Investigating water quality in Coffs coastal estuaries and the relationship to adjacent land use

Part 2: Water quality

Final Report - Coffs Harbour City Council Environmental Levy Program

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Executive Summary

Blueberry farming has become a dominant horticultural industry in the Coffs Harbour LGA. Many coastal catchments in this region are occupied by blueberry farms that drain to the Solitary Islands Marine Park [SIMP]. However, the influence of intensive horticulture on regional water quality remains poorly understood. As a result, Southern Cross University was engaged by Coffs Harbour City Council to perform water quality investigations in Double Crossing Creek, a tributary of Hearnes Lake, draining to SIMP.

A time series site was established to sample water for nutrients and the greenhouse gas nitrous oxide [N_2O]. Daily sampling was undertaken between 27 January and 3 April 2018. Three rain events >50 mm were captured. After rain on 24 February, Hearnes Lake overtopped the sand barrier and drained to the ocean.

Overall, the results reveal significant nitrate + nitrite [NO_X] loads and large aquatic N_2O emissions to the atmosphere consistent with leaching of nitrogen from fertilised soils upstream.

NO_X was the dominant nitrogen [N] species accounting for 78% of total dissolved N [TDN] concentrations. The highest NO_X sample was 287 µM, 100 fold greater than the Australia and New Zealand Environment and Conservation Council [ANZECC] trigger value. 55% of NO_X samples were at least 50 fold greater than the ANZECC trigger values.

Three distinct hydrological stages were observed. Dry was characterised by high salinity as well as low N_2O and NO_X. Rain and Wet experienced low salinity as well as hyper-saturated N_2O and consistently high NO_X.

Nutrient loads in Double Crossing Creek reflected the fertiliser intensive land uses upstream and subsequent runoff during rain events. NO_X loads in rain were 695 fold greater than the dry period. These NO_X loads were amongst the highest reported for catchments on the East Coast of Australia, and similar to loads in rivers throughout China, Europe and India with strong agricultural or urban influences.

Assuming that our 66 days of observations represent an annual average, and that farmers use the recommended fertiliser dose, the calculated fertiliser loss to waterways would potentially be ~20% of applied fertiliser.

The water shifted from being a sink of atmospheric N_2O during dry conditions to a source of N_2O to the atmosphere during wet and rain. Our N_2O emissions estimates are some of the highest ever described for global aquatic systems, reaching 2859 µmol m^2 day^{-1} on 24 Feb and related to NO_X cycling in soils and waterways.

Considering the large observed aquatic nitrogen loads, there are clear opportunities for decreasing fertiliser use, altering land use practices as well as capturing N on farms before excess N is lost to creeks and the ocean.

While there are no data on ecological communities, we speculate that these high loads of nitrogen will drive eutrophication and alter the ecological communities of the SIMP, particularly in enclosed waterways such as Hearnes Lake. We strongly recommend site-specific management to reduce N runoff.

1. Introduction

Coffs Harbour City Council, as part of the Environmental Levy Grants program, engaged Southern Cross University to perform water quality investigations within the Hearnes Lake Catchment, NSW Australia, of which Double Crossing Creek is the primary tributary. This project was motivated by community concerns over the impacts of intensive agriculture activity in the catchment on the water quality of Hearnes Lake and the Solitary Islands Marine Park [SIMP]. The majority of banana farms in the catchment have been converted to blueberry farms, consistent with the trends seen throughout the Coffs Harbour Local Government Area [LGA] (Bevan, 2006; Rural Lands Council, 2016). In September 2002, 19% of the catchment was banana farms and 0.5% was blueberry farms (Conrad et al., 2018). In December 2017, banana farms occupied 4% and blueberry farms occupied 15.9% of the catchment (Google Earth Pro, 2017).

In accordance with the Coffs Harbour City Council Biodiversity Action Strategy 2012–2030, Coffs Harbour City Council has an environmental and planning responsibility to be aware of any land use change and if this change detrimentally affects local waterways (Coffs Harbour City Council, 2012). White and Santos (2018) highlighted that blueberry-dominated catchments had high loads of nitrogen (N) in creeks, particularly during flushing events. The catchment of Hearnes Lake contains multiple blueberry farms, as well as other forms of intensive horticulture.

Coffs Harbour City Council has undertaken two Eco health catchment sampling surveys of Hearnes Lake providing vital information for environmental management. However, these sporadic surveys may miss a vital understanding of phase shifting in Double Crossing Creek and the importance of flushing events. With the land use shift from bananas to blueberries and the evidence of nutrient leaching provided in White and Santos (2018), scientific knowledge is essential to manage any nutrient runoff that may impact the valuable ecosystems within Hearnes Lake and the SIMP.

Blueberries are presumably fertilised with N (121 kg N ha yr^{-1}) and phosphorus [P] (83 kg ha yr^{-1}) using commercially available fertilisers (Barker & Pilbeam, 2015; Doughty et al., 1988). When these fertilisers run off into waterways, there is an increasing possibility of algal blooms and hypoxia occurring within the receiving waters (Backer et al., 2015; Hoagland et al., 2002; Jeppesen et al., 1998).

Flushing of nutrients can occur when rainfall mobilises nutrients deposited in the upper soil layers via overland runoff (Creed & Band, 1998). Groundwater pathways may also deliver nutrients to creeks. During rain events, vertical flows along the soil increase the subsurface hydraulic head of the upper catchment, stimulating groundwater seepage and surface water nutrient peaks from hours to days after rainfall events (Burt & Arkell, 1987). Previous studies have found a clear link between groundwater pollution and agriculture, though the timescales of pollution from farm to creek via groundwater can be decades to centuries (Eckhardt & Stackelberg, 1995; Helena et al., 2000; Zhang et al., 1996).

N_2O is a potent greenhouse gas that is long lived, contributing to the destruction of ozone in the atmosphere (Montzka et al., 2011; Portmann et al., 2012). Increases in the release of N_2O to the atmosphere are largely due to anthropogenic factors such as fertilisers, industrial waste and sewage (Smith et al., 1997). As an intermediate and by-product of both the nitrification ($NH_4^+ \rightarrow NO_3^- \rightarrow NO_2^-$) and denitrification ($NO_3^- \rightarrow N_2$) processes, N_2O can be produced in soils and saturated sediments (Bange, 2006; Statham, 2012). N_2O can also be dissolved in water and travel downstream to lakes and the ocean where emissions to the atmosphere can be relatively high (Murray et al., 2015).

In this report, we describe observations performed over 66 days during a dry period and subsequent rain events to better understand the drivers and loads of nitrogen within Double Crossing Creek. We specifically test how rain events affect water quality and nitrogen loads in the creek.

Our analysis includes:

1) A comparison of the results to Australia and New Zealand Environment and Conservation Council [ANZECC] pollution trigger values for lowland streams in NSW.

2) A comparison of nutrient loads between dry periods, rain events and post rain events.

3) An assessment of water pathways into creeks, i.e., whether nutrients are delivered via surface runoff following rain events or by groundwater inflows.

4) Whether nitrate loads are related to emissions of nitrous oxide.

5) Estimates of potential fertiliser loss from upstream land uses.

