Seasonal and spatial controls on N\textsubscript{2}O concentrations and emissions in low-nitrogen estuaries: Evidence from three tropical systems

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Abstract

Estuarine N\textsubscript{2}O emissions contribute to the atmospheric N\textsubscript{2}O budget, but little is known about estuary N\textsubscript{2}O fluxes under low dissolved inorganic nitrogen (DIN) conditions. We present high-resolution spatial surveys of N\textsubscript{2}O concentrations and water-air fluxes in three low-DIN (NO\textsubscript{3}\textsuperscript{-} < 30 \textmu mol L\textsuperscript{-1}) tropical estuaries in Queensland, Australia (Johnstone River, Fitzroy River, Constant Creek) during consecutive wet and dry seasons. Constant Creek had the lowest concentrations of dissolved inorganic nitrogen (DIN; 0.01 to 5.4 \textmu mol L\textsuperscript{-1} of NO\textsubscript{3}\textsuperscript{-} and 0.09 to 13.6 \textmu mol L\textsuperscript{-1} of NH\textsubscript{4}\textsuperscript{+}) and N\textsubscript{2}O (93–132\% saturation), and associated lowest N\textsubscript{2}O emissions (−1.4 to 8.4 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1}) in both seasons. The other two estuaries exhibited higher DIN inputs and higher N\textsubscript{2}O emissions. The Johnstone River Estuary had the highest N\textsubscript{2}O concentrations (97–245\% saturation) and emissions (0.03 to 25.7 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1}), driven by groundwater inputs from upstream sources, with increased N\textsubscript{2}O input in the wet season. In the Fitzroy River Estuary, N\textsubscript{2}O concentrations (100–204\% saturation) and emissions (0.03–19.5 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1}) were associated with wastewater inputs, which had a larger effect during the dry season and were diluted during the wet season. Overall N\textsubscript{2}O emissions from the three tropical estuaries were low compared to previous studies, and at times water-air N\textsubscript{2}O fluxes were actually

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negative, indicating that N\textsubscript{2}O consumption occurred. Low water column NO\textsubscript{3}\textsuperscript{-} concentration (i.e. < 5 \(\mu\)mol L\textsuperscript{-1}) appears to promote negative water-air N\textsubscript{2}O fluxes in estuary environments; considering the number of estuaries and mangrove creeks where DIN falls below this threshold, negative water-air N\textsubscript{2}O fluxes are likely common.

Keywords: nitrous oxide, estuary, groundwater, wastewater

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1. Introduction

Humans have greatly altered the nitrogen cycle in estuarine and coastal waters through excess nitrogen loads from agriculture, wastewater and urban runoff (Howarth, 2008; Vitousek et al., 1997). Nitrogen over-enrichment drives the production of excess organic matter (eutrophication), which is one of the greatest threats to coastal ecosystems worldwide (Howarth and Marino, 2006; de Jonge et al., 2002). Nitrogen is biologically processed in estuaries via many pathways including assimilatory uptake and microbially-mediated redox-regulated processes (e.g. Salk et al., 2017; An and Gardner, 2002; Cook et al., 2004; Eyre et al., 2016). Some of these pathways produce nitrous oxide (N\textsubscript{2}O), which is a potent greenhouse gas that contributes about 8% of the radiative ‘greenhouse gas’ effect (Bouwman et al., 1995; Stocker et al., 2013) and causes ozone depletion in the stratosphere (Ravishankara et al., 2009).

In coastal areas, the most common biological pathways of N\textsubscript{2}O production are nitrification and denitrification. Denitrification is the reduction of NO\textsubscript{3}\textsuperscript{-} to NO\textsubscript{2}\textsuperscript{-}, N\textsubscript{2}O, and N\textsubscript{2} (Firestone et al., 1980; Firestone and Davidson, 1989). Typically, heterotrophic microbes are responsible for denitrification, however autotrophic ammonia-oxidising bacteria can reduce NO\textsubscript{2}\textsuperscript{-} to N\textsubscript{2}O and N\textsubscript{2} via ‘nitrifier-denitrification.’ In contrast with denitrification, nitrification involves oxidation of NH\textsubscript{4}\textsuperscript{+} to N\textsubscript{2}O, NO\textsubscript{2}\textsuperscript{-}, and NO\textsubscript{3}\textsuperscript{-} (Arp et al., 2002; Belser and Schmidt, 1978). Denitrification occurs in anoxic environments, such as anoxic layers of soil or sediment (Davidson and Swank, 1986; Firestone et al., 1979).
Thomas et al. (1994), while nitrification occurs in both sediment (Jenkins and Kemp 1984; Usui et al. 2001) and the water column (Damashek et al. 2016; Iriarte et al. 1998; Somville 1984), where O$_2$ is available.

High concentrations of nitrate (NO$_3^-$) in estuarine waters are linked to increased N$_2$O water-air emissions (Murray et al. 2015), although this may be attenuated by the estuarine flushing time (Wells et al. 2018). High NH$_4^+$ concentrations are also known to enhance N$_2$O production (De Wilde and De Bie 2000). Most studies of N$_2$O in tidal aquatic environments have been undertaken in disturbed estuaries with high DIN concentrations (up to 500 µmol L$^{-1}$) (Murray et al. 2015). Additionally, most N$_2$O water concentration sampling has been undertaken in temperate or higher-latitude estuaries, with only 11 water-air N$_2$O emission studies in estuaries located between 25$^\circ$S and 25$^\circ$N (Table 1). Waters low in dissolved inorganic nitrogen (DIN) can be a net sink for N$_2$O, particularly in small mangrove-lined creeks (Erler et al. 2015; Maher et al. 2016; Wells et al. 2018; Murray et al. 2018). N$_2$O undersaturation may be prevalent in mangrove creeks, but the extent and seasonal dynamics of N$_2$O undersaturation are not well understood due to the limited number of studies and lack of seasonal sampling.

There can be significant variability in water-air N$_2$O fluxes across larger estuaries due to N$_2$O exchange, groundwater input, and benthic/water-column microbial activity. Large spatial N$_2$O concentration gradients have been observed at ‘hot spots’ of N$_2$O influx (Mueller et al. 2016; Wong et al. 2013). However, most estuarine N$_2$O surveys employ discrete sampling at coarse resolution, which may not capture the full range of variation. Continuous sampling, employing real-time N$_2$O concentration monitoring, is emerging as a way of investigating spatial variability in estuaries at a very fine scale (Bange et al. 1998; Brase et al. 2016; Mueller et al. 2016; Wells et al. 2018), however there has only been one such sampling campaign in a tropical estuary (Mueller et al. 2016).

In the current study, we present real-time N$_2$O concentration measurements and interpret the drivers of N$_2$O production and loss in three Queensland estu-
turies during the wet and dry seasons, focusing on catchments which are only slightly to moderately affected by anthropogenic disturbance. We hypothesise that in such environments, water-air $N_2O$ fluxes should be positive and increase with DIN concentration, however $N_2O$ may be undersaturated at very low DIN concentrations. The DIN–$N_2O$ relationship may provide some indication of the biogeochemical conditions under which a tropical estuary can transition from a net sink to a net source of $N_2O$.

Table 1: Range of $N_2O$ concentrations and water-air $N_2O$ fluxes in tropical estuaries.

<table>
<thead>
<tr>
<th>Study Location</th>
<th>$N_2O$ saturation (%)</th>
<th>$N_2O$ flux ($\mu$mol m$^{-2}$ day$^{-1}$)</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andaman Island, Indian Ocean</td>
<td>102 to 208</td>
<td>−2.4 to 7.2</td>
<td>Barnes et al. (2006)</td>
</tr>
<tr>
<td>Jiulong River, China</td>
<td>112 to 4133</td>
<td>1.1 to 93.8</td>
<td>Chen et al. (2015)</td>
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<tr>
<td>Pearl River, China</td>
<td>101 to 3799</td>
<td>0.1 to 733</td>
<td>Lin et al. (2016)</td>
</tr>
<tr>
<td>Tianjin, China</td>
<td>100 to 1300</td>
<td>−6.2 to 49.9</td>
<td>Liu et al. (2015)</td>
</tr>
<tr>
<td>Various estuaries in Australia</td>
<td>50 to 123</td>
<td>−3.4 to 0.7</td>
<td>Maher et al. (2016)</td>
</tr>
<tr>
<td>Northwestern Borneo</td>
<td>102 to 1679</td>
<td>3.6 to 33</td>
<td>Mueller et al. (2016)</td>
</tr>
<tr>
<td>Queensland, Australia</td>
<td>86 to 154</td>
<td>−2.2 to 9.4</td>
<td>Murray et al. (2018)</td>
</tr>
<tr>
<td>Adyar River, India</td>
<td>−</td>
<td>3.6 to 84.9</td>
<td>Rajkumar et al. (2008)</td>
</tr>
<tr>
<td>Various estuaries in India</td>
<td>72 to 5902</td>
<td>−1.1 to 14.21</td>
<td>Rao and Sarma (2013)</td>
</tr>
<tr>
<td>Pichavaram Mangrove, India</td>
<td>112 to 157</td>
<td>10.1 to 31.2</td>
<td>Senthilkumar (2008)</td>
</tr>
<tr>
<td>Various estuaries in Australia</td>
<td>∼90 to 400</td>
<td>−0.6 to 11.6</td>
<td>Wells et al. (2018)</td>
</tr>
</tbody>
</table>

2. Study Locations

Surveys were conducted during March (wet season) and September (dry season) in northern Queensland, Australia, along the lengths of three estuaries: the Fitzroy River Estuary, the Johnstone River Estuary, and Constant Creek Estuary (Figure 1). These are wet and dry tropical estuaries where most of the rainfall occurs in summer, with a mean annual rainfall of 3152 mm in the Johnstone catchment, 1705 mm in the Constant Creek catchment, and 646 mm in the Fitzroy catchment (Queensland Department of Environment and...
In the Johnstone and Fitzroy estuaries there is a strong seasonality in freshwater supply, as can be seen in data from upstream river gauges (Figure 2). Under high flows, salt water can flush fully to the mouth and during the dry season these systems can become hypersaline due to high evaporation and low freshwater input (Eyre, 1995, 1994).

