Kim, G., 2013. Dissolved organic matter in the subterranean estuary of a volcanic island, Jeju: importance of dissolved organic nitrogen fluxes to the ocean. Journal of Sea Research, 78, 18–24.

Knee, K., L., Layton, B., A., Street, J., H., Boehm, A., B., Paytan, A. 2008. Sources of nutrients and fecal indicator bacteria to near shore waters on the north shore of Kauaì (Hawaiì, USA). Estuaries and Coasts 31: 607–622.

Kovacic, D.A., David, M.B., Gentry, L.E., Starks, K.M. and Cooke, R.A., 2000. Effectiveness of constructed wetlands in reducing nitrogen and phosphorus export from agricultural tile drainage. Journal of Environmental Quality, 29(4), 1262-1274.

Kroeger, K. D. Swarzenski, P. W. Greenwood, W. J. Reich, C. 2007. Submarine groundwater discharge to Tampa Bay: Nutrient fluxes and biogeochemistry of the coastal aquifer. Marine Chemistry.104, 85– 97.

Kroeger, K.D. and Charette, M.A., 2008. Nitrogen biogeochemistry of submarine groundwater discharge. Limnology and Oceanography, 53(3), 1025.

Kroeger, K.D., Cole, M., L., Valiela, I. 2006. Groundwater transported dissolved organic nitrogen exports from coastal water sheds. Limnology and Oceanography 51: 2248–2261.

Lomas, M.W., Burke, A.L., Lomas, D.A., Bell, D.W., Shen, C., Dyhrman, S.T. and Ammerman, J.W., 2010. Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP). Biogeosciences Discussions, 6(5), 10137.

Maher, D. & Eyre, B. D. 2011. Benthic carbon metabolism in southeast Australian estuaries: habitat importance, driving forces, and application of artificial neural network models. Marine Ecology-Progress Series 439, 97-115, doi:10.3354/meps09336.

Maher, D. & Eyre, B. D. 2012. Carbon budgets for three autotrophic Australian estuaries: Implications for global estimates of the coastal air-water CO2 flux. Global Biogeochemical Cycles 26, GB1032, doi:10.1029/2011GB004075.

Mayorga, E., Seitzinger, S.P., Harrison, J.A., Dumont, E., Beusen, A.H., Bouwman, A.F., Fekete, B.M., Kroeze, C. and Van Drecht, G., 2010. Global nutrient export from WaterSheds 2 (NEWS 2): model development and implementation. Environmental Modelling & Software, 25(7), 837-853.

Michael, H.A., Mulligan, A.E. and Harvey, C.F., 2005. Seasonal oscillations in water exchange between aquifers and the coastal ocean. Nature, 436 (7054), 1145-1148.

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

Moore, W.S., 2010. The effect of submarine groundwater discharge on the ocean. Annual Review of Marine Science, 2, 59-88.

Moore, W.S., Blanton, J.O. and Joye, S.B., 2006. Estimates of flushing times, submarine groundwater discharge, and nutrient fluxes to Okatee Estuary, South Carolina. Journal of Geophysical Research: Oceans, 111(C9).

Mozdzer, T.J., Zieman, J.C. and McGlathery, K.J., 2010. Nitrogen uptake by native and invasive temperate coastal macrophytes: importance of dissolved organic nitrogen. Estuaries and Coasts, 33(3), 784-797.

Murrell, M.C., Hagy, J.D., Lores, E.M. and Greene, R.M., 2007. Phytoplankton production and nutrient distributions in a subtropical estuary: importance of freshwater flow. Estuaries and Coasts, 30(3), 390-402.

Porubsky, W.P., Weston, N.B., Moore, W.S., Ruppel, C. and Joye, S.B., 2014. Dynamics of submarine groundwater discharge and associated fluxes of dissolved nutrients, carbon, and trace gases to the coastal zone (Okatee River estuary, South Carolina). Geochimica et Cosmochimica Acta, 131, 81-97.

Redfield, A.C. 1934. On the proportions of organic derivatives in seawater and their relation to the composition of plankton. In James Johnson memorial volume, ed. R.J. Daniel, 177–192. Liverpool: Liverpool Univ. Press.

Rodellas, V., Garcia-Orellanaa, J., Masquéa, P., Feldmane, M., Weinsteine, Y. 2015. Submarine groundwater discharge as a major source of nutrients to the Mediterranean Sea. Proceedings of the National Academy of Sciences, 112.13, 3926-3930.

Ruprecht, J.E., Timms, W.A., 2010. Hat Head Effluent Disposal Scheme ‑ Ongoing Monitoring Results to September 2010. WRL Technical Report 2010/31.

Sadat-Noori M., Maher D. T. Santos I. R. 2016. Groundwater Discharge as a Source of Dissolved Carbon and Greenhouse Gases in a Subtropical Estuary. Estuaries and Coasts, 39, 639-656.

Sadat-Noori, M., I. Santos, D. Maher, C. Sanders, and L. Sanders. 2015. Groundwater discharge into an estuary using spatially distributed radon time series and radium isotopes. Journal of Hydrology, 528, 703‑719.

Sánchez-Carrillo, S., Sánchez-Andrés, R., Alatorre, L.C., Angeler, D.G., Álvarez-Cobelas, M. and Arreola-Lizárraga, J.A., 2009. Nutrient fluxes in a semi-arid microtidal mangrove wetland in the Gulf of California. Estuarine, Coastal and Shelf Science, 82(4), 654-662.