2. Methods

2.1. Study area

Hearnes Lake (-30.1362, 153.1975) is located approximately 25 km north of Coffs Harbour, in the Coffs Harbour LGA. It is situated within in the NSW north coast bioregion on Gumbaynggirr Aboriginal Country and forms part of both the SIMP and the Coffs Coast Regional Park (Office of Environment and Heritage, 2017; Roper et al., 2011). Typically the Intermittently Closed and Open Lake or Lagoon [ICOLL] has an open water surface area of 10 ha, though this figure is highly variable depending on the state of the lake mouth (Haines, 2009). As part of the SIMP, Hearnes Lake is zoned 'habitat protection', restricting commercial activities and highlighting the importance of the connectivity between the ICOLL and the wider SIMP (Haines, 2009). The catchment drains 6.8 km^2, dominantly through Double Crossing Creek. The area receives average annual rainfall of 1685 mm per year, with >60% of this rainfall occurring between January and May (Department of Land and Water Conservation, 2001). Roper et al. (2011) estimated that base flow increased 48% and surface flow increased 10.1% post clearing of the catchment for agricultural practices.

As an ICOLL, Hearnes Lake has inconstant entrance conditions. When the mouth is open, it is hydraulically connected to the Pacific Ocean, allowing tidal flows in and out of the lake with an upper tidal limit of 2 km (Haines, 2009). Longshore currents continuously deliver sand across the mouth of the lake, periodically forming a sand barrier isolating Hearnes Lake from the ocean. During the periods of mouth closure, the lake is dominantly fed by groundwater as well as surface water flows via Double Crossing Creek during rain events (Haines, 2009). In high rainfall events the lake can fill and overtop the sand barrier, draining the lake and scouring a new mouth.

Within the catchment there are recognised increasing pressures from agricultural and urban development, as well as groundwater extraction and growing pressures from climate change, all of which influence the impact of flooding during high rainfall events (Haines, 2009). The runoff from these pressures is likely to contain high concentrations of nutrients, increasing the risk of eutrophication and algal blooms after rainfall (Haines, 2009).

Within the Northern Rivers Regional Biodiversity Management Plan, Hearnes Lake is considered regionally important with high conservation value aquatic habitats: swamp sclerophyll forest (an Endangered Ecological Community); known habitat for the endangered *Sternula albifrons* and vulnerable *Crinia tinnula*; as well as threatened flora (*Marsdenia longiloba, Niemeyera whitei*, *Senna* *acclinis* and *Thesium australe)* (Coffs Harbour City Council, 2012; Department of Environment Climate Change and Water NSW, 2010).

2.2. *Time series site*

The time series observations were performed at Double Crossing Creek (-30.1364, 153.1903) downstream of the agricultural activities. A small 2 m^2 shed was set up on private land next to Double Crossing Creek, powered by a battery system fed by solar panels and a top up generator (Figure 1). Water was continuously pumped from 30 cm below the surface of the creek to the shed, giving a constant supply of creek water to the instruments. Discrete sampling was conducted on 107 occasions between the 27th January and 3rd April 2018. Continuous monitoring of water quality parameters and the groundwater tracer ^{222}Rn, was conducted by autonomous instruments (Santos et al., 2012). A calibrated Hydrolab MS5 measured 10 minute time steps of dissolved oxygen [DO], pH, salinity and temperature.

During the time series three hydrological events were classified, covering a dry period (<50 mm rain per day), three rain periods (> 50 mm of rain per day and the following day) and wet periods (days after >50 mm of rain). The catchment upstream of the site was identified by creating polygons following the upper limits of 1 m interval contour data to create an upstream watershed delineation in Environmental Systems Research Institute [ESRI] ArcGIS™ mapping software (Geoscience Australia, 2015). ESRI mapping software, aerial imagery and field scouting were used, as well as consultation with local landholders and CHCC staff, enabling classification of the catchment into land uses based on December 2017 imagery (Google Earth Pro, 2017; Land and Property Information NSW, 2017). Land use (m^2 and % catchment) were calculated as reported in Table 1.

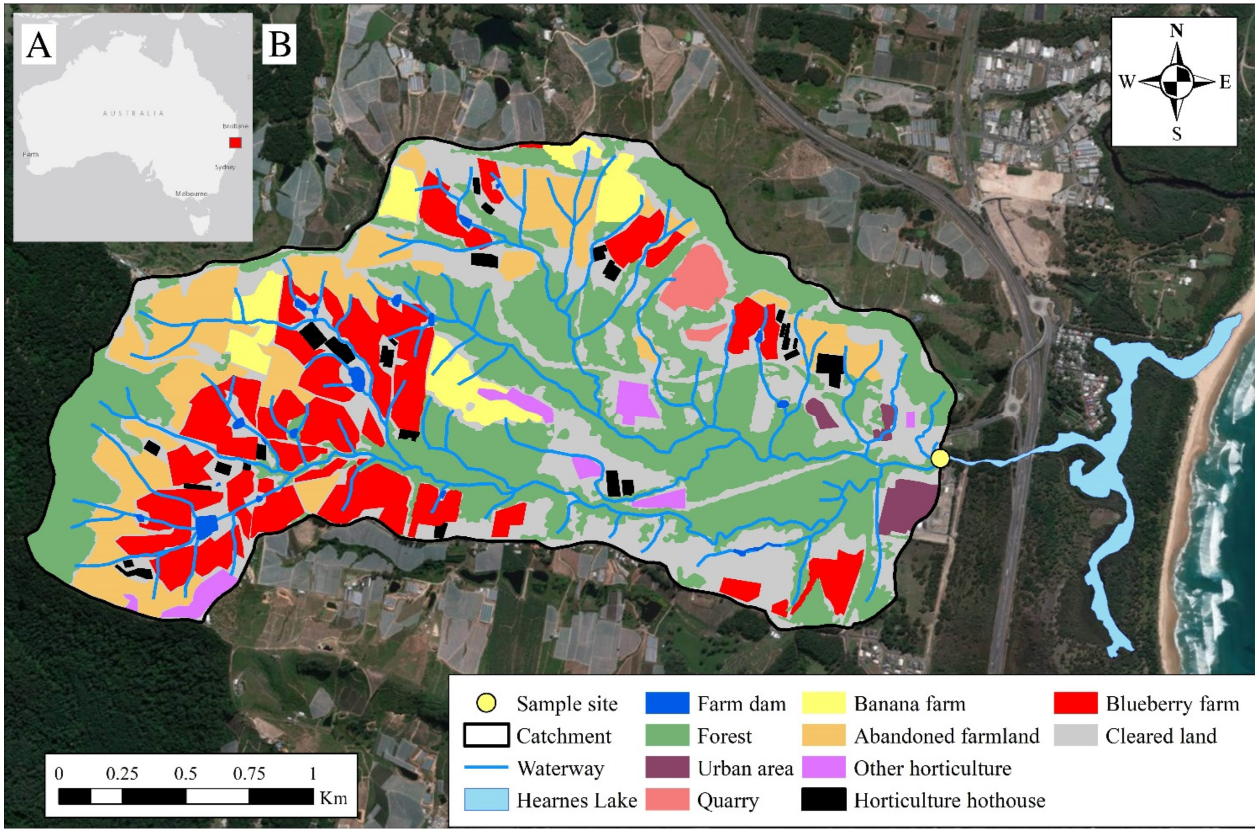

Figure 1: A: Location of study site on the east coast of Australia. B: Classification of land uses upstream of the time series site at Double Crossing Creek. The Forest classification incorporates wet and dry sclerophylls, rainforests and introduced species. The Other Horticulture classification incorporates macadamia, avocado and nursery horticulture. Cleared land incorporates pasture, houses and roads.

Table 1: Land use classifications of the catchment upstream of the study site at Double Crossing Creek, NSW on 17th December, 2017.