The Johnstone River is furthest north, at 17.5°S latitude, draining a catchment of 2320 m². The mouth of the Johnstone River is just 5 km east of the city of Innisfail, QLD, which sits at the confluence of two major tributaries: the North Johnstone River and the South Johnstone River. In this catchment there is a sewage treatment plant located along a mangrove-lined creek, which empties into the Johnstone River about 2.5 km upstream of the mouth of the estuary (Figure 1a). The major land uses are banana and sugarcane cultivation.

Constant Creek is located north of Mackay, QLD at about 21°S latitude, lined by mangroves and draining sugarcane cultivation and grazing lands (Figure 1b). The mouth of the Fitzroy River is located at about 23°S latitude, draining a catchment of 142,570 km², and emptying into the ocean downstream of Rockhampton, QLD. In the Fitzroy catchment, grazing and production forestry are the most common land uses. Several sewage treatment plants release effluent into the estuary just downstream of Rockhampton, near the upstream end of the estuary (Figure 1c).

3. Methods

3.1. Sample Collection and Analysis

Spatial surveys were performed on board a small vessel, starting at high tide at the mouth of each estuary and then moving upstream to the head of the estuary (Eyre, 2000). In the case of the Johnstone River estuary, the South Johnstone tributary was surveyed for about 1 km before a return trip to the fork in the river and a survey of the North Johnstone tributary. Water was continuously sampled from just below the water line through a water pump and hose, which were suspended from the side of the boat. This water was then fed...
Figure 1: The three estuaries surveyed along the coast of Queensland, Australia: a) the Johnstone River Estuary, b) Constant Creek, and c) the Fitzroy River Estuary.
into a shower-head style equilibrator to allow any dissolved gases to come into equilibrium between the water and a head-space of air (Johnson, 1999).

The head-space was vented into a second equilibrator head-space, which was itself vented into the ambient air. This assured there would be no pressure build-up in the equilibrator, while minimising atmospheric contamination of the sample. The head-space in the primary equilibrator was connected by 4 mm Bev-A-line tubing into a Picarro cavity ring-down spectrometer (CRDS) instrument (details described below). A Drierite™ column was connected to this tubing, between the equilibrator and the analyser inlet, to reduce humidity in the incoming air stream and minimise infrared interference from H₂O. The analyser outlet was connected back to the equilibrator so that the CRDS and equilibrator formed a loop through which air continuously flowed. Initial experimentation revealed that there was a small lag (∼ 5 min) between water sampling and full equilibration of the water with the head-space.

Two different CRDS instruments were used to measure N₂O concentration. In the wet season (March), the Picarro G5101-I isotopic N₂O analyser (Picarro Inc., Santa Clara, CA. USA) was used (Erler et al., 2015). In the dry season (September) technical problems prevented the use of this device, so a G2308 Picarro was used. Both of these detect N₂O by measuring the ‘ring-down’ time of infrared light, however there is a difference in precision; The G5101-I has a 1-minute 1-σ precision of ∼ 0.3 ppbv while the G2308 is less precise (∼ 8 ppbv). In both seasons a 350 ppbv N₂O standard gas mixture was analysed to check for instrument drift before and after each deployment, and no significant instrument drift was recorded.

In addition to continuous N₂O measurements, discrete water samples were collected about every 2 ppt of salinity along the length of the survey. These samples were filtered (0.45 µm, Whatman GF/F), stored in 10 mL polycarbonate vials, and frozen for later DIN and δ¹⁵N–DIN analysis. Salinity, temperature and luminescent dissolved oxygen (LDO) were measured every 5 minutes using a Hydrolab DS5X Sonde (AquaLab), which was suspended from the side of the vessel, just below the water line. This sonde was re-calibrated for salinity be-
fore and after each survey. \(^{222}\text{Rn}\), a groundwater tracer, was measured every 10 minutes by a radon-in-air analyser (RAD7, Durridge) connected by a loop of tubing to the shower-head exchanger (Santos and Eyre 2011). \(^{222}\text{Rn}\) data was only collected in the dry season.

Wind speed, required for \(\text{N}_2\text{O}\) water-air flux calculations, was measured using an anemometer and augmented with 1-minute wind speed data procured from three Bureau of Meteorology (BOM) stations — Rockhampton (station number 039083), South Johnstone (032037), and MacKay (033045) (near Constant Creek). Depth datapoints came from a Garmin GPS unit on-board the boat. Discharge data (m\(^2\) s\(^{-1}\) of stream flow) came from two stream gauges upstream of the Johnstone River (stream gauge numbers 112004A and 112101B), and one stream gauge upstream of the Fitzroy River (stream gauge number 130005A) which were obtained from the Water Monitoring Information Portal of the Queensland Department of Natural Resources and Mines.

Discrete water samples were analysed for nitrate (NO\(^{-3}\)), dissolved organic nitrogen (DON), and ammonium (NH\(^{4+}\)) on a Lachat-flow injection device (see Eyre and Pont (2003); Eyre et al. (2011) for methods, errors and detection limits). Before \(\delta^{15}\text{N}\) analysis, NO\(^{-3}\) was converted to \(\text{N}_2\text{O}\) by denitrifying bacteria following the method of Sigman et al. (2001). The resulting \(\text{N}_2\text{O}\) was then stripped from the solute by helium sparging and then analysed in a Thermo Fisher GasBench II which fed into a Thermo Delta V Plus IRMS.

3.2. Calculations

The dissolved \(\text{N}_2\text{O}\) and saturation values were calculated based on the solubility equations of Weiss and Price (Weiss and Price 1980), and apparent oxygen utilisation (AOU) was derived from LDO using the solubility equations of Benson and Krause (1984). Excess \(\text{N}_2\text{O}\) (\(\Delta\text{N}_2\text{O}\)) was calculated as the difference between measured concentration of \(\text{N}_2\text{O}\) (in nmol L\(^{-1}\)) and the theoretical concentration at 100% saturation, which we refer to as the "background" concentration:
Figure 2: Stream discharge (m$^3$ s$^{-1}$) measurements from three tributaries upstream of the Johnstone and Fitzroy Rivers, at the locations of (a) ‘Tung Oil’ upstream of the North Johnstone River, (b) ‘Central Mill’ upstream of the South Johnstone River, and (c) ‘The Gap’ upstream of the Fitzroy River.
\[ \Delta \text{N}_2\text{O} = \text{N}_2\text{O}_{\text{measured}} - \text{N}_2\text{O}_{\text{background}} \]

There are many parameterisations available for estimating water-to-air fluxes. The commonly-cited options can produce very different results (Musenze et al., 2014; Rosentreter et al., 2017), so fluxes were calculated using 6 different parameterisations (equations in Appendix Table A1). The mean fluxes presented in this study represent the average of all 6 parameterisations, and the ranges represent the full range of all calculated values. Gas fluxes were calculated at 1-minute intervals, and any missing temperature, salinity, or wind data was linearly interpolated from the nearest measured values. The resulting water-air \text{N}_2\text{O} fluxes then were extrapolated over the area of the main channel of each estuary. To calculate the average area-weighted estuary water-to-air flux, it was first necessary to define a shape-file outlining the areal extent of each transect. This was done by manually digitising Landsat 8 satellite images for each estuary using QGIS software. After this step, the 1-minute-average water-air flux values (in \( \mu \text{mol N}_2\text{O m}^{-2} \text{d}^{-1} \)) were extrapolated over the water surface area at \( \sim 3 \) m resolution, using an inverse cost function – specifically, the GRASS GIS ‘v.surf.icw’ function (developed by Hamish Bowman) was used for this purpose. Finally, the area-weighted values were calculated as the average \text{N}_2\text{O} flux of all of the pixels in the resulting geoTIFF raster image.

Once the total water-air \text{N}_2\text{O} flux (\( \mu \text{mol d}^{-1} \)) was calculated, it was compared with various inputs into the estuary, such as the total DIN load (the DIN concentration of freshwater multiplied by the total freshwater discharge into each estuary) and the load of \text{NO}_3^- \text{ and NH}_4^+. Additionally, the depth (m), salinity, and \text{N}_2\text{O} concentration (nmol L\(^{-1}\)) datasets were extrapolated using the same method as the water-air fluxes – the inverse-cost function – over the same area in order to calculate the total water volume of each estuary and the total volume of freshwater. The freshwater fraction was calculated using the QGIS ‘raster calculator’ function at each pixel of the ‘depth’ geoTIFF as:
Freshwater fraction = \( (S_{\text{mouth}} - S_{\text{measured}}) / S_{\text{mouth}} \).