Sanders, C.J., Santos, I.R., Maher, D.T., Sadat-Noori, M., Schnetger, B. and Brumsack, H.J., 2015. Dissolved iron exports from an estuary surrounded by coastal wetlands: can small estuaries be a significant source of Fe to the ocean? Marine Chemistry, 176, 75-82.

Santos, I. R., Bryan, K. R., Pilditch, C. A., Tait, D. R., 2014. Influence of porewater exchange on nutrient dynamics in two New Zealand estuarine intertidal flat. Marine Chemistry, 167, 57–70.

Santos, I., R., Burnett, W., C., Dittmar, T., Suryaputra, I., G., N., A., Chanton, J. 2009. Tidal pumping drives nutrient and dissolved organic matter dynamics in a Gulf of Mexico subterranean estuary. Geochimica et Cosmochimica Acta, 73, 1325–1339.

Santos, I.R., Beck, M., Brumsack, H.-J., Maher, D.T., Dittmar, T., Waska, H., Schnetger, B., 2015. Porewater exchange as a driver of carbon dynamics across a terrestrial-marine transect: Insights from coupled ^{222}Rn and $p$$CO_2$ observations in the German Wadden Sea. Marine Chemistry 171, 10-20.

Santos, I.R., Cook, P.L.M., Rogers, L., de Weys, J., Eyre, B.D., 2012. The “salt wedge pump”: convection-driven pore-water exchange as a source of dissolved organic and inorganic carbon and nitrogen to an estuary. Limnology and Oceanography, 57, 1415‐1426.

Santos, I.R., de Weys, J., Tait, D.R., Eyre, B.D., 2013. The contribution of groundwater discharge to nutrient exports from a coastal catchment: post-flood seepage increases estuarine N/P ratios. Estuaries and Coast 36, 56‐73.

Santos, I.R., et al., 2008. Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. Limnology and Oceanography, 53 (2), 705–718.

Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., Bouwman, A. F., 2005. Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application, Global Biogeochemical Cycles, 19, GB4S01, doi:10.1029/2005GB002606.

Seitzinger, S. P., Kroeze, C., Bouwman, A. F., Caraco, N., Dentener, F., Styler, R. V., 2002b. Global Patterns of Dissolved Inorganic and Particulate Nitrogen Inputs to Coastal Systems: Recent Conditions and Future Projections. Estuaries, 2, 640–655.

Seitzinger, S. P., R. W. Sanders, and R. V. Styles. 2002a. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. Limnology and Oceanography, 47,353–366.

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

Su, N., Burnett, W.C., Macintyre, H.L., Liefer, J.D., Peterson, R.N., Viso, R., 2014. Natural radon and radium isotopes for assessing groundwater discharge into Little Lagoon, AL: implications for Harmful Algal Blooms. Estuaries and Coast, 37, 893‐910.

Sugimoto, R., Honda, H., Kobayashi, S., Takao, Y., Tahara, D., Tominaga, O., Taniguchi, M. 2015. Seasonal Changes in Submarine Groundwater Discharge and Associated Nutrient Transport into a Tideless Semi-enclosed Embayment (Obama Bay, Japan). Estuaries and Coasts, DOI: 10.1007/s12237-015-9986-7

Tait, D.R., Erler, D.V., Santos, I.R., Cyronak, T.J., Morgenstern, U., Eyre, B.D., 2014. The influence of groundwater inputs and age on nutrient dynamics in a coral reef lagoon. Marine Chemistry, 166, 36-47.

Taniguchi, M., Ishitobi, T. and Shimada, J., 2006. Dynamics of submarine groundwater discharge and freshwater/seawater interface. Journal of Geophysical Research: Oceans, 111(C1).

Urquidi-Gaume, M. Santos, I. R. Lechuga-Deveze, C. 2016. Submarine groundwater discharge as a source of dissolved nutrients to an arid coastal embayment (La Paz, Mexico). Environmental Earth Sciences, 75:154

Volkmann, C., Halbedel, S., Voss, M. and Schubert, H., 2016. The role of dissolved organic and inorganic nitrogen for growth of macrophytes in coastal waters of the Baltic Sea. Journal of Experimental Marine Biology and Ecology, 477, 23-30.

Wang, J., Yan, W., Chen, N., Li, X. and Liu, L., 2015. Modeled long-term changes of DIN: DIP ratio in the Changjiang River in relation to Chl-α and DO concentrations in adjacent estuary. Estuarine, Coastal and Shelf Science, 166, 153-160.

Weinstein, Y., Yechieli, Y., Shalem, Y., Burnett, W., C., Swarzenski, P., W., Herut, B. 2011. What Is the Role of Fresh Groundwater and Recirculated Seawater in Conveying Nutrients to the Coastal Ocean? Environmental science & technology, 45(12), 5195-5200.

Wong, W.W., Grace, M.R., Cartwright, I., Cardenas, M.B., Zamora, P.B. and Cook, P.L., 2013. Dynamics of groundwater-derived nitrate and nitrous oxide in a tidal estuary from radon mass balance modelling. Limnology and Oceanography, 58(5), 1689-1706.

Zhang, Y., Li, H., Wang, X., Zheng, C., Wang, C., Xiao, K., Wan, L., Wang, X., Jiang, X., Guo, H. 2016. Estimation of submarine groundwater discharge and associated nutrient fluxes in eastern Laizhou Bay, China using 222Rn. Journal of Hydrology, 533, 103–113.

Zirino, A., Elwany, H., Facca, C., Neira, C. and Mendoza, G., 2016. Nitrogen to phosphorus ratio in the Venice (Italy) lagoon (2001–2010) and its relation to macroalgae. Marine Chemistry. 180, 33-41.