Classification	Area (km^2)	% Catchment
Farm Dam	0.03	0.61
Quarry	0.05	1.12
Urban area	0.05	1.13
Horticulture hothouse	0.06	1.32
Other horticulture	0.08	1.65
Banana farm	0.19	4.06
Abandoned farmland	0.58	12.45
Blueberry farm	0.75	15.96
Cleared land	1.18	25.27
Forest	1.70	36.42
Total catchment	4.67	100.0

2.3. ^{222}Rn sampling

Insight into groundwater inflow was obtained using the natural radiogenic isotope radon [^{222}Rn; $T_{1/2}$=3.83 days]. ^{222}Rn is used routinely to examine surface water and groundwater connectivity in freshwater rivers, lakes and streams (Cook et al., 2003; Ellins et al., 1990; Hamada et al., 1997). Two Durridge Company gas equilibration shower head systems (Dulaiova et al., 2005) were set up to receive ~1 L of creek water per minute. The equilibrated headspace air in the device was pumped through a closed gas loop via Drierite Desiccant to a RAD7 radon in air monitor (Durridge Company). Temperature and salinity was used to calculate the partitioning of radon between its' liquid and gas phases (Schubert et al., 2012). ^{222}Rn (dpm L^{-1}) observations were made every 10 mins for 66 days and data was integrated to every 3 hours for visualisation purposes. The detection limits and approach are described in detail elsewhere (Burnett et al., 2001).

2.4. Nitrous oxide

N_2O was sampled by syringing 500 mL of gas from within the two shower head gas equilibration devices to gas tight sample bags. Gas in the bags was analysed on a Picarro G2308, calibrated before and after sampling using standard gases (0 and 0.35 ppm) (Erler et al., 2015). Detectable drift was not observed. The N_2O concentrations in water were estimated from the headspace concentrations using solubility constants (Weiss & Price, 1980). Fluxes of N_2O at the boundary of air and water were calculated using;

$$\boldsymbol{F = k\alpha\Delta pN_2O}$$

where k is the piston velocity (gas transfer coefficient) of N_2O, α is the solubility coefficient (Weiss & Price, 1980) and ΔpN_2O is the variance between atmospheric N_2O and the water partial pressure (air-water gradient). We used two piston velocity models that take into account flow velocity, wind speed and depth for *k,* to estimate a range of N_2O flux potential. The Raymond and Cole (2001) model was determined for estuaries as a function of wind and depth, while the piston velocity model of Borges et al. (2004) was determined for three estuaries in Europe using wind, depth and current. The *k* values were aligned with in situ Schmidt numbers at *k*600 using salinity and temperature, assuming linear salinity dependence between 0 and 35 ppm. Constant atmospheric N_2O of 0.326 ppm from occasional air sampling was used in calculations. Wind data was obtained from Coffs Harbour Airport (Australian Bureau of Meteorology, 2018b). Depth was measured using an in situ Unidata

Starflow Ultrasonic Doppler. Current velocity was calculated as a function of horizontal area, depth, runoff and catchment area (Australian Bureau of Meteorology, 2018a).

2.5. Nutrient sampling and analysis

Nutrients (phosphate [PO_4], nitrate + nitrite [NO_X], ammonium [NH_4] and total dissolved N [TDN]) were sampled using a sample rinsed 60 mL polyethylene syringe. 0.7 µm glass fibre syringe filters were used to filter samples into a 10 mL rinsed and capped polyethylene sample tube. Sample tubes were labelled, kept in the dark on ice for <5 hours and frozen for laboratory analysis. Dissolved nutrients (NO_X, NH_4, PO_4) were analysed colourimetrically using a Lachat Flow Injection Analyser [FIA]. Total dissolved N [TDN] was determined colourimetrically using an FIA post persulfate digestion. Dissolved organic nitrogen [DON] concentrations were calculated as TDN minus NO_X and NH_4. Eyre and Ferguson (2005) describes the detection limits and analytical approach of this methodology.

2.6. Hydrology

Lower soil moisture and runoff data was acquired from the Australian Landscape Water Balance model (Australian Bureau of Meteorology, 2018a). Runoff is a modelled assessment calculated by using soil infiltration and soil saturation, whereby estimating surface runoff. Baseflow is factored using data on groundwater and modelling deep soil drainage (Australian Bureau of Meteorology, 2018a). The AWRA-L model is used in these calculations to estimate lower soil moisture, calibrated by remotely sensed soil moisture and evapotranspiration data, as well as surface flow observations (Australian Bureau of Meteorology, 2018a). Rainfall data was collected on site using a rain gauge, with rainfall recorded at each of the 107 discrete samples.

2.7. Interpretation

We produced histograms of solutes to compare against ANZECC trigger values for lowland streams (eastern NSW) (ANZECC, 2000) and understand the sink / source behaviour of N_2O. Data summaries are means and standard error unless otherwise noted. One way ANOVA with Tukeys Post-hoc analysis was performed using independent samples to assess differences between dry, wet and rain sample groups. MANOVA was considered for nutrient analysis, but considering the different environmental and solubility behaviours of NH_4, PO_4 and NO_X, ANOVA was preferred.

The load (flux per area, per time) of nutrients was calculated using the equation:

$$\boldsymbol{F = \frac{CMQ}{A}}$$

where F is the flux of nutrients (kg ha day^{-1}), C is the concentration of nutrient (µmol L^{-1}), M is the molecular weight of the element (g per mol), Q is discharge (m^3 day^{-1}) and A is catchment area (ha). Appropriate unit conversions were applied to data. The loss of fertiliser was calculated as the recommended fertiliser (kg ha yr^{-1}) divided by the mean creek flux of nitrogen species.

3. Results and Discussion

3.1. Time series observations

During the 66 day sampling period, there were three rain events >50 mm day (24 February, 107 mm; 6 March, 83 mm; 24 March, 161 mm) that drove changes in hydrology (Figure 2) and water quality. A clear shift in nutrients and N_2O was seen before and after the rainfall on 24 February. This rainfall was sufficient to overtop the sand barrier and trigger ICOLL drainage to the ocean with a drop of 0.84 m in lake level in only 48 hours. The ICOLL remained open to the Pacific Ocean and wider SIMP during the remainder of the time series. The total change in depth was 1.9 m from maximum to minimum.

There were three distinct stages in hydrology that we have classified as dry, rain and wet. The dry period was characterised by high salinity and high DON (Table 2). N_2O, NO_X and NH_4 were very low during the dry period. Conversely, during rain and wet periods, low salinity and DON, and super saturated N_2O (34 fold and 27 fold higher than dry in rain and wet respectively on average) were observed. The NO_X concentrations were 145 fold and 105 fold higher in the rain and wet periods respectively, as compared to the dry. NH_4 was 1.8 fold higher in rain than dry, and 2.9 fold higher in wet than dry. ^{222}Rn was 3 fold higher in rain and 2.5 fold higher in wet than dry periods. The PO_4 concentrations increase substantially as a pulse during rain, found to be 4 fold higher in rain than either dry or wet.