Where \( S_{\text{mouth}} \) is the salinity at the mouth of the estuary (the oceanic salinity) and \( S_{\text{measured}} \) is the salinity as measured (or extrapolated from measured values) at each point. The freshwater fraction values were multiplied by the depth and surface area at each pixel as:

\[
\text{Freshwater m}^3 \text{ per pixel} = \text{Freshwater fraction} \times \text{pixel area} \times \text{depth}
\]

The sum of all values in the resulting raster image, calculated using the 'raster statistics' function in QGIS, was then the total amount (in m\(^3\)) of freshwater in the estuary. This information, along with the freshwater discharge data, was required to calculate the freshwater flushing time using the fraction of freshwater method \( [\text{Kennish, 1986}] \), where the total freshwater volume is divided by the freshwater discharge at the upstream gauge. Instead of using the discharge on the day previous to sampling, however, the discharge of preceding days was summed until the total freshwater volume was reached \( [\text{Eyre, 2000; Kaul and Froelich, 1984}] \). The exception was at Constant Creek, where freshwater residence time was not calculated due to the absence of upstream discharge data.

The discharge data and total \( \text{N}_2\text{O} \) flux data were used to estimate the contribution of ventilation of river \( \text{N}_2\text{O} \) to the total \( \text{N}_2\text{O} \) flux within each estuary \( [\text{Abril et al., 2000; Borges and Abril, 2011}] \). This value represents the proportion of the positive water-air \( \text{N}_2\text{O} \) flux which would be needed to offset all of the excess dissolved \( \text{N}_2\text{O} \) (\( \Delta \text{N}_2\text{O} \)) delivered by the river at the upstream end of the estuary channel. It is possible for this proportion to be greater than 100% in estuaries where the water-air \( \text{N}_2\text{O} \) flux is too low to fully account for all incoming dissolved \( \text{N}_2\text{O} \) – i.e. in estuaries where freshwater-derived \( \text{N}_2\text{O} \) is exported to the ocean.
Independently, the theoretical ventilation time (the time required to equilibrate the entire water column with overlying air) was estimated as the ratio between the average depth and average gas transfer velocity (Bender et al., 2011; De Wilde and De Bie, 2000; Reuer et al., 2007). In addition, where N\textsubscript{2}O concentrations fell below the conservative salinity mixing line, the amount of N\textsubscript{2}O removed from the water column (R\textsubscript{N\textsubscript{2}O}), was calculated as the sum of the deviations between observed N\textsubscript{2}O concentrations and expected N\textsubscript{2}O concentrations at each point.

For consistency, the area of each transect was defined as the maximum area that had sampling coverage for both seasons. In the Fitzroy, the survey extended from the mouth of the estuary to a point just downstream of the Rockhampton weir. In the Johnstone, the sampling vessel traveled up the South and North Johnstone for a few km. In Constant Creek the surveyed area extended upstream to a bridge just inland of the boat ramp.

4. Results

4.1. Johnstone River Estuary

Nitrous oxide concentrations in the Johnstone River Estuary ranged from 132 to 245% saturation in the wet season and from 97 to 228% saturation in the dry season (Table 2; Figure 3e,f). Water-air N\textsubscript{2}O fluxes were higher than in the Fitzroy River Estuary and Constant Creek, with a wide range of 0 to 47.5 \( \mu \text{mol m}^{-2} \text{d}^{-1} \) over the salinity gradient in the wet season (Table 2; Figure 3g,h) and an average area-weighted water-air flux of 5.6 \( \mu \text{mol m}^{-2} \text{d}^{-1} \) (Table 2). The range over the salinity gradient in the dry season was – 0.3 to 28.8 \( \mu \text{mol m}^{-2} \text{d}^{-1} \) and the average area-weighted water-air flux was 3.6 \( \mu \text{mol m}^{-2} \text{d}^{-1} \). Nitrous oxide concentrations were generally highest at the freshwater end-member, particularly in the South Johnstone (Figure 4a,b), where N\textsubscript{2}O saturations reached as high as 245% in the wet season and 225% in the dry season. In the North Johnstone, N\textsubscript{2}O reached a maximum saturation of 204% in the wet season and 160% in the dry season.
The freshwater flushing time in the Johnstone River was 0.59 days (14 h) in the wet season, during which time the theoretical water-column ventilation time was about 2.02 days. The potential contribution of riverine \( \text{N}_2\text{O} \) evasion to \( \text{N}_2\text{O} \) emissions was about 450% (Figure 5) corresponding to a total riverine input of 70 mol of excess \( \text{N}_2\text{O} \) per day, as compared with the total water-air evasion of 15.4 mol d\(^{-1}\). In the dry season, the freshwater residence time was 2.3 days, similar to the theoretical ventilation time of 2.26 days. The contribution of riverine \( \text{N}_2\text{O} \) was 124%; 9.8 mol d\(^{-1}\) \( \text{N}_2\text{O} \) was emitted to the atmosphere, while the total excess freshwater \( \text{N}_2\text{O} \) contribution was 12.3 mol d\(^{-1}\).

The Johnstone River was consistently the least saline of the three estuaries, with salinity range of < 1 to 34 in the dry season and < 1 to 12 in the wet season. In both seasons there was a negative relationship between salinity and \( \text{N}_2\text{O} \).

In both seasons, \( \text{N}_2\text{O} \) concentrations measured downstream of the confluence of the North and South Johnstone fell below the salinity–\( \text{N}_2\text{O} \) conservative mixing line, resulting in a total deficit of 6.3 mol in the wet season and 1.4 mol in the dry season (Figure 7). Over the same area, the total water-air \( \text{N}_2\text{O} \) flux was 8.9 mol d\(^{-1}\) (wet season) and 4.2 mol d\(^{-1}\) (dry season). Additionally, the freshwater residence times were lower below the confluence of the North and South Johnstone Rivers — 7 h for the wet season and 21 h for the dry season — and over the residence time the water-air \( \text{N}_2\text{O} \) flux could account for 41% and 260% of the missing \( \text{N}_2\text{O} \) in the wet and dry season, respectively. The ratio of the \( \text{N}_2\text{O} \) emissions (\( \mu \text{mol d}^{-1} \)) to total DIN load (\( \mu \text{mol d}^{-1} \)) was 0.02% in the wet season and 0.09% in the dry season.

In the dry season, \( \text{NO}_3^- \) concentrations were lower (mean value of 3.5 \( \mu \text{mol L}^{-1} \)) and \( \text{NH}_4^+ \) values higher (mean of 1.3 \( \mu \text{mol L}^{-1} \)) (Figure 3b,d) than in the wet season (mean of 6.0 \( \mu \text{mol L}^{-1} \) for \( \text{NO}_3^- \) and 0.1 \( \mu \text{mol L}^{-1} \) for \( \text{NH}_4^+ \)) (Figure 3a,c). There was a strong positive correlation between \( \text{NO}_3^- \) and \( \text{N}_2\text{O} \) in dry season (\( r^2 = 0.77; \ p < 0.001 \)) and a weak and non-significant relationship in the wet season (Figure 8a). Ammonium concentrations were low and showed no correlation with \( \text{N}_2\text{O} \) concentrations (Figure 8b). Nitrate levels decreased with increasing salinity in both seasons (Appendix Figure A1a), but \( \text{NH}_4^+ \) showed no
clear correlation with salinity (Appendix Figure A1b). Dissolved oxygen levels varied between 90% and 100% saturation, with AOU values falling between 7 and 36 µmol L\(^{-1}\) in the wet season and –30 and 16 µmol L\(^{-1}\) in the dry season (Appendix Figure A2a,b). Excess N\(_2\)O (\(\Delta\)N\(_2\)O) ranged from 2 to 10 nmol L\(^{-1}\) in the wet season and 0 to 4 nmol L\(^{-1}\) in the dry season.

The \(^{222}\)Rn concentrations were negatively correlated with salinity and positively correlated with both NO\(_3^-\) and N\(_2\)O concentration in the dry season (Figure 9e,g,h). Overall, wet season \(\delta^{15}\)N–NO\(_3^-\) values (+7.7 to +9.9‰) were higher than dry season values (+4.8 to +7.3‰) (Figure 10a,b), with the lowest wet season value near the mouth of the estuary, and the highest value in the high-N\(_2\)O reaches of the north arm.

Table 2: N\(_2\)O concentrations (saturation %) and water-air N\(_2\)O fluxes, for the Johnstone River, the Fitzroy River, and Constant Creek, including area-weighted values.