Table 1. A summary of the key hydrological variables in wet and dry seasons.

Hydrological variables	Wet Season	Dry Season
Salinity range	7.4 − 34.7	3.9 − 37.8
Rainfall (mm) - over preceding month	375	103
Surface water discharge (m^3 s^{-1})	3.0	2.3
Fresh GW discharge (m^3 s^{-1})	0.71±0.25	0.04±0.01
Saline GW discharge (m^3 s^{-1})	0.33±0.09	0.19±0.23

Table 2. Surface water nutrient concentrations, estuary-wide and catchment nutrient export. Uncertainty was calculated following on the basic rules of error propagation.

	Wet			Dry			Average	
	Median Conc. (μmol L^{-1})	Surface water export from estuary (μmol m^{-2} estuary d^{-1})	Surface water export from catchment (μmol m^{-2} catchment d^{-1})	Median Conc. (μmol L^{-1})	Surface water export (μmol m^{-2} estuary d^{-1})	Surface water export from catchment (μmol m^{-2} catchment d^{-1})	Surface water export (μmol m^{-2} estuary d^{-1})	Surface water export from catchment (μmol m^{-2} catchment d^{-1})
NO_3	0.42	1053±211	7±2	0.62	758±152	5±1	905±182	6±1
NH_4	3.08	8395±1679	54±11	3.15	2741±548	18±4	5568±1114	36±7
DON	17.93	55479±11096	358±72	30.62	2502±5005	161±32	40252±8050	260±52
TDN	19.57	64927±12985	419±84	35.75	28525±5705	184±37	46726±9345	302±60
PO_4	0.20	490±98	3±1	0.31	399±79	3±1	443±89	3±1
DOP	0.35	871±174	6±1	0.32	473±94	3±1	672±134	4±1
TDP	0.55	1361±272	9±2	0.63	868±174	6±1	1115±223	7±2

Note that TDN may not exactly equal DIN+DON as median values are used.

Table 3. Groundwater-derived nutrient fluxes based on the area of the estuary (µmol m^{-2} estuary d^{-1}). Fresh and saline groundwater discharge rates were calculated using a radium mass balance as described in Sadat-Noori et al. (2015). Uncertainty was calculated following on the basic rules of error propagation.

	Wet		Dry	
	Median Conc. (µmol L^{-1})	GW input (µmol m^{-2} estuary d^{-1})	Median Conc. (µmol L^{-1})	GW input (µmol m^{-2} estuary d^{-1})
		Saline		
SGD (m^3 s^{-1})		0.33±0.09		0.19±0.23
NO_3	0.18±1.28	43.7±9.7	0.71±0.87	100.5±123.8
NH_4	5.54±0.85	1360.4±316.5	8.46±6.13	1195.1±1110.3
DON	11.49±0.97	516.6±109.7	62.85±26.46	8881.8±8024.4
TDN	18.30±1.74	4492.6±965.4	66.48±31.83	9395.3±8487.9
PO_4	1.10±0.06	271.0±56.1	0.62±0.73	88.3±80.9
DOP	0.15±0.05	38.0±11.3	0.20±0.16	28.8±31.6
TDP	1.21±0.08	296.6±61.8	0.53±0.47	74.8±587.4
		Fresh		
SGD (m^3 s^{-1})		0.71±0.25		0.04±0.01
NO_3	5.68±2.07	3001.4±3001.4	5.68±2.07	148.0±328.0
NH_4	6.98±4.98	3687.1±3687.1	6.98±4.98	181.8±112.0
DON	23.98±13.61	12663.7±12663.7	23.98±13.61	624.3±493.4
TDN	55.17±38.77	29135.5±29135.5	55.17±38.77	5984.8±3300.2
PO_4	0.34±0.48	180.0±180.0	0.34±0.48	8.9±35.4
DOP	0.47±0.19	250.4±250.4	0.47±0.19	12.3±9.8
TDP	1.24±1.47	654.0±654.0	1.24±1.47	134.3±526.4
		Total		
SGD (m^3 s^{-1})		1.0±0.3		0.2±0.2
NO_3		3045.1±743.8		248.4±61.1
NH_4		5047.5±3204.6		1376.9±338.9
DON		13180.3±5498.7		9506.1±2339.9
TDN		33628.1±8948.5		15380.2±3785.9
PO4		451.0±740.5		97.2±23.9
DOP		288.4±182.8		41.2±10.1
TDP		950.6±2591.5		209.1±24.6

Estuary area 116,160 m^2; catchment area 18 km^2.

Figure 1. A Map of the study area (Hat Head, NSW). Red points indicate groundwater sampling locations and blue point shows surface water sampling area. Inset C shows rainfall events occurred at Hat Head in 2013. Image modified from Sadat-Noori et al. (2015).