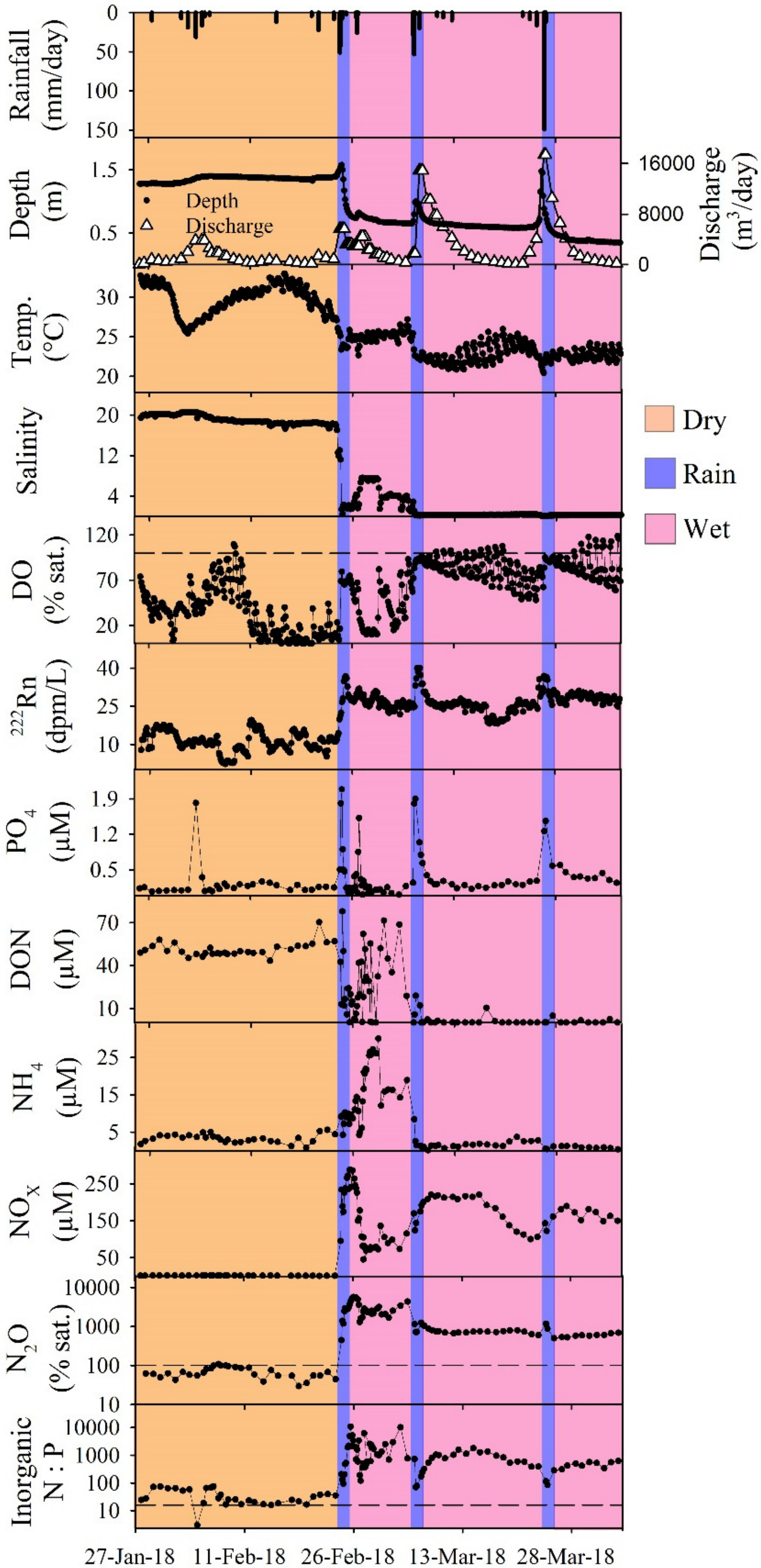

Figure 2: Time series observations over a 66 day time period at Double Crossing Creek, NSW. Note the different y axes. The differing colours identify dry, rain and wet periods.

Table 2: Mean and standard errors of observations over a 66 day time series at Double Crossing Creek, NSW. Data are broken into dry, rain and wet periods as indicated in Figure 2.

	pH	Depth (m)	Discharge (m^3 day^{-1})	Temp. (°C)	Salinity (ppt)	DO (% Sat.)	Rn in Water (dpm L^{-1})	PO_4 (µM)	DON (µM)	NH_4 (µM)	NO_X (µM)	N_2O (% Sat.)	Inorganic N : P
Overall	**6.78**	**0.91**	**3173.9**	**25.6**	**7.0**	**59.3**	**22.4**	**0.3**	**25.5**	**7.0**	**116.0**	**1376.3**	**956.0**
Std. error	0.02	0.03	349.6	0.3	0.8	3.1	0.9	0.0	2.3	0.7	8.8	144.5	163.9
Dry	**7.09**	**1.36**	**1193.8**	**29.6**	**18.5**	**39.7**	**10.2**	**0.2**	**51.2**	**3.3**	**1.4**	**64.8**	**36.0**
Std. error	0.01	0.01	192.8	0.3	0.6	5.6	0.7	0.1	0.9	0.2	0.1	4.3	3.8
Rain	**6.50**	**0.97**	**6887.8**	**23.6**	**1.2**	**77.6**	**30.7**	**0.8**	**16.1**	**5.9**	**202.4**	**2241.1**	**1535.3**
Std. error	0.03	0.06	1149.5	0.2	0.2	3.1	1.1	0.1	4.1	0.8	12.4	351.3	539.0
Wet	**6.69**	**0.64**	**2797.5**	**24.0**	**2.8**	**63.8**	**26.0**	**0.2**	**14.6**	**9.5**	**146.6**	**1776.8**	**1248.1**
Std. error	0.01	0.02	328.3	0.2	0.4	4.9	0.4	0.0	2.9	1.3	8.0	188.2	214.9

3.2. ANZECC comparisons

3.2.1. PO_4

During the 66 days of observations, 8.4% of 107 PO_4 samples (Figure 3A) were above the ANZECC trigger value of 0.645 µM for lowland streams (eastern NSW) (ANZECC, 2000). The highest PO_4 value was 2.09 µM, observed in the rain period. The dry period contained only 1% of total PO_4 samples above the trigger value. ANOVA revealed significant differences ($p=<0.01$) between dry and rain, as well as wet and rain. There was no significant difference between dry and wet, indicating PO_4 pulses during rain events. These results are consistent with other studies, showing that PO_4 is bound to soil particles and deposits as sediment relatively quickly (Vimpany & Lines-Kelly, 2004). PO_4 likely originated from the flushing of the upper soil zone (0-5 cm) in P fertilised lands during rain events (Sharpley, 1985; Sharpley et al., 1996).

3.2.2. NH_4

NH_4 concentrations were found to be above the ANZECC trigger values of 1.43 µM (ANZECC, 2000) during rain, dry and wet events (Figure 3B). The highest sample was measured during the wet period and was 21 fold higher than the trigger value. ANOVA revealed significant differences ($p=<0.01$) between dry and wet, and no significant difference between dry and rain or wet and rain. The high values seen in NH_4 were inconsistent across the wet dataset. The highest concentrations were observed during a flushing event after the first rain (Figure 2). Lang et al. (2013) showed that a medium mass NH_4 first flush can occur after a rain event, consistent with our results. Though NH_4 was above the ANZECC guidelines in 76.6 % of samples, NH_4 accounted for only 4.7 % of TDN across the time series. This is consistent with Cuadra and Vidon (2011), where NH_4 accounted for <7 % of TDN over 4 storm events in tile drains from a soybean farm (applying 180 kg N ha yr^{-1}) within a watershed of 8.1 ha in Indiana (USA).