<table>
<thead>
<tr>
<th>Location</th>
<th>N(_2)O saturation (%)</th>
<th>N(_2)O flux (µmol m(^{-2}) day(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>Johnstone River</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wet season</td>
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<td>245</td>
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<tr>
<td>dry season</td>
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<td>Constant Creek</td>
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<td>139</td>
</tr>
<tr>
<td>dry season</td>
<td>103</td>
<td>204</td>
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4.2. Constant Creek Estuary

N\(_2\)O concentrations were lower in Constant Creek than the Johnstone and Fitzroy river estuaries, ranging from 92.9% to 104.4% saturation in the wet season and 97.3% to 131.5% saturation in the dry season (Table 2, Figure 4c,d).
Figure 3: Box plots of wet and dry season NO$_3^-$, NH$_4^+$ concentrations, N$_2$O saturations, and water-air N$_2$O fluxes for the three estuaries.
Figure 4: The spatial variability of \(N_2O\) concentration (% saturation) in the Johnstone River Estuary, Constant Creek, and Fitzroy River Estuary in the wet and dry seasons.
In the dry season N\textsubscript{2}O concentrations were highest at the seawater end-member and showed non-conservative behaviour with an uptake in the middle reaches of the estuary (Figure 4c). In the wet season water-air N\textsubscript{2}O fluxes were negative over a large portion of the estuary (range of − 2.2 to 1.2 µmol m\textsuperscript{-2} d\textsuperscript{-1}) (Table 2), reflecting slightly undersaturated N\textsubscript{2}O concentrations (93%-100%) in the middle of the estuary. The highest water-air fluxes (up to 15.1 µmol m\textsuperscript{-2} d\textsuperscript{-1}) (Table 2), occurred during the dry season, when N\textsubscript{2}O saturations reached ∼ 130% in the outer estuary (Figure 4d).

Theoretical water-column ventilation times were 2.1 days in the wet season and 1.2 days in the dry season, the difference caused by an increase in wind speed in the dry season. The total water-air flux was much lower in the wet season (1.4 mol d\textsuperscript{-1}) than in the dry season (8.9 mol d\textsuperscript{-1}). In both seasons, N\textsubscript{2}O concentrations fell below the conservative mixing line, with an apparent total N\textsubscript{2}O deficit of 1.4 mol in the wet season and 9.9 mol in the dry season. For water-air N\textsubscript{2}O emissions to make up for this deficit, it would require ∼ 28 days in the wet season and only ∼ 1 day in the dry season.

Constant Creek was the most saline of the three estuaries, with salinity ranging from 11 to 35 in the wet season and 30 to 35 in the dry season. NO\textsubscript{3}\textsuperscript{-} concentrations were lower than in the Johnstone and Fitzroy river estuaries, ranging from 0.2 to 0.4 µmol L\textsuperscript{-1} in the wet season and from 0 to 5.4 µmol L\textsuperscript{-1} in the dry season (Figure 3a,b). Similar to the Fitzroy and Johnstone river estuaries, NH\textsubscript{4}\textsuperscript{+} concentrations were extremely low in the wet season, ranging from 0.1 to 0.4 µmol L\textsuperscript{-1} (Figure 3c), but increased in the dry season, ranging from 0.4 to 13.6 µmol L\textsuperscript{-1} (Figure 3d). In the wet season the highest NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} concentrations were at the seawater end-member. In contrast, in the dry season the highest NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} concentrations were at the river end-member (Appendix Figure A1c,d).

Neither N\textsubscript{2}O, NO\textsubscript{3}\textsuperscript{-} nor NH\textsubscript{4}\textsuperscript{+} were correlated with \textsuperscript{222}Rn (Figure 9i,j,k); \textsuperscript{222}Rn increased at lower salinities (Figure 9l) while DIN and N\textsubscript{2}O concentrations were highest in the outer estuary (Figure 4d). In the dry season dissolved oxygen was saturated (∼ 100%), with AOU values between – 8 and 13 µmol
Figure 5: Residence time vs. the proportion of water-air $\text{N}_2\text{O}$ flux explained by ventilation of river-derived (freshwater-derived) $\text{N}_2\text{O}$ from upstream sources (%), for the Johnstone River Estuary and Fitzroy River Estuary.

L$^{-1}$ (Appendix Figure A2d). In the wet season dissolved oxygen was slightly undersaturated (85%), with AOU values between –19 and 34 µmol L$^{-1}$. AOU and $\Delta\text{N}_2\text{O}$ show a negative correlation in the wet season (Appendix Figure A2c). Due to low $\text{NO}_3^-$ concentrations, $\delta^{15}\text{N}–\text{NO}_3^-$ values were only measured at two locations during the dry season, when they were 2.8 and 4.2‰.

4.3. Fitzroy River Estuary

In the Fitzroy River Estuary, $\text{N}_2\text{O}$ concentrations ranged from 100% to 139% saturation, in the wet season and 103% to 204% in the dry season (Table 2; Figure 3e,f). Despite higher $\text{N}_2\text{O}$ concentrations in the dry season, water-air fluxes were higher in the wet season (area-weighted mean of 2.2 µmol m$^{-2}$ d$^{-1}$ in wet and 1.5 µmol m$^{-2}$ d$^{-1}$ in dry) due to higher k-values during the wet season (Appendix Table A2). In both seasons $\text{N}_2\text{O}$ concentrations decreased from the upstream end to the ocean. However in the wet season there was a slight increase in the middle reaches of the estuary, near the mouth of small mangrove-lined tributary at about 30 km downstream of Rockhampton.

The freshwater flushing time was 5.7 days in the wet season, and the average ventilation time of the water-column was 0.9 days. With a freshwater excess $\text{N}_2\text{O}$ load of 151 mol $\text{N}_2\text{O}$ and a total water-air $\text{N}_2\text{O}$ flux of 477 mol over the residence time, the ventilation of the freshwater (riverine) $\text{N}_2\text{O}$ accounted for 32% of the $\text{N}_2\text{O}$ emissions (Figure 5). In the dry season the flushing time was 72.6 days and the ventilation time was 2.2 days. The excess freshwater $\text{N}_2\text{O}$ load was 67 mol, and over the duration of the residence time, the estimated total
water-air flux was 4150 mol, meaning that ventilation of river N$_2$O inputs can explain 1.6% of the water-air flux. In both seasons, N$_2$O concentrations showed non-conservative mixing, (Figure 6c); N$_2$O was as much as 3 nmol L$^{-1}$ below the conservative mixing line despite N$_2$O saturation remaining above 100%. The estimated total N$_2$O deficit was 1.3 mol N$_2$O in the wet season and 150 mol in the dry season. Over the duration of the residence time, the water-air flux could account for 5100% and 2800% of the lost N$_2$O in the wet season and dry season, respectively. The N$_2$O water-air flux (µmol d$^{-1}$) accounted for 0.05% and 1.12% of the total DIN load (µmol d$^{-1}$) in the wet and dry seasons respectively.

Salinity was lower during the wet season, ranging from < 1 to 29 as compared to 24 to 35 in the dry season. In the dry season, NO$_3^-$ and NH$_4^+$ concentrations were elevated (Figure 3b,d) compared to the Johnstone River Estuary and Constant Creek, showing a positive correlation with salinity (Appendix Figure A4,f). The N$_2$O saturation was positively correlated with both NO$_3^-$ and NH$_4^+$ concentrations in the dry season (Figure 8e,f). In contrast, in the wet season NO$_3^-$ and NH$_4^+$ concentrations were lower (Figure 3a,c) and not correlated with N$_2$O concentrations (Figure 8e,f).

AOU values varied from 24 to 59 µmol L$^{-1}$ in the wet season, increasing along the length of the freshwater plug until it reached a peak at the transition between freshwater (salinity < 0.5) and brackish water (Appendix Figure A2f). AOU increased again until about 30 km from Rockhampton, where both AOU and ΔN$_2$O reach a secondary, mid-estuary peak. In the dry season, AOU fell between 14 and 41 µmol L$^{-1}$. The highest AOU values were observed at a salinity less than 25, where ΔN$_2$O was elevated in the upper estuary. At this location there was a positive correlation between AOU and salinity (Appendix Figure A2f). At a salinity of ~ 27 and a distance of ~ 11 km downstream of Rockhampton, the AOU–ΔN$_2$O relationship changes, but the values further downstream still show a positive correlation.

The $^{222}$Rn concentrations showed a positive correlation with NO$_3^-$ concentrations (Figure 9i) and a maximum at intermediate salinity values — (up to 3 pCi L$^{-1}$ between salinities of 26 and 28) (Figure 9l). At the lowest salinity
values (< 25), where $^{222}\text{Rn}$ was at intermediate concentration, $\text{NO}_3^-$, $\text{N}_2\text{O}$ and $\text{NH}_4^+$ were all relatively high, diverging from a simple linear correlation with $^{222}\text{Rn}$. Nitrate $\delta^{15}\text{N}$ values were higher in the dry season (+ 8.7 to + 11.7‰), than in the wet season (+ 4.1 to + 7.0‰) (Figure 10) and the lowest wet-season $\delta^{15}\text{N}–\text{NO}_3^-$ values were found in the low-salinity upper reaches of the estuary.

5. Discussion

5.1. Johnstone River Estuary

The highest concentrations of $\text{N}_2\text{O}$ (both wet and dry seasons) over the three estuarine systems were found in the Johnstone River Estuary. In contrast to the two other systems, $\text{N}_2\text{O}$ concentrations in the Johnstone River Estuary were higher during the wet season rather than the dry season. Below we discuss these differences in terms of the potential sources of $\text{N}_2\text{O}$, the observed seasonal pattern in $\text{N}_2\text{O}$ concentration, and the distribution of $\text{N}_2\text{O}$ within the Johnstone River Estuary.

Compared with the other two estuaries, the Johnstone River Estuary is subject to much higher freshwater input from its tributaries (Figure 2a,b,c). As such, the estimated $\text{N}_2\text{O}$ loads are high enough, and the residence time is low enough, that some of the $\text{N}_2\text{O}$ arriving from upstream sources is exported to the ocean. In both the wet and dry season, the proportion of $\text{N}_2\text{O}$ emissions explained by ventilation of riverine $\text{N}_2\text{O}$ inputs is greater than 100% (Figure 5). In other words the potential $\text{N}_2\text{O}$ ventilation is higher than the observed $\text{N}_2\text{O}$ water-air flux, and any in situ production of $\text{N}_2\text{O}$ is overwhelmed by the river load.