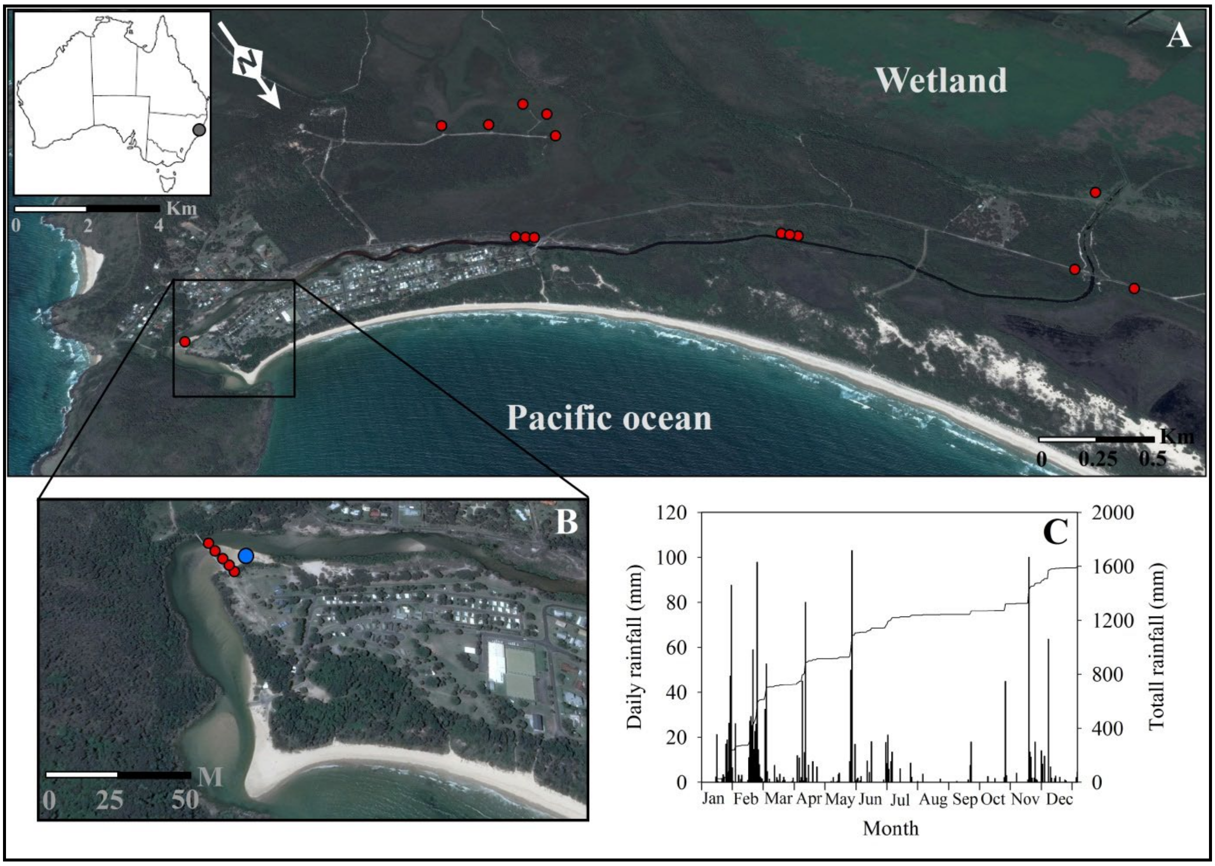


Figure 2. Surface water depth (m), salinity, nutrient concentration (µmol L^{-1}) and radium (dpm $100L^{-1}$) time series at Hat Head Estuary, during the wet and dry seasons. Ancillary data originally reported in Sadat-Noori et al. (2015).