3.2.3. NO_X

During the rain, the NO_X concentration reached the highest level at 287.11 µM, which is 100 fold higher than the ANZECC trigger value of 2.85 µM for lowland streams (eastern NSW) (ANZECC, 2000). 50.4 % and 20.5 % of total samples (Figure 3C) exceeding the ANZECC trigger value were in wet and rain periods respectively (ANZECC, 2000). 55.1% of total samples (19.6% rain and 35.5% wet) were between 50 and 100 fold higher than the trigger values. Post Hoc ANOVA revealed NO_X was significantly different between rain and dry, wet and rain, and wet and dry.

An NO_X first flush was seen after the first rain event (Figure 2), indicating that N had been stored in soils and flushed during rains (Van Meter et al., 2016; Worrall et al., 2015). As NO_X is soluble, the continued leaching from soils and groundwater seepage maintained the higher concentrations during wet, pulsed with additional NO_X during subsequent rain events (Puckett, 1994). NO_X accounted for 78.1 % of total N over the time series, also consistent with Cuadra and Vidon (2011), where over 4 storm events, NO_X accounted for 53-92 % of TDN concentrations. In the nearby Bucca Bucca Creek, NO_X in sites downstream of blueberry farms accounted for 61.1% of TDN, whereas at sites not influenced by blueberries, NO_X accounted for only 10.2 % of TDN (White & Santos, 2018).

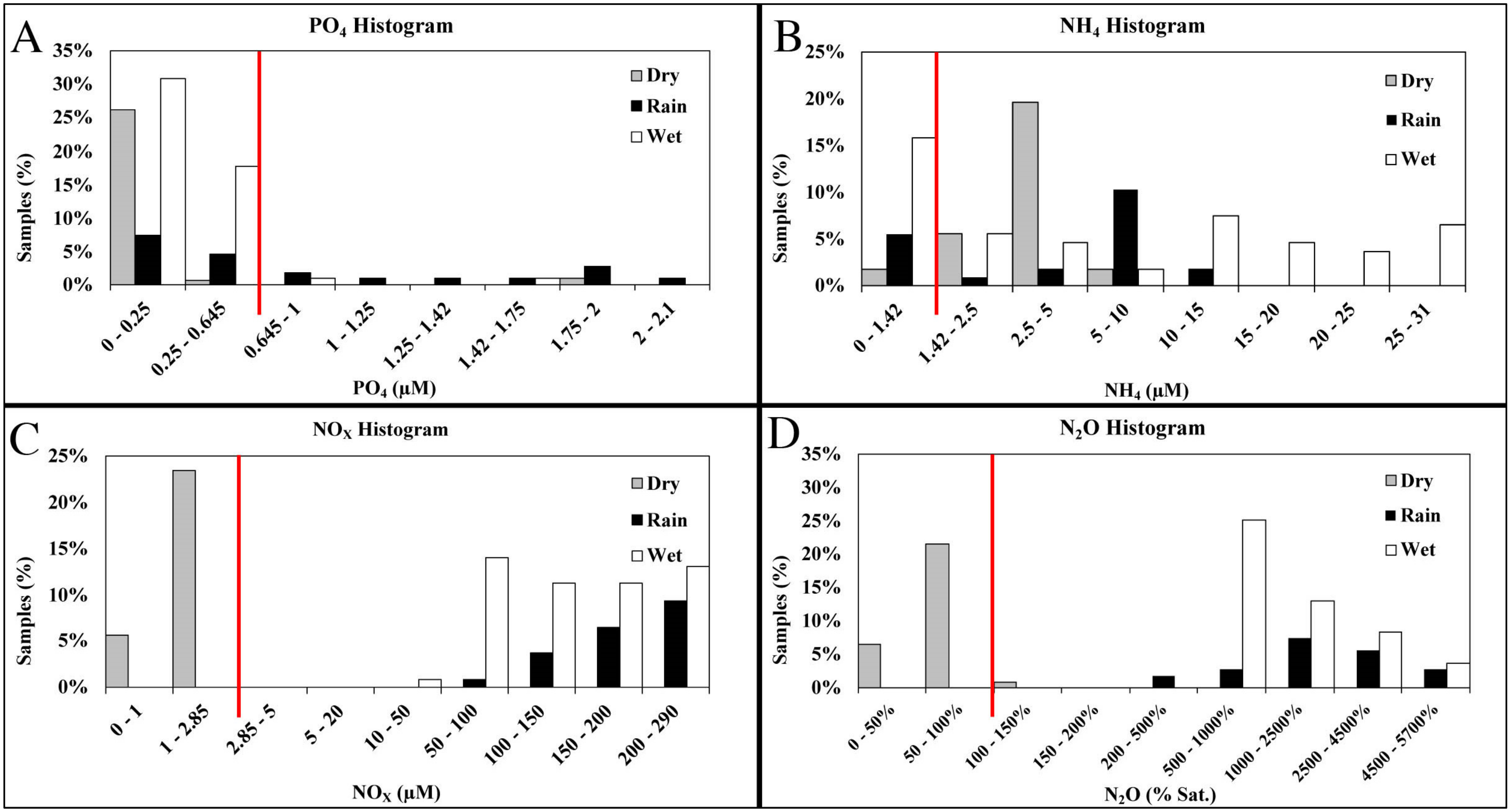

Figure 3: Histograms of dissolved inorganic nutrients and N_2O observations during dry, rain and wet periods at Double Crossing Creek, NSW. Red lines on plots A, B and C indicate the ANZECC trigger value for lowland streams in NSW, observations to the right of this line are above the trigger value. Red line on plot D indicates 100% saturation of N_2O in water. Observations to the left of this line indicate a sink and observations to the right of the line indicate a source to the atmosphere.

3.3. Phase shifts

The input of nutrients from anthropogenic sources such as fertilisers has changed the cycling of N and subsequent export of nutrients downstream in many catchments worldwide. Changes in biogeochemical processes have been driven by the modification of natural cycles, permitting concentrations of N in altered watersheds to be many fold higher than catchments with natural vegetation (Martin et al., 2004; Schilling & Libra, 2000; Van Herpe & Troch, 2000). Fertilisers rich in N were once thought to be denitrified in soils, though recent evidence has shown that soils can accumulate between 25 and 70 kg N ha^{-1} (Van Meter et al., 2016). Once saturated with rainfall, soils can release this N via overland runoff to streams or through nutrient rich waters feeding groundwater aquifers (Van Meter et al., 2016; Worrall et al., 2015). Therefore, the concentrations of nutrients in streams where watersheds contain fertilised soils are often driven by rainfall that flushes the nutrients from the soils, which are deposited and accumulate during the dry periods. This allows a phase shift in downstream areas receiving this runoff, modifying natural waterways from N deficient to N enriched (Vink et al., 2007).

Our time series at Double Crossing Creek revealed clear phase shifts (Figures 2 and 4). These shifting phases caused significant modifications in the nutrient loads during different hydrologic conditions. NO_X, N_2O and ^{222}Rn plotted as clear population clusters, before and after the first rain event: wet and rain are similar, whereas dry in all three was identified as a different population (Figure 5B, 5D and 5F). This is consistent with the flushing hypothesis for NO_X (Creed & Band, 1998), and the groundwater flow hypothesis for both NO_X and ^{222}Rn (Burt & Arkell, 1987). The similarities between populations of NO_X and ^{222}Rn may indicate that the source of NO_X is groundwater, though the scale of increase in NO_X when compared to ^{222}Rn indicates a weak correlation. There may be interactivity between overland flushing and groundwater flows contributing to this relationship.