Discharge-driven increases in estuarine $\text{N}_2\text{O}$ concentration are relatively common. For example, across 28 estuaries in India, high wet-season $\text{N}_2\text{O}$ concentrations resulted from mobilisation of $\text{N}_2\text{O}$ from upstream sources [Rao and Sarma, 2013]. Similar to the Johnstone River, the Saribas and Lupar Rivers in Borneo also exhibited greater $\text{N}_2\text{O}$ variability and higher maximum $\text{N}_2\text{O}$ concentrations in the wet season, with a clear source of $\text{N}_2\text{O}$ near the midpoint of
Figure 6: $N_2O$ concentrations plotted as a function of salinity in wet and dry seasons in the Johnstone River Estuary (a), Constant Creek (b) and Fitzroy River Estuary (c).
the spatial transect \cite{Mueller et al., 2016}. In the dry season however, \cite{Mueller et al., 2016} found that $N_2O$ concentrations were less variable and most of the $N_2O$ came from upstream, freshwater inputs.

One of the main differences between the Johnstone River and the two rivers in Borneo is the relationship between $N_2O$ and $NO_3^-$. \cite{Mueller et al., 2016} found no correlation between DIN and $N_2O$ in either season, and noted that despite the relatively low DIN concentrations of the waterways (10–37 $\mu$mol L$^{-1}$) $N_2O$ was present in very high concentrations in some places (up to 1679% saturation). In contrast, in the Johnstone, $N_2O$ concentrations showed a correlation with $NO_3^-$ in both seasons (Figure 8a,b), indicating that $N_2O$ production was enhanced by the higher $NO_3^-$ concentrations, or that $N_2O$ and $NO_3^-$ were entering the system together.

The salinity–$NO_3^-$ mixing plots indicate that most of the $NO_3^-$ in the Johnstone River was from freshwater sources from the North and South Johnstone tributaries (Appendix Figure A1a); $NO_3^-$ was not generated in large quantities below the confluence of the river. It is difficult to tell if any $N_2O$ was produced in the estuary. In both seasons, the $N_2O$ load from freshwater input is high enough to more than account for all of the emitted $N_2O$ (Figure 5) and in-situ production is not needed to explain the observed patterns. In some estuaries and coastal waters, a positive correlation between $N_2O$ and apparent oxygen utilization has been interpreted as a sign of in-situ nitrification \cite{Nevison et al., 2003, Goncalves and Brogueira, 2017}, however this correlation was not observed in the Johnstone (Figure A2a,b), and neither did we observe a negative correlation between $N_2O$ and $NH_4^+$ (Figure 8b), as would be expected if nitrification were consuming large quantities of $NH_4^+$.

Another possible pathway of $N_2O$ production or consumption is denitrification. Sediments and groundwater can be major sites of denitrification and $N_2O$ production \cite{Marzadri et al., 2017}, and the higher $\delta^{15}N–NO_3^-$ values observed in the wet season could indicate a greater influence of denitrification during the high-$N_2O$ season (Figure 10). Denitrification increases the $\delta^{15}N–NO_3^-$ in the remaining $NO_3^-$ pool \cite{Granger et al., 2008, Middelburg and Nieuwenhuize}. 

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therefore the higher $\delta^{15}$N–NO$_3^-$ could result from an increased inflow of DIN from sediment pore-water or groundwater, where denitrification is likely to occur. However, similar to nitrification, there was little evidence that denitrification occurred in-situ; dissolved N$_2$O could have come from upstream sources.

A denitrification pathway for N$_2$O production would be consistent with the strong correlation between $^{222}$Rn and both NO$_3^-$ and N$_2$O in the dry season (Figure 9a,c), which suggest that at least some NO$_3^-$ and N$_2$O came from groundwater inputs. The CO$_2$ and CH$_4$ concentrations were also correlated with $^{222}$Rn suggesting a similar groundwater source [Rosentreter et al., 2018]. Although we were unable to obtain $^{222}$Rn concentrations for the wet season, it seems likely that groundwater input would increase with higher precipitation. This would drive pore-water NO$_3^-$ and N$_2$O into the upper river systems. Overall, we propose that the higher concentration of N$_2$O in the Johnstone River Estuary relative to the Constant Creek and the Fitzroy River Estuaries, and the increase in N$_2$O concentration in the wet season relative to the dry season, is a consequence of higher rainfall and increased groundwater flow.

### 5.1.1. Spatial Variability

The Johnstone Estuary itself has two main sections (see Figure 1): the North and South tributaries. The South Johnstone tributary was the strongest source of N$_2$O-rich freshwater in both the wet and dry seasons, accounting for 51–55% of the N$_2$O load despite only contributing 32–34% of the freshwater volume (according to the upstream gauges). This high N$_2$O concentration water mixed within the main body of the estuary with water from the North Johnstone tributary.

Below the confluence of the North and South Johnstone, N$_2$O concentrations fall below the conservative mixing line in both the wet and dry seasons (Figure 6a). If N$_2$O concentrations were near or below 100% saturation, this mid-estuary minimum of N$_2$O might indicate N$_2$O reduction to N$_2$, as has been observed in some low-DIN tidal waterways [Daniel et al., 2013; Rao and Sarma, 2013; Erler et al., 2015; Maher et al., 2016; Murray et al., 2018]. However, where N$_2$O is
supersaturated, as in the Johnstone River Estuary, it doesn’t seem likely that
\( \text{N}_2\text{O} \) consumption could explain the loss of \( \text{N}_2\text{O} \).

The \( \text{N}_2\text{O} \)–salinity relationship in the Johnstone River Estuary is similar
to the eutrophic Pearl River in China (Lin et al., 2016), where \( \text{N}_2\text{O} \) was non-
conservative despite dissolved \( \text{N}_2\text{O} \) concentrations consistently above 100% sat-
uration (101–3799%). Lin et al. (2016) estimated \( \text{N}_2\text{O} \) removal rates which
nearly balanced out water-air \( \text{N}_2\text{O} \) fluxes, suggesting that all of the apparent
\( \text{N}_2\text{O} \) loss could be explained by evasion.

In the Johnstone River, in contrast, there was a net export of freshwater-
derived \( \text{N}_2\text{O} \) (55 mol d\(^{-1}\)) in the wet season, despite the fact that evasion could
only explain \( \sim 40\% \) of the \( \text{N}_2\text{O} \) lost below the confluence of the North and
South Johnstone. In the dry season, this \( \text{N}_2\text{O} \) loss was dwarfed by the water-air
evasion (280%), a fact that might indicate in-situ \( \text{N}_2\text{O} \) production, yet the net
export of freshwater-derived \( \text{N}_2\text{O} \) was lower (2.4 mol d\(^{-1}\)). The residence time
was very low below the confluence of the North and South Johnstone in both
seasons, and a small change in either residence time or water volume could have
a large effect on the calculations.

5.2. Constant Creek Estuary

In contrast to the Johnstone River, the low DIN and \( \text{N}_2\text{O} \) concentrations
in Constant Creek suggest relatively low anthropogenic input of nitrogen from
agriculture or other sources. Similar to the Johnstone River Estuary, \( \text{N}_2\text{O} \) concentrations in Constant Creek fall below the conservative mixing line (Figure
6c). In this case, however, \( \text{N}_2\text{O} \) concentrations in the middle reaches of the
estuary are close to or slightly below 100% saturation. This suggests that the
\( \text{N}_2\text{O} \) deficit results from consumption of \( \text{N}_2\text{O} \) by denitrifiers.

In the wet season there was some evidence for in-situ consumption. While
the overall area-weighted flux was positive, negative water-air fluxes (as low as
\( \sim 2.2 \text{ µmol m}^{-2} \text{ d}^{-1} \)) were observed in the middle section of the transect (Table
2). The undersaturation of \( \text{N}_2\text{O} \) has been observed previously in other relatively
pristine creeks in Australia (Erler et al., 2015; Maher et al., 2016; Murray et al.)
Figure 7: $\text{N}_2\text{O}$ mixing plot for the Johnstone River. The map shows the difference, in nmol $\text{N}_2\text{O}$ between the measured $\text{N}_2\text{O}$ concentration and the value expected from saltwater/freshwater mixing alone, with ‘hot spots’ indicated in red.

Johnstone River
However, \( \textit{N}_2\text{O} \) undersaturation is not observed in all pristine estuaries. Barnes et al. (2006) documented \( \textit{N}_2\text{O} \) saturations between 100\% and 208\% in a pristine mangrove creek where \( \textit{NO}_3^- \) values were 0–5 \( \mu \text{mol L}^{-1} \) and \( \textit{NH}_4^+ \) values were 0–25 \( \mu \text{mol L}^{-1} \), similar to values found at Constant Creek (0–5.4 \( \mu \text{mol L}^{-1} \) \( \textit{NO}_3^- \) and 0–13.6 \( \mu \text{mol L}^{-1} \) \( \textit{NH}_4^+ \)). The creek on Andaman Island had relatively low salinity (0–28) compared with Constant Creek (10–35); the shared characteristics of undersaturated estuaries seem to be low DIN and high salinity (Maher et al., 2016; Rao and Sarma, 2013). Saline conditions can inhibit water-column nitrification (Rysgaard et al., 1999), and this might help to prevent in-situ \( \textit{N}_2\text{O} \) production.