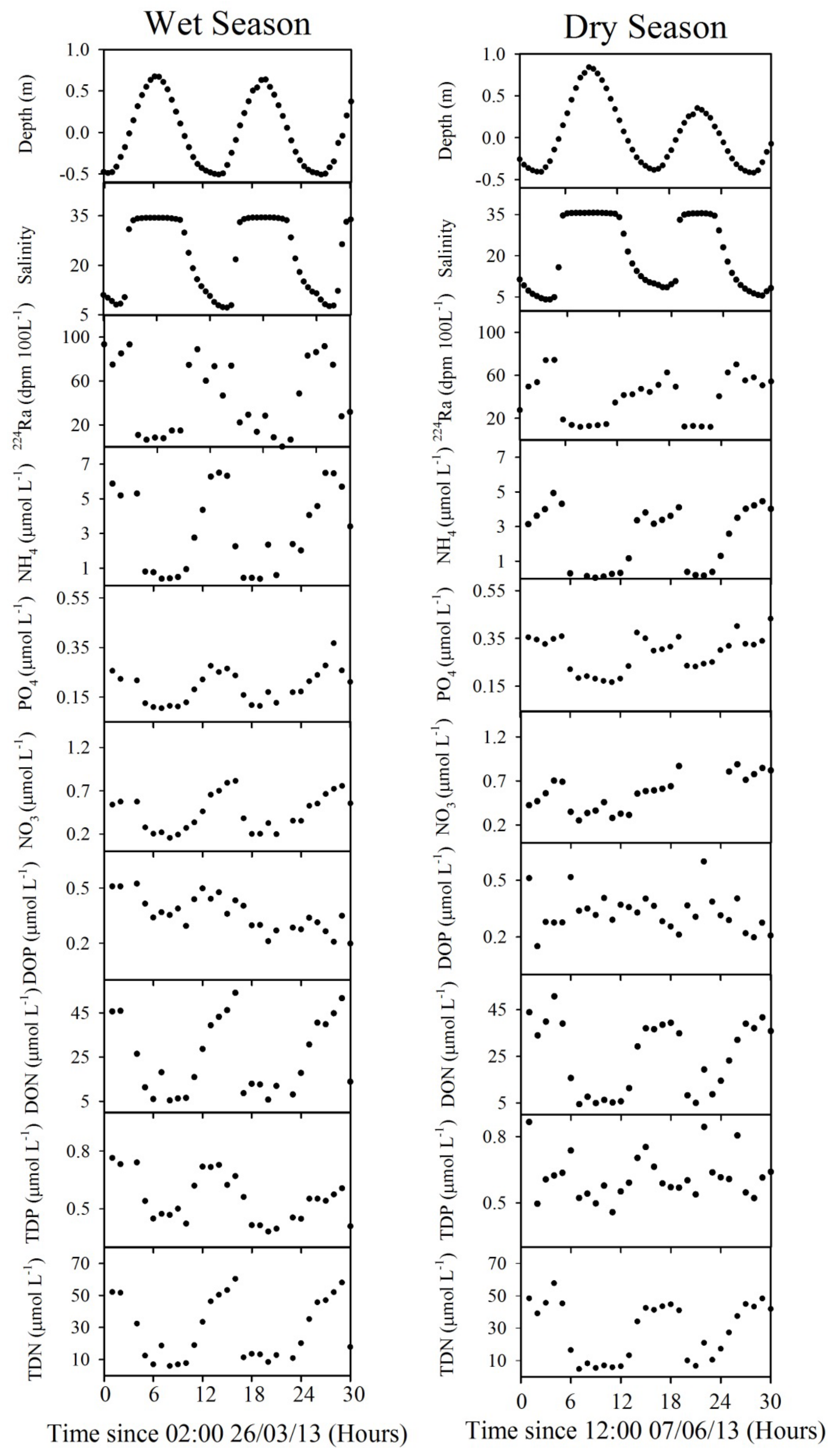


Figure 3. Pie charts showing the relative contribution of the different nitrogen species to the TDN pool in surface and groundwater in wet and dry seasons. Flood and ebb pie chart are based on export rates. TDN import and export rates are in units of µmol m^{-2} catchment d^{-1}.

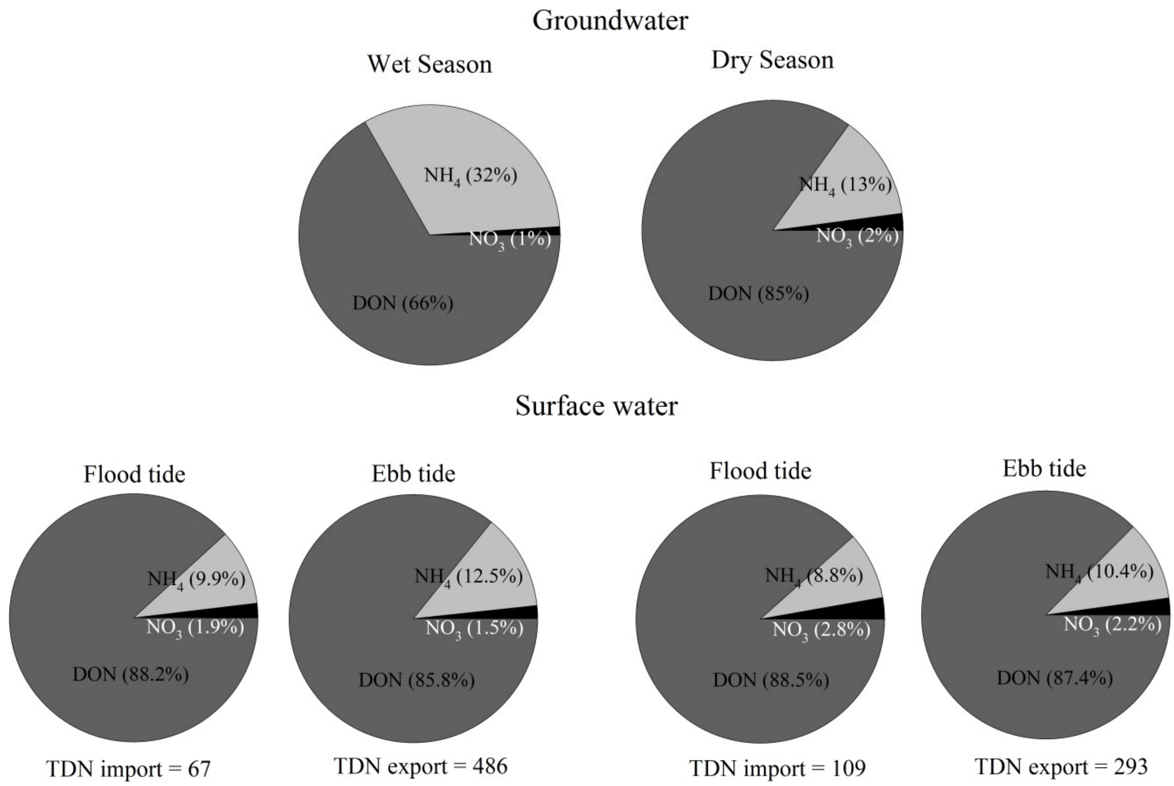


Figure 4. A groundwater 2D nutrient transect sampled in the wet season at low tide.