3.3.1. N:P ratios

The mean N:P ratio of Double Crossing Creek was 35.99±3.7 in dry, rising to 1535±538 in rain and 1248±214 in wet (Figure 5E). Inorganic N:P ratios and concentrations are useful predictors of the possibility of algal composition and/or blooms in certain conditions (Zhang et al., 2018). The Redfield ratio of 16N:1P is the optimum ratio of nutrients for algal growth and ratios above or below 16 can indicate if a system is N limited or P limited (Howarth, 1988; Redfield, 1934; Slomp & Van Cappellen, 2004). Limiting nutrients for primary production can vary significantly, though the global average in rivers and coastal waters is 18 (Smith, 2003). The limiting nutrient in freshwater is often P, whereas N is often the limiting nutrient in estuaries and coastal marine systems (Fabricius, 2005; Redfield, 1934; Smith et al., 2003). Therefore, when freshwater systems experience large influxes of N or P, the freshwater creeks or receiving waters of estuaries and coastal marine systems can experience rapid eutrophication and algal blooms (Howarth, 1988; Howarth et al., 1996; Nixon et al., 1996). The high N:P ratios show that the creek was P limited in the water column, indicating that release of P can facilitate algal growth. The pulse of P on 4 February, after a small rain event (Figure 2) dropped the N:P ratio to 3, indicating an N limited system for ~24 hours. Following this small rain event there was a slick of algal growth observed in the creek (personal observation).

Figure 4: Images of Double Crossing Creek at the time series site over 7 days during dry (21st Mar), rain (24th Mar.) and wet (28th Mar.) periods.

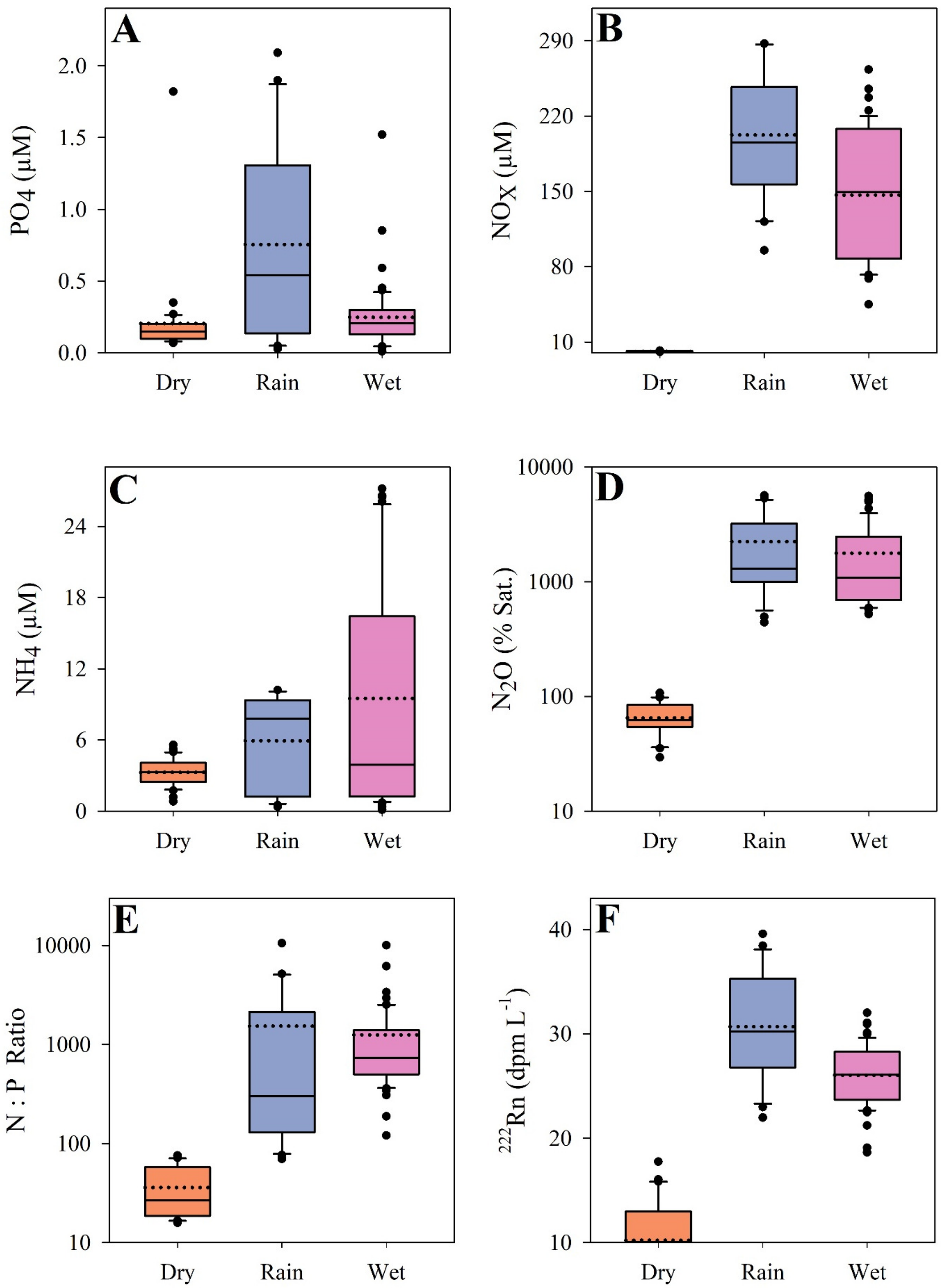

Figure 5: Box plots of nutrient (A, B and C), gas (D and F) and N:P ratio (E) observations during dry, rain and wet periods at Double Crossing Creek, NSW. Boxes indicate 25th and 75th quartile. Lines in boxes indicate median, dotted lines indicate mean. Whiskers are 10th and 90th percentiles. Outliers are plotted as dots.

3.4. Loads and drivers

Nutrient loads in Double Crossing Creek reflect the upstream fertiliser intensive land uses and the subsequent expected losses during and after rain events (Table 3). Phase shifts were evident in nutrient loads: NO_X loads in rain and wet respectively were 695 fold higher and 242 fold higher than dry; NH_4 loads were between 5.5 and 5.9 fold higher than dry in wet/rain; TDN was 7 fold and 20 fold higher than dry in wet and rain respectively; PO_4 in rain was 15 fold greater than dry and 7 fold greater than wet.

Table 3: Nutrient loads observed at time series site on Double Crossing Creek.

	NO_X (Kg ha yr^{-1})	NH_4 Kg ha yr^{-1})	TDN (Kg ha yr^{-1})	PO_4 (Kg ha yr^{-1})
Overall	**5.31**	**0.21**	**6.10**	**0.043**
Std. error	0.72	0.03	0.73	0.010
Dry	**0.02**	**0.05**	**0.72**	**0.010**
Std. error	0.00	0.01	0.11	0.005
Rain	**13.90**	**0.29**	**15.08**	**0.148**
Std. error	1.94	0.04	1.92	0.038
Wet	**4.86**	**0.27**	**5.53**	**0.019**
Std. error	0.77	0.04	0.77	0.003

Variable N loads are seen across the world (Figure 6) and are highly dependent on population, land use, atmospheric deposition and underlying geology (Seitzinger et al., 2002). Australian east coast mean N loads are estimated at <1 kg N ha yr^{-1} (Seitzinger et al., 2002). These loads can be up to >5 fold higher in the more populated areas of China, Europe and India (Seitzinger et al., 2002). Loads in the Tuckean Swamp, NSW where sugarcane is a major land use have been reported at 8.5 kg N-TDN ha yr^{-1} (Santos et al., 2013) and loads in a relatively pristine estuary at Hat Head, NSW were reported at 0.3 kg N-NO_3 ha yr^{-1} (Sadat-Noori et al., 2016). At Bucca Bucca Creek, White and Santos (2018) reported N loads in sites downstream of blueberry farms at 21.8 kg N-NO_X ha yr^{-1}, whereas at sites with no blueberries, loads were 1.6 N-NO_X ha yr^{-1}. Here, we found that N loads normalised to catchment areas were 6.1 fold higher than the modelled Australian east coast average (Figure 6), 0.3 fold lower than the Tuckean Swamp, 17 fold greater than Hat Head, 4 fold higher than sites with no blueberry farms in Bucca, and 3 fold lower than sites downstream of blueberry farms in Bucca. Combined, these observations demonstrate the very high nitrogen loads from the Hearnes Lake catchment.