In the dry season, it was not clear that \( \textit{N}_2\text{O} \) was consumed in the estuary, due to the fact that that \( \textit{N}_2\text{O} \) concentrations were generally elevated above 100\% (Figure 3). Constant Creek was the only estuary where the highest \( \textit{N}_2\text{O} \) concentrations were found at the downstream end of the transect, and we propose that the extra \( \textit{N}_2\text{O} \) was most likely produced on the extensive shallow shoals which are found in the outer estuary (Figure 4). Shallow benthic sediments are known to be a strong source of \( \textit{N}_2\text{O} \) in many estuaries (e.g. Usui et al., 2001; Ferrón et al., 2007). Due to the downstream \( \textit{N}_2\text{O} \) source, the salinity–\( \textit{N}_2\text{O} \) data-points to deviate below the conservative mixing line. Considering that \( \textit{N}_2\text{O} \) concentrations remain at or above 100\% over the transect, we cannot say that the non-conservative behaviour of \( \textit{N}_2\text{O} \) is due to in-situ consumption. Furthermore, the water-air \( \textit{N}_2\text{O} \) flux would require only 1.1 days to balance out the negative deficit, which is not an unreasonably long time.

In the dry season, \( ^{222}\text{Rn} \) concentrations were highest at low \( \textit{N}_2\text{O} \) concentrations, indicating that groundwater was not a strong source of \( \textit{N}_2\text{O} \) (Figure 9). Water-column nitrification is also unlikely to produce \( \textit{N}_2\text{O} \) in this environment.

As mentioned previously, a positive linear correlation between AOU and \( \Delta \textit{N}_2\text{O} \) is considered a sign of nitrification activity because nitrification produces \( \textit{N}_2\text{O} \) and consumes \( \text{O}_2 \). However in Constant Creek there is a clear negative correlation between excess \( \textit{N}_2\text{O} \) and AOU in the wet season (Appendix Figure A2).
suggesting that nitrification was not a strong source of N₂O, but that denitrifiers reduced N₂O to N₂, especially under low-DIN conditions.

5.3. Fitzroy River Estuary

In the Fitzroy River Estuary, there was a clear source of N₂O at the upstream end of the survey (Figure 4e,f), with higher concentrations during the dry season (Figure 4). Similar to Constant Creek, but in contrast to the Johnstone River Estuary, the seasonal differences in N₂O concentrations reflect a fundamental shift in the source and/or processing of DIN, and not just a change in freshwater discharge. While total freshwater discharge was higher in the wet season, this extra freshwater did not have enough N₂O to increase N₂O concentration higher than in the dry season (Figure 6c), and freshwater may even dilute N₂O concentrations. In the dry season the weak relationship between N₂O and ²²²Rn shows that pore-water/groundwater was not the only source of N₂O in the Fitzroy River Estuary (Figure 9k). Near Rockhampton, there was a source of low-salinity water with relatively low ²²²Rn concentrations but high N₂O, NO₃⁻ and NH₄⁺ concentrations (Figure 9i,j,k,l).

Looking at the strong correlation between N₂O saturation and DIN (Figure 7e,f) and the relationship between ²²²Rn and DIN, it seems likely that the wastewater treatment plants located near the head of the Fitzroy River Estuary (Figure 1) are the ultimate source of a large portion of the NO₃⁻, N₂O and NH₄⁺ present in the waterway. In the case of N₂O, the treatment plants may be a direct or indirect source: N₂O may be discharged directly as a result of wastewater processing, or alternately the organic matter and DIN from the wastewater treatment plants may spur N₂O production downstream of the wastewater outlet. The low-salinity, low-²²²Rn wastewater had a greater effect on NH₄⁺ and N₂O concentrations than on NO₃⁻ concentrations (Figure 9j,k).

For a given NO₃⁻ concentration in the dry season N₂O concentrations were much lower in the Fitzroy than in the Johnstone where NO₃⁻ and N₂O were sourced from groundwater (Figure 3b,f). This suggests that although most of the N₂O and some of the NO₃⁻ were sourced from the wastewater treatment
Figure 8: NO$_3^-$ and NH$_4^+$ vs N$_2$O concentrations for the Johnstone River Estuary, Constant Creek, and the Fitzroy River Estuary.
Figure 9: $^{222}$Rn vs. NO$_3^-$, NH$_4^+$, and N$_2$O (nmol L$^{-1}$) concentrations, and salinity vs. $^{222}$Rn concentration, for the Johnstone River Estuary, Constant Creek, and the Fitzroy River Estuary.

**Johnstone dry season**

- a) $R^2 = 0.64$, $p < 0.001$
- b) $R^2 = 0.83$, $p < 0.001$
- c) $R^2 = 0.91$, $p < 0.001$
- d) $R^2 = 0.81$, $p = 0.001$

**Constant Creek dry season**

- e) $R^2 = 0.64$, $p < 0.001$
- f) $R^2 = 0.83$, $p < 0.001$
- g) $R^2 = 0.91$, $p < 0.001$
- h) $R^2 = 0.81$, $p = 0.001$

**Fitzroy dry season**

- i) $R^2 = 0.64$, $p < 0.001$
- j) $R^2 = 0.83$, $p < 0.001$
- k) $R^2 = 0.91$, $p < 0.001$
- l) $R^2 = 0.81$, $p = 0.001$
plant the N\textsubscript{2}O was not directly linked to the NO\textsubscript{3}\textsuperscript{−}. Nitrification of wastewater-derived NH\textsubscript{4}\textsuperscript{+}, occurring at or just downstream of the wastewater outlet could also have elevated N\textsubscript{2}O and NO\textsubscript{3}\textsuperscript{−}.

Wastewater effluent is associated with increased NH\textsubscript{4}\textsuperscript{+} concentrations and N\textsubscript{2}O production in other tropical and subtropical estuaries. For example, in the Adyar River in southeast India high NH\textsubscript{4}\textsuperscript{+} concentrations resulted from wastewater and use of diammonium phosphate fertiliser led to elevated N\textsubscript{2}O driven by water-column nitrification ([Rajkumar et al. 2008]). Many of the estuaries on the east and west coast of India, where N\textsubscript{2}O production is attributed to water-column nitrification, receive wastewater effluent as well and show a strong correlation between NH\textsubscript{4}\textsuperscript{+} and N\textsubscript{2}O concentration ([Rao and Sarma 2013]). Similarly, strong DIN–N\textsubscript{2}O correlations were observed in the wastewater-affected Pearl River in China ([Lin et al. 2016]).

Upstream freshwater N\textsubscript{2}O inputs could not account for the entire water-air N\textsubscript{2}O flux in either season, which indicates that there is a secondary source of N\textsubscript{2}O downstream of Rockhampton, either from tributary/groundwater inputs or in-situ production. In the wet season, some of this extra N\textsubscript{2}O entered the estuary about 30 km downstream from Rockhampton, where there was an obvious increase in N\textsubscript{2}O concentration over a region of constant salinity. Considering that this occurs near the mouth of a creek where we observed high N\textsubscript{2}O concentrations, it seems likely that some of this extra N\textsubscript{2}O was allochthonous. However the N\textsubscript{2}O increase was also associated with an increase in AOU, indicating a possible role of nitrification. AOU declines again downstream of the mid-estuary N\textsubscript{2}O peak, indicating that nitrification was likely responsible for very little N\textsubscript{2}O production in the low-N\textsubscript{2}O lower reaches of the estuary.

In the dry season, the total contribution of freshwater-derived N\textsubscript{2}O is not well known because freshwater N\textsubscript{2}O concentrations were not directly measured (minimum salinity in the estuary is 22). Additionally, estimating ‘freshwater’ N\textsubscript{2}O concentration is difficult where wastewater inputs contribute to N\textsubscript{2}O production, as wastewater could have an extremely high N\textsubscript{2}O concentration. While excess N\textsubscript{2}O (ΔN\textsubscript{2}O) was assumed to be similar to the highest observed values...
at the upstream end of the estuary (8.0 nmol L\(^{-1}\)), if we assume the average freshwater \(\Delta N_2O\) was close to wet season values (\(\sim 2.8\) nmol L\(^{-1}\)), the riverine contribution to \(N_2O\) production would be 0.4%. At the high value of 20 nmol L\(^{-1}\) the contribution would be 4%, and to reach 100%, the average freshwater \(\Delta N_2O\) would have to be \(\sim 500\) nmol L\(^{-1}\).

Unlike the wet season, the mid-estuary tributaries don’t seem to have a huge effect on \(N_2O\) concentration. Above the salinity of \(\sim 27\) transition at \(\sim 11\) km from Rockhampton, some \(N_2O\) production could result from nitrification; AOU concentrations were slightly higher at salinities below 25 (up to 1.3 mg L\(^{-1}\)) where they exhibited a positive relationship with \(\Delta N_2O\) (Appendix Figure A2). However, given that low-O\(_2\) waters were likely quickly mixed with more oxygenated waters further downstream, it is possible that the AOU\(−\Delta N_2O\) pattern is merely the result of mixing and \(N_2O\) evasion, which could cause both AOU and \(\Delta N_2O\) to decline.