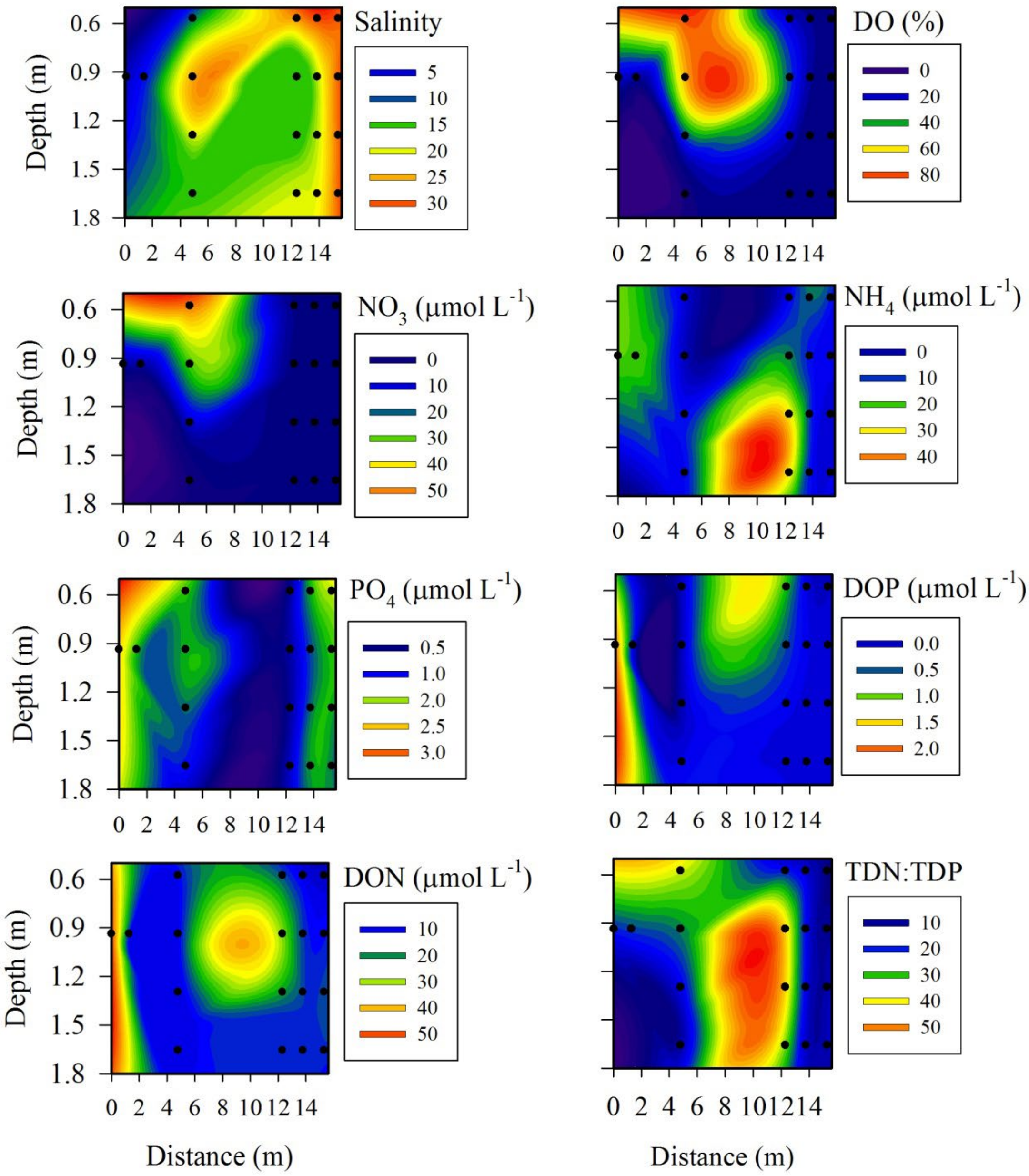


Figure 5. Groundwater and surface water DIN:DIP and TDN:TDP plots in wet and dry seasons. The dashed line indicates the Redfield Ratio.