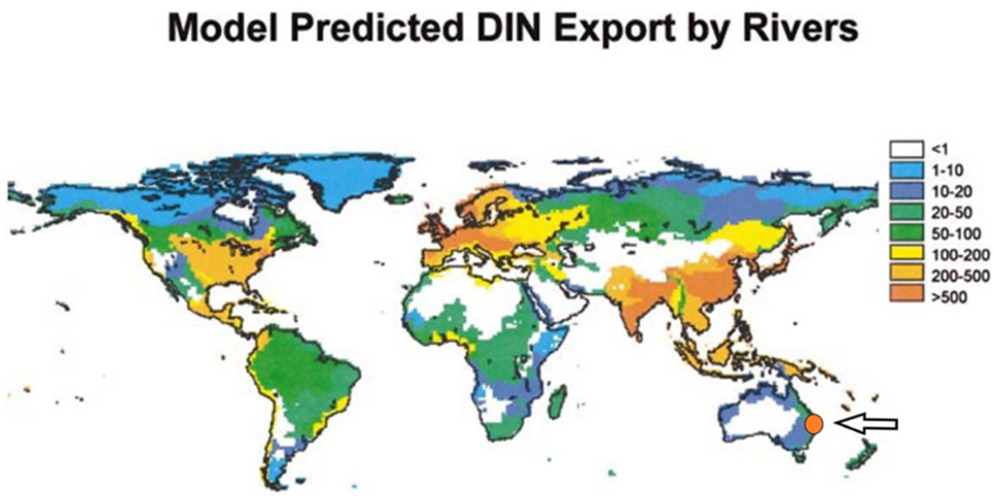

Figure 6: Model predicted global DIN export to rivers based on population, sewage, synthetic fertiliser use and atmospheric deposition. Units are kg dissolved inorganic N [DIN] km^2 yr^{-1} normalised to watershed area. Adapted from (Seitzinger et al., 2002). Orange dot shows the DIN load calculated in this study (552.4 kg DIN km^2 yr^{-1}) compared to global modelled loads.

Land use is a key factor in downstream nutrient loads (Harris, 2001) and fertiliser leaching from agricultural landscapes often dominates nutrient inputs to waterways (Puckett, 1994; Seitzinger et al., 2005). NH_4 is more easily adsorbed on soils, therefore NO_X is the most likely inorganic N species in groundwater and surface runoff as a result of fertiliser inputs on agricultural lands (De Boer & Kowalchuk, 2001; Puckett, 1994; Vimpany & Lines-Kelly, 2004). White and Santos (2018) showed a significant correlation between blueberry land use and NO_X in streams within the nearby Bucca Bucca catchment. We plotted Double Crossing Creek data against Bucca Bucca Creek (Figure 7). Double Crossing Creek plots above the regression line in NO_X concentrations, indicating additional leaching of nitrogen in the Hearnes Lake catchment.

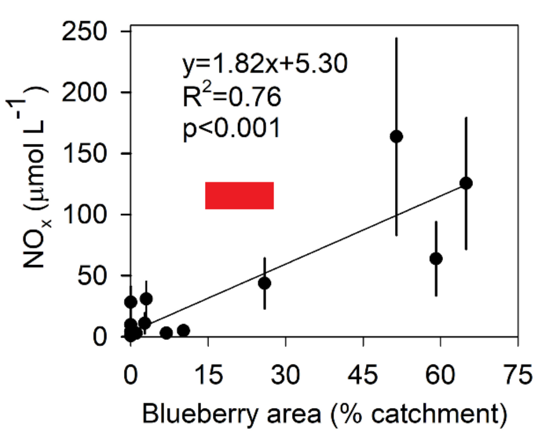

Figure 7: Plot of mean NO_X concentrations against blueberry land use (as a percentage of the catchment) observed in the Bucca Bucca Creek catchment, NSW, taken from White and Santos (2018). Additional red box represents mean concentration from this study at Double Crossing Creek. Box denotes ±SE and land use (calculated on total horticulture and only blueberry land use). Error bars are standard error.

Nutrients are sourced not only from blueberry farming, but all horticulture in the catchment as well as the possibility of legacy runoff from abandoned banana or other farms. Unfortunately, we cannot directly separate those nitrogen sources with the data available. Hunter and Walton (2008) reported loads downstream of banana farms at 0.38 kg N-TDN ha yr^{-1}. Our results are 16.5 fold higher than this, indicating that banana farms are not a likely a major source of N to Double Crossing Creek. The lack of historical nitrogen enrichments in Hearnes Lake sediments shown in our companion report (Conrad et al., 2018) is further evidence that nitrogen runoff is a recent development in this catchment, or that most of the nitrogen is exported to the ocean.

The dominant fertiliser intensive land uses upstream of Double Crossing Creek are bananas, cucumbers, and blueberries. Bananas require 100 kg N ha yr^{-1} (Newley et al., 2008), cucumbers in hothouses require 270 kg N ha yr^{-1} (Shen et al., 2010) and blueberries require 121 kg N ha yr^{-1} (Doughty et al., 1988). However, the actual amount and timing of fertilisers applied by local farmers are unknown. Assuming that our 66 days of observations represent an annual average, farmers are using the recommended fertiliser dose and our observations can be up scaled to annual loads, the calculated fertiliser loss to waterways would be between 19.7 % (calculated on N-NO_X) and 22.6 % (calculated on N-TDN). White and Santos (2018) estimated N losses in Bucca Bucca Creek between 18 % (calculated on N-NO_X) and 25 % (calculated on N-TDN).

Plotting NO_X against water parameters revealed distinct populations of samples (Figure 8). NO_X and ^{222}Rn dry samples plotted as a very different population to wet and rain (Figure 8A). As indicated earlier, this may be an interconnected contribution of groundwater and surface runoff to NO_X. Discharge and NO_X (Figure 8B) also supports the possibility of dual groundwater and runoff pathways, where during high rainfall, surface runoff dominates NO_X, followed by steady groundwater inflows presumably rich in NO_X. Salinity and NO_X have distinct populations, showing the phase shift between dry and rain/wet when the ICOLL opened (Figure 8C). The source of NO_X is clearly freshwater flushed from upstream land uses. NO_X exhibited a threshold limit of soil storage and subsequent NO_X release at above 40% soil moisture (Figure 8D), though continued to show high NO_X concentrations at high soil moistures. This is likely due to the solubility of NO_X and the continued flushing of soil storages and groundwater inflows. The general inverse relationship between DON and NO_X may suggest that decomposition of DON could be a source of NO_X, however the scale of NO_X increase reveals that this is not possible. Therefore, flushing of NO_X from agricultural soils, coupled with groundwater inflows are the likely sources of NO_X to Double Crossing Creek.