Considering the estimated freshwater \(N_2O\) inputs and water-air fluxes, it seems that the Fitzroy was the only estuary where residence times were long enough for significant in-situ \(N_2O\) production to occur in both seasons. This raises the possibility that denitrification at the sediment-water interface could also contribute \(N_2O\). Previous research has identified a relationship between residence time and denitrification in temperate estuaries (Eyre et al., 2016; Nixon et al., 1996), which would predict that over a residence time of 72 days (as in the dry season) about 25% of \(NO_3^-\) inputs should be consumed by denitrifiers. For residence times of less than 1 month, as in the wet season and in the Johnstone River, the predicted consumption of \(NO_3^-\) by denitrifiers would be much lower than 25%. In theory, at higher temperatures these values could increase (Barnes and Owens, 1999), however we should note that \(NO_3^-\) concentrations do not seem to show non-conservative behaviour indicative of significant \(NO_3^-\) consumption along the length of the estuary (Appendix Figure A1b).

In contrast to the Johnstone River, the \(\delta^{15}N−NO_3^-\) data in the Fitzroy seem to indicate more intense denitrification of \(NO_3^-\) during the dry season, rather than the wet season, which could reflect processing during wastewater...
treatment and subsequent NO$_3^-$ consumption by denitrifiers in the sediment downstream of the wastewater inlet (Figure 10c,d). Without the wastewater source and long residence time, we might expect that the Fitzroy dry season δ$^{15}$N−NO$_3^-$ values would be lower than the wet season values, perhaps similar to the dry season values observed at Constant Creek. However the Fitzroy is similar to the other two estuaries in that the seasonal increase in NO$_3^-$ input is associated with increased δ$^{15}$N−NO$_3^-$ values and higher N$_2$O concentrations.

5.4. Nitrous oxide load and residence time

Residence time is an important control on the amount of nitrogen and phosphorus processing that occurs in estuaries, with greater processing as residence time increases (Balls 1994, Nixon et al. 1996, McKee et al. 2000, Eyre et al. 2016). Here, we show that residence time is also an important control on the freshwater N$_2$O load that is lost as an estuarine water-air N$_2$O flux (i.e. res-
idence time vs. the % riverine ventilation; Figure 5). This is similar to the
findings that residence time affects the amount of freshwater DIC that is lost as
a water-air CO$_2$ flux, (i.e. residence time vs. the % riverine ventilation) (Borges
and Abril, 2011).

In the Johnstone River, N$_2$O was delivered along with freshwater (surface
water and/or groundwater), causing a clear negative relationship between N$_2$O
concentration and salinity (Figure 6a) and a wet-season dominance of N$_2$O
(Figure 4a,b). This is typical of many temperate (Barnes and Owens, 1999;
Robinson et al., 1998; Zhang et al., 2010) and some tropical estuaries (Rao and
Sarma, 2013); in these cases, the dominant control on N$_2$O concentration is
delivery of freshwater rather than in-situ N$_2$O production. In the Johnstone
River, the dominance of freshwater-derived N$_2$O can be seen in Figure 5, where
the amount of freshwater-derived N$_2$O exceeds the total water-air N$_2$O flux over
the surface area of the transect, i.e. the proportion of water-air fluxes that can
be explained by riverine N$_2$O inputs is greater than 100%.

When residence time increases, however, freshwater inputs play a lesser role
compared with in-situ processes. For example, when N$_2$O concentrations are
higher in the dry season (Chen et al., 2015; Rajkumar et al., 2008; Senthilkumar,
2008), often N$_2$O production is attributed to stagnation of DIN-rich water in
river or estuary water bodies, leading to water-column nitrification. In the wet
season, the in-situ nitrification source of N$_2$O is suppressed because of the lower
residence time and higher flushing rate (Chen et al., 2015). A similar pattern
is evident in the Fitzroy River, and can be seen in the relationship between
residence time and % riverine N$_2$O ventilation (Figure 5). In the wet season
the larger freshwater input dilutes the wastewater effluent and decreases NO$_3^-$,
NH$_4^+$ and N$_2$O concentrations in the estuary. This leads to a lower residence
time and a higher proportion of freshwater-derived N$_2$O, even though overall
N$_2$O concentrations are lower (Figure 4c,d). In the dry season, freshwater input
is low and the residence time is high (~ 72 days), strengthening the relative
contribution of in-situ production to the water-air N$_2$O flux.
Figure 11: (a) Average annual NO$_3^-$ concentration ($\mu$mol L$^{-1}$) vs N$_2$O water-air flux ($\mu$mol m$^{-2}$ day$^{-1}$; modified from Murray et al., 2015). (b) Data from the Johnstone River Estuary, Constant Creek, and the Fitzroy River Estuary, plotted against data presented in Murray et al., 2015 along with results from several mangrove creeks (Barnes et al., 2006; Maher et al., 2010; Murray et al., 2018) and southeast Queensland estuaries (Wells et al., 2018).
Table 3: NO$_3^-$ and NH$_4^+$ concentrations in tropical marine systems.

<table>
<thead>
<tr>
<th>Citation</th>
<th>Environment</th>
<th>Country</th>
<th>NH$_4^+$ (µmol L$^{-1}$)</th>
<th>NO$_3^-$ (µmol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agawin et al. (1996)</td>
<td>seagrass</td>
<td>Philippines</td>
<td>1.6 to 1.9</td>
<td>0.4 to 0.8</td>
</tr>
<tr>
<td>Carruthers et al. (2005)</td>
<td>seagrass</td>
<td>Panama</td>
<td>0.20 to 0.26</td>
<td>0.20 to 0.27</td>
</tr>
<tr>
<td>Erftemeijer and Herman (1994)</td>
<td>seagrass</td>
<td>Indonesia</td>
<td>2.2 to 3.2</td>
<td>0.9 to 1.4</td>
</tr>
<tr>
<td>Heminga et al. (1994)</td>
<td>seagrass</td>
<td>Kenya</td>
<td>0.4 to 0.8</td>
<td>0.3 to 0.45</td>
</tr>
<tr>
<td>Uku and Björk (2005)</td>
<td>seagrass</td>
<td></td>
<td>1.6 to 1.9</td>
<td>0.4 to 0.8</td>
</tr>
<tr>
<td>Boto and Wellington (1988)</td>
<td>mangrove</td>
<td>Australia</td>
<td>0.1 to 1.6</td>
<td>&lt; 0.1 to 5.8</td>
</tr>
<tr>
<td>Davis et al. (2001a)</td>
<td>mangrove</td>
<td>Florida</td>
<td>0.1 to 5.2</td>
<td>0.1 to 5.8</td>
</tr>
<tr>
<td>Davis et al. (2001b)</td>
<td>mangrove</td>
<td>Florida</td>
<td>0.1 to 6.3</td>
<td>0.2 to 5.8</td>
</tr>
<tr>
<td>Ohowa et al. (1997)</td>
<td>mangrove</td>
<td>Kenya</td>
<td>0.3 to 3</td>
<td>0.2 to 8</td>
</tr>
<tr>
<td>Rivera-Monroy et al. (1995)</td>
<td>mangrove</td>
<td>Mexico</td>
<td>1.1 to 51.7</td>
<td>0.2 to 4.9</td>
</tr>
<tr>
<td>Rivera et al. (2007)</td>
<td>mangrove</td>
<td>Florida</td>
<td>&lt; 0.1 to 1.4</td>
<td>1.8 to 11.8</td>
</tr>
<tr>
<td>Eyre and Balls (1999)</td>
<td>estuary main channel</td>
<td>Australia</td>
<td>&lt; 0.1 to 4</td>
<td>&lt; 0.1 to 7</td>
</tr>
<tr>
<td>Eyre (1994)</td>
<td>estuary main channel</td>
<td>Australia</td>
<td>—</td>
<td>2.3 to 31.2</td>
</tr>
</tbody>
</table>

5.5. Role of water column DIN concentrations and N$_2$O emissions

The low Fitzroy River Estuary and Johnstone River Estuary N$_2$O concentrations were typical of some tropical or subtropical estuaries or creeks at lower salinity which have a low freshwater source of DIN (Barnes et al. 2006; Maher et al. 2016; Senthilkumar 2008; Wells et al. 2018) (Table 1). For example, most estuaries surveyed in India exhibited N$_2$O saturations between 100% and 300% (Rao and Sarma 2013), with the exception of a few which had large anthropogenic N inputs. Similar values were observed in the more saline, downstream reaches of more eutrophic estuaries (Lin et al. 2016; Mueller et al. 2016; Rao and Sarma 2013), where a strong upstream N$_2$O source is diluted by mixing with seawater. More anthropogenically disturbed tropical estuaries, with a large population living in the catchment and significant wastewater or agricultural DIN inputs, can reach much higher maximum saturations, typically at the upstream, freshwater end of the estuary (Chen et al. 2015; Lin et al. 2016; Liu et al. 2015; Rao and Sarma 2013).
Like N$_2$O saturations, calculated N$_2$O water-air fluxes across the three estuaries were at the low end of the range typical for estuarine waters. This reflects relatively low DIN concentrations across the three estuaries (below 30 µmol L$^{-1}$ for both NO$_3^-$ and NH$_4^+$). Over a large range of NO$_3^-$ concentrations (i.e. 0 to 500 µmol L$^{-1}$ of NO$_3^-$) water-column NO$_3^-$ concentrations appear to be a driver of N$_2$O water-air fluxes (Figure 11a) (Murray et al., 2015). Including more recent work in mangrove creeks (Daniel et al., 2013; Erler et al., 2015; Maher et al., 2016; Murray et al., 2018) and other low concentration estuaries (Wells et al., 2018), it appears that negative water-air fluxes occur where water column NO$_3^-$ concentration falls below $\sim$ 5 µmol L$^{-1}$ (Figure 11b), despite the weaker relationship over the smaller NO$_3^-$ range. NO$_3^-$ concentrations below 5 µmol L$^{-1}$ are commonly found in many undisturbed and slightly disturbed tropical estuaries and mangrove creeks (Table 3), suggesting N$_2$O uptake may be widespread.