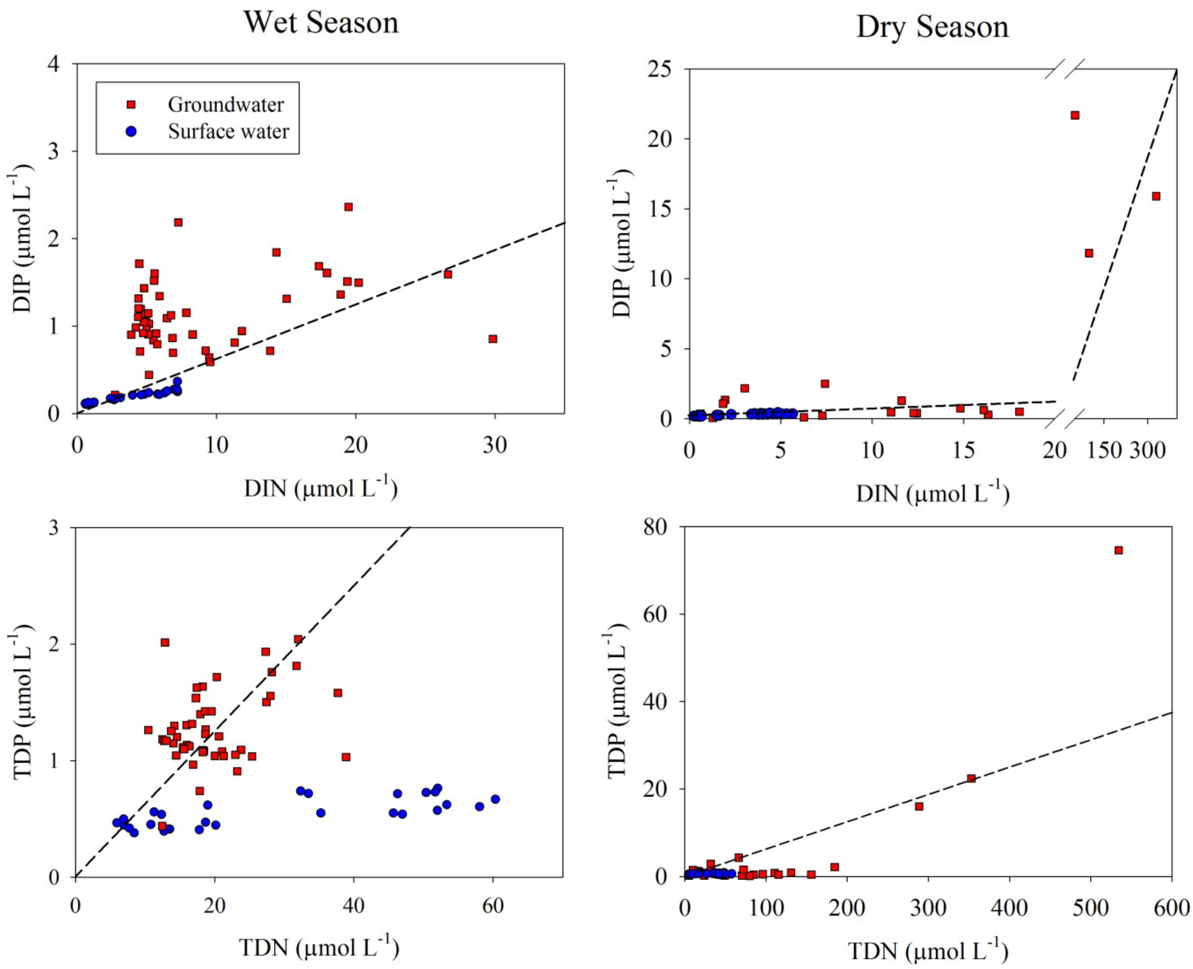


Figure 6. The contribution of groundwater-derived nutrient to total estuary nutrient export in wet and dry seasons (upper plots), and export rates for estuary surface water, fresh GW and saline GW in both seasons (lower plots). Note that export scale is in log scale.