The ratio of N$_2$O emissions to total DIN load was quite low (0.02 – 0.09%), except for the Fitzroy dry season (1.12%). For comparison, N$_2$O emissions accounted for 0.26% of DIN load in the Changjiang River in China (Zhang et al., 2010), about 0.29% of TN in the Colne River (Robinson et al., 1998), and 0.3% of DIN is assumed to be converted to N$_2$O in estuaries in some global models of coastal N dynamics (Kroeze and Seitzinger, 1998). However, the ratio between DIN load and N$_2$O emissions, referred to as the emissions factor, can vary significantly and lower values are common. In a review of emissions factors in rivers, Hu et al. (2016) found a range of values from 0.003% to 7.13%, with a median of 0.15%. They found that the emissions factor increases as freshwater discharge declines, which might explain why the value was so high in the Fitzroy River during the dry season (1.12%), when discharge was low (Figure 2c) and residence time was high (Figure 5).
6. Conclusions

In the Johnstone River, N₂O came from a freshwater source upstream of the sampled estuary, with the highest contribution of N₂O coming from the South Johnstone River. The N₂O concentration of freshwater was similar in both the wet and the dry season, but the amount of freshwater delivered to the estuary in the wet season was much greater. In both seasons, the freshwater residence time was low enough that DIN and dissolved N₂O moved through the estuary with little evidence of in-situ production or consumption. Apart from the N₂O emitted through water-air exchange, dissolved N₂O was largely exported to the ocean.

The Fitzroy River was affected by wastewater input from the sewage treatment plants near Rockhampton. This was most obvious in the dry season, when freshwater input was low, and led to a stronger production and water-air flux of N₂O. The residence time was long, compared with the Johnstone River; Excess N₂O from the riverine source was completely lost to the atmosphere and additional N₂O from in-situ processes and downstream tributaries was added along the length of the transect.

Constant Creek was the site of N₂O consumption in the wet season, due to the unusually low concentrations of DIN in the water-column. In the dry season there was a slight N₂O production in some offshore shoals, but the N₂O concentration and fluxes in the creek itself remained very low. Comparing these results with previous studies, it seems that a NO₃⁻ concentration of less than 5 μmol L⁻¹ is conducive to a negative water-air N₂O flux.

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Table A1: The parameterization equations used to calculate gas transfer k-values (in cm s\(^{-1}\)) from U\(_{10}\) (wind speed adjusted to 10 m altitude, in m s\(^{-1}\))

<table>
<thead>
<tr>
<th>Citation</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clark et al. (1995)</td>
<td>[ k = (2 + 0.24 \times U_{10}^2) \times (Sc/600)^{-0.5} ]</td>
</tr>
<tr>
<td>Wanninkhof (2014)</td>
<td>[ k = 0.251 \times U_{10}^2 \times (Sc/600)^{-0.5} ]</td>
</tr>
</tbody>
</table>
| Liss and Merlivat (1986) | \[
\begin{align*}
0.17 \times U_{10} \times (Sc/600)^{-2/3} & \quad \text{if } U_{10} \leq 3.6 \\
(2.85 \times U_{10} - 9.65) \times (Sc/600)^{-0.5} & \quad \text{if } 3.6 > U_{10} > 13 \\
(0.59 \times U_{10} - 49.3) \times (Sc/600)^{-0.5} & \quad \text{if } U_{10} > 13
\end{align*}
\] |
| Ro and Hunt (2006)  | \[ k = 5.9 \times U_{10}^{1.81} \times (Sc/600)^{-0.5} \]                                                                                  |
| Nightingale et al. (2000) | \[ k = (0.222 \times U_{10}^2 + 0.333) \times U_{10} \times (Sc/600)^{-0.5} \]                                                          |
| Raymond and Cole (2001) | \[ k = 1.91 \times e^{0.35 \times U_{10}} \times (Sc/600)^{-0.5} \]                                                               |

Table A2: Calculated k-values using 6 different parameterisations. The mean of all k-values is in parentheses.

<table>
<thead>
<tr>
<th>Location/season</th>
<th>k value (cm s(^{-1}))</th>
<th>C 95</th>
<th>W 14</th>
<th>L&amp;M 86</th>
<th>R&amp;H 06</th>
<th>N 2000</th>
<th>R&amp;C 01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnstone River wet season</td>
<td>2.2–12.6 (5.8)</td>
<td>0–11.3 (4)</td>
<td>0–1.2 (0.7)</td>
<td>0–7.3 (2.8)</td>
<td>0–11.9 (4.6)</td>
<td>2.1–18.8 (7.7)</td>
<td></td>
</tr>
<tr>
<td>Johnstone River dry season</td>
<td>2.2–12.2 (5.4)</td>
<td>0–10.8 (3.4)</td>
<td>0–1.2 (0.6)</td>
<td>0–7.1 (2.4)</td>
<td>0–11.4 (4)</td>
<td>2.1–17.8 (7.1)</td>
<td></td>
</tr>
<tr>
<td>Constant Creek wet season</td>
<td>4.7–12.6 (8.5)</td>
<td>2.8–11.4 (6.9)</td>
<td>–0.8–9 (4.6)</td>
<td>2.1–7.4 (4.6)</td>
<td>3.5–11.9 (7.6)</td>
<td>6.2–18.8 (11.6)</td>
<td></td>
</tr>
<tr>
<td>Constant Creek dry season</td>
<td>8–18.5 (13.6)</td>
<td>6.5–17.9 (12.5)</td>
<td>4.3–14 (9.9)</td>
<td>4.4–11.1 (8)</td>
<td>7.2–18 (12.9)</td>
<td>10.9–33.2 (21.3)</td>
<td></td>
</tr>
<tr>
<td>Fitzroy River wet season</td>
<td>4.8–34.6 (16.9)</td>
<td>2.8–35.3 (16)</td>
<td>–0.9–24.7 (12.2)</td>
<td>2.1–20.7 (10)</td>
<td>3.6–34 (16.2)</td>
<td>6.3–91.4 (29.8)</td>
<td></td>
</tr>
<tr>
<td>Fitzroy River dry season</td>
<td>2.5–18.6 (7.7)</td>
<td>0.5–18.3 (6.3)</td>
<td>–5.6–14 (3.9)</td>
<td>0.4–11.2 (4.2)</td>
<td>0.9–18.2 (6.9)</td>
<td>3.1–36 (11)</td>
<td></td>
</tr>
</tbody>
</table>
Figure A1: Salinity vs NO$_3^-$ and NH$_4^+$ during the wet and dry season in the Johnstone River Estuary, Constant Creek, and the Fitzroy River Estuary.
Figure A2: AOU vs $\Delta N_2O$ during the wet and dry season in the Johnstone River Estuary, Constant Creek, and the Fitzroy River Estuary.
Table A3: Results of calculations for water-air N\textsubscript{2}O flux, using 6 different parameterisations. The mean flux is in parentheses.

<table>
<thead>
<tr>
<th>Location/season</th>
<th>C 95</th>
<th>W 14</th>
<th>L&amp;M 86</th>
<th>R&amp;H 06</th>
<th>N 2000</th>
<th>R&amp;C 01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnstone River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wet season</td>
<td>1.4–31.9</td>
<td>0–28.8</td>
<td>0–3.12</td>
<td>0–18.5</td>
<td>0–30</td>
<td>1.4–47.5</td>
</tr>
<tr>
<td>dry season</td>
<td>– 0.2–20.9</td>
<td>0–17.3</td>
<td>0–2.4</td>
<td>0–11.5</td>
<td>– 0.24–19.0</td>
<td>– 0.24–28.8</td>
</tr>
<tr>
<td>Constant Creek</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wet season</td>
<td>– 1.4–1.0</td>
<td>– 1.2–0.7</td>
<td>– 1.0–0.7</td>
<td>– 0.7–0.5</td>
<td>– 1.2–0.7</td>
<td>– 2.2–1.2</td>
</tr>
<tr>
<td>dry season</td>
<td>– 0.5–8.4</td>
<td>– 0.5–8.2</td>
<td>– 0.5–6.5</td>
<td>– 0.2–5.0</td>
<td>– 0.48–8.16</td>
<td>– 0.7–15.1</td>
</tr>
<tr>
<td>Fitzroy River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wet season</td>
<td>0–14.9</td>
<td>0–14.9</td>
<td>0–11.0</td>
<td>0–8.9</td>
<td>0–14.4</td>
<td>0–33.4</td>
</tr>
<tr>
<td>dry season</td>
<td>0.5–19.5</td>
<td>0.2–17.3</td>
<td>4.8–13.7</td>
<td>0.2–11.3</td>
<td>0.2–18.2</td>
<td>0.5–28.6</td>
</tr>
</tbody>
</table>