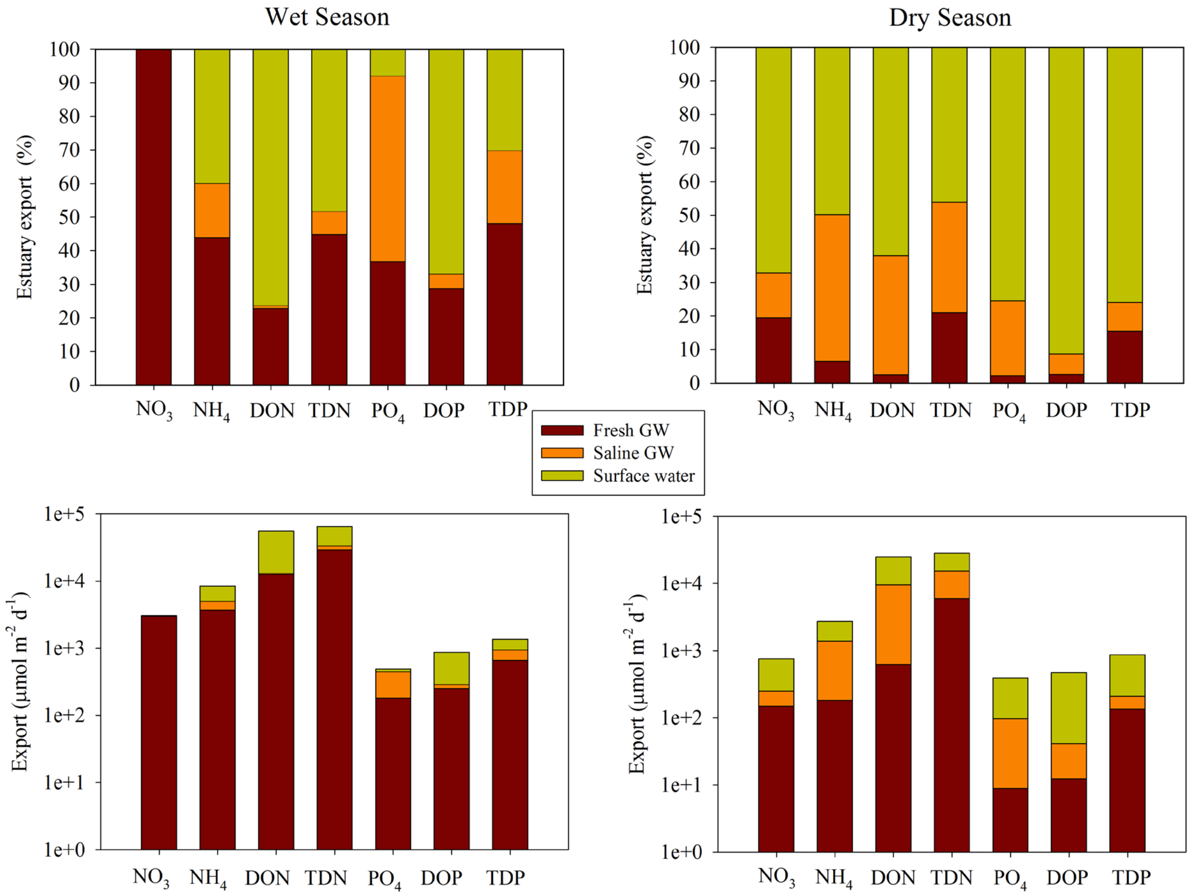
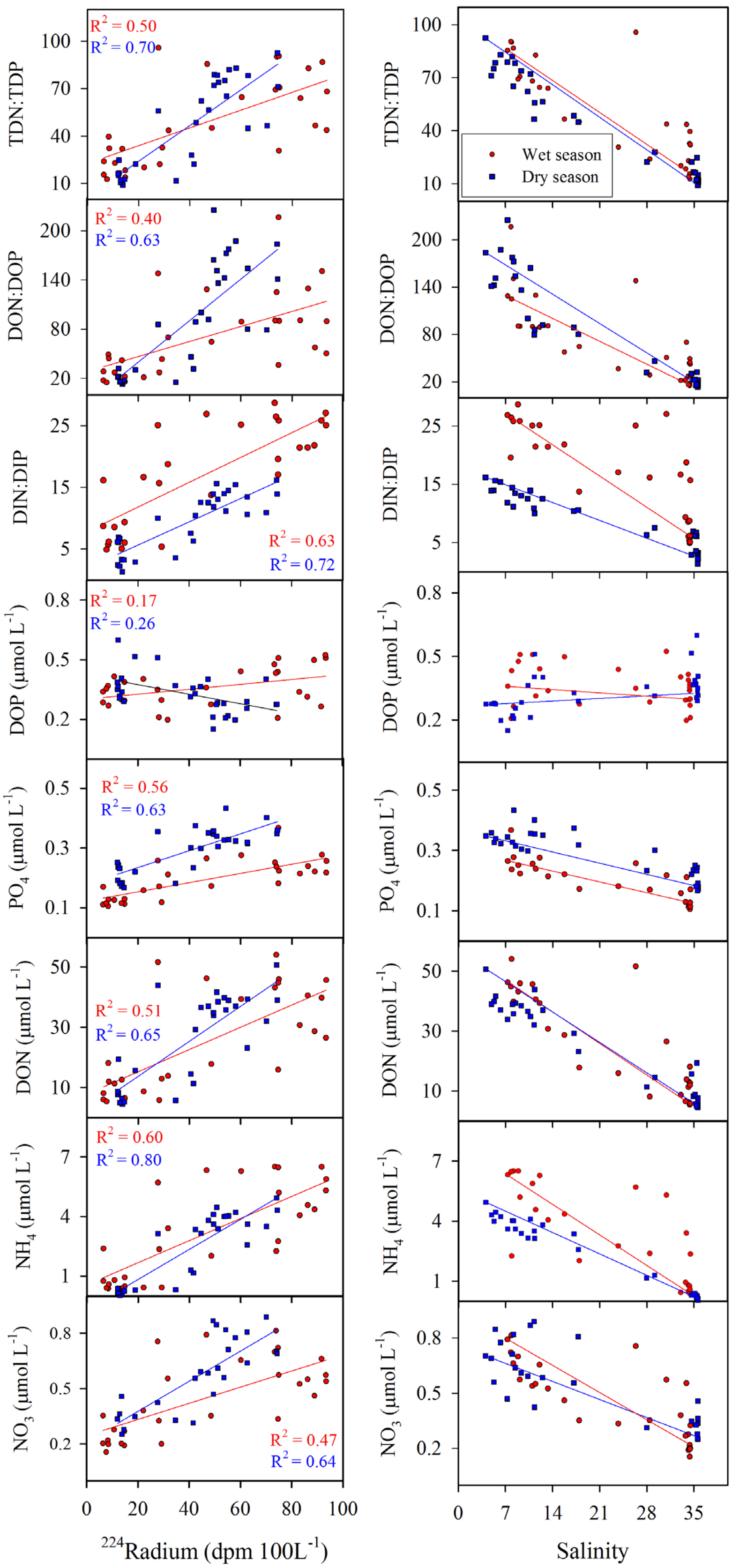
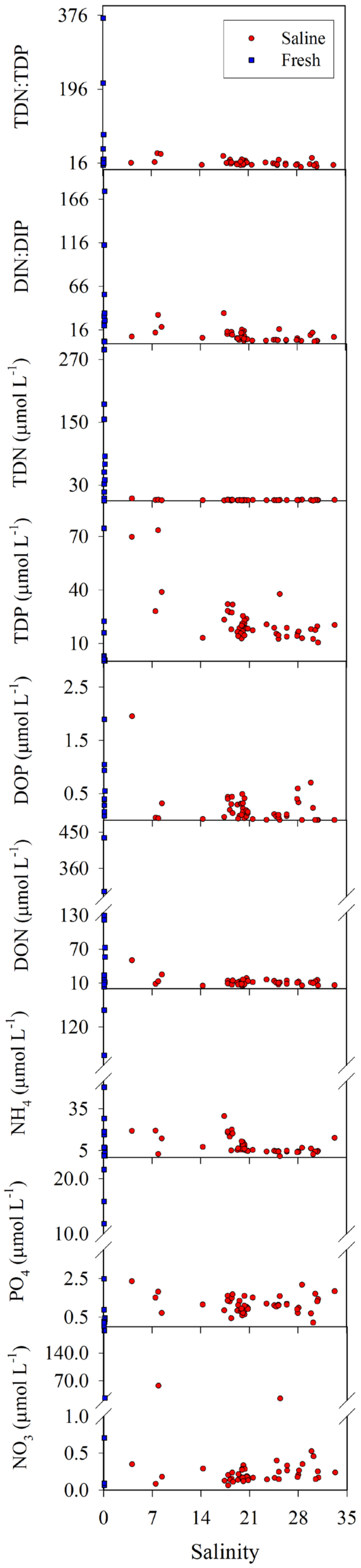


Figure 7. Surface water radium-224 and salinity vs nutrient concentrations and N:P ratios. The lines on the salinity mixing plots represent the theoretical conservative mixing line.



755 Figure 8. Groundwater nutrients concentration and N:P ratios vs salinity scatter plots.



756

Figure 9. Nutrient ratios during the surface water time series. The red dotted line indicates the Redfield Ratio. Dashed lines indicate high tide mark.