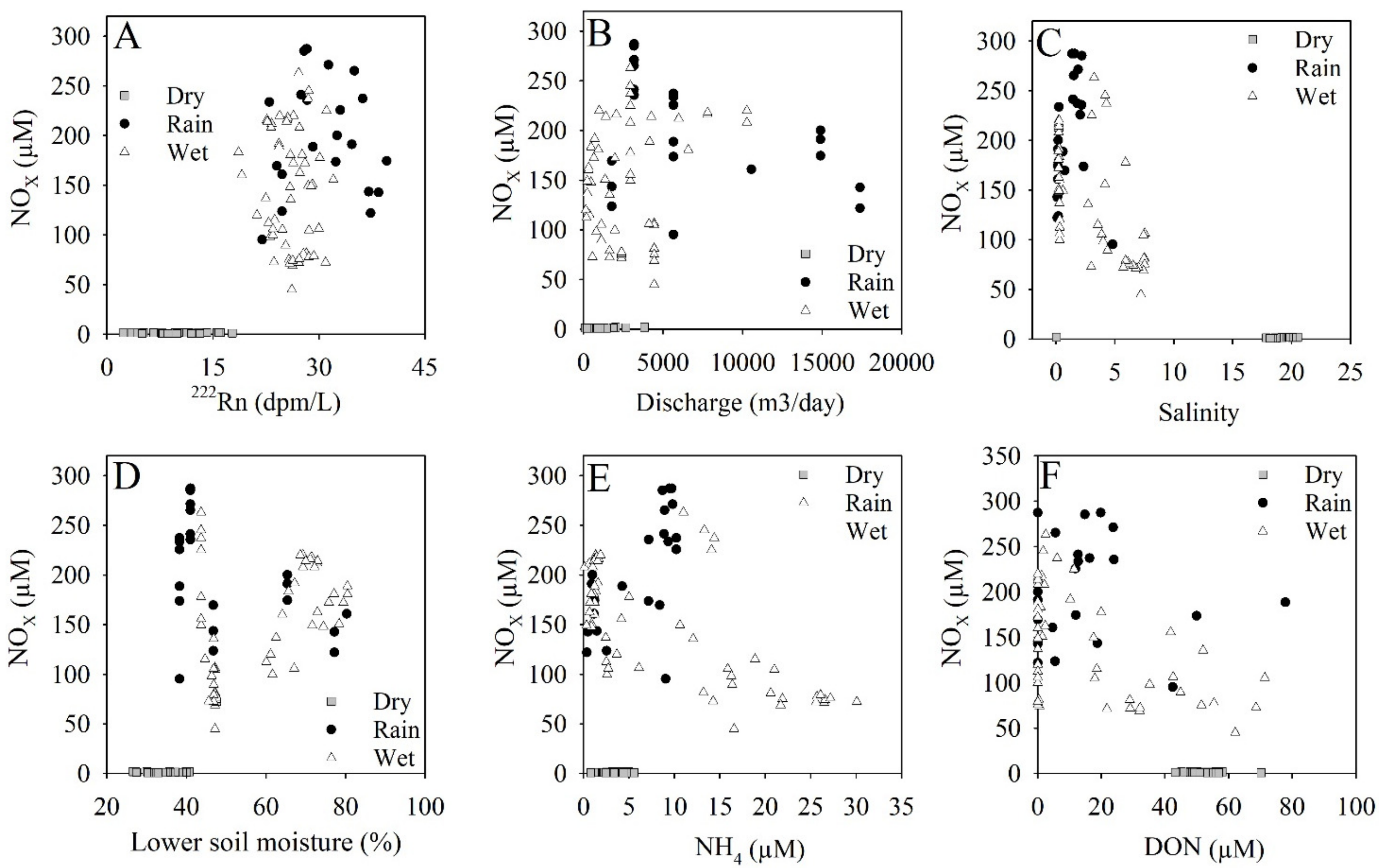

Figure 8: Scatter plots of NO_X versus potential drivers revealing population clusters during dry, rain and wet conditions.

3.5. N_2O

The water shifted from being a sink of atmospheric N_2O during dry conditions to a source of N_2O to the atmosphere during the wet and rain periods. Any N_2O values below 100% indicate that the water was a sink of atmospheric N_2O, and any values above 100% indicate the water was a source of N_2O to the atmosphere. In rain, N_2O reached the highest level at 5655 % saturation. From 50.4 % to 20.5 % of total samples (Figure 3C) over the 100% saturation state were in wet and rain periods respectively. 41.1 % of total samples (15.8 % rain and 25.2 % wet) were between 1000 % and 5700 % saturation. Results of Post-Hoc ANOVA revealed N_2O was significantly different ($p=<0.01$) between rain and dry as well as wet and dry periods. There was no significant difference between wet and rain. Production of N_2O in water can be a function of NO_X and NH_4 availability, oxygen saturation and groundwater discharges (Barnes et al., 2006; Wong et al., 2013). Therefore, as the availability of inorganic N species increases, there is an increased likelihood of N_2O production and subsequent release to the atmosphere.

Our estimates of water N_2O emissions to the atmosphere (450.07±59.87 µmol m^2 day^{-1} or 490.74±56.43 µmol m^2 day^{-1} depending on assumptions) are potentially the highest ever described in natural waterways, reaching 2859 µmol m^2 day^{-1} on 24 February. For example: Bange et al. (1998) reported emissions between 0.3 and 7.2 µmol m^2 day^{-1}, near the Oden Estuary, Germany; Barnes and Upstill-Goddard (2011) reported emissions between 2.4 and 76.8 µmol m^2 day^{-1} in 7 estuaries in the UK; de Wilde and de Bie (2000) found between 9.6 and 528 µmol m^2 day^{-1} from the Scheldt River in France; Dong et al. (2005) reported between 4.3 and 266 µmol m^2 day^{-1} from 10 UK estuaries; Hashimoto et al. (1999) reported between 1.44 and 153 µmol m^2 day^{-1} in Tokyo Bay. More locally, Brisbane River was reported to emit between 2.16 and 76.8 µmol m^2 day^{-1} (Musenze et al., 2014) and Coffs Creek, NSW was found to emit between -0.6 and 36.7 µmol m^2 day^{-1} (Reading et al., 2017). The highest emissions we could find in the literature was in the River Colne, UK, where Robinson et al. (1998) reported N_2O emissions between 0 and 1339.2 µmol m^2 day^{-1} with a mean of 31.2 µmol m^2 day^{-1}. The River Colne is classified as hypernutrified and has significant N inputs including sewage effluent and agricultural land runoff from the 500 km^2 of catchment (Robinson et al., 1998).

The Double Crossing Creek sink and source behaviour drives many of the populations of N_2O when plotted against various parameters. N_2O and ^{222}Rn concentrations are similar to NO_X, where dry is a sink and wet/rain are a source (Figure 9A). A possible combined groundwater and runoff component may be the driver of these populations. Discharge is considered a weak driver of N_2O due to the scattered populations of rain and wet (Figure 9B). Salinity and N_2O indicates that the origin of N_2O in Double Crossing Creek is the upstream freshwater catchment (Figure 9C).

The origin of N_2O is likely to be associated with flushing of N_2O rich soils, groundwater release and denitrification or nitrification between farm and sample site within the creek (Barnes et al., 2006; Statham, 2012; Wong et al., 2013). When N is transported via streamflow, instream cycling of N via mineralisation, assimilation, nitrification and denitrification occurs (Peterson et al., 2001). Nitrification of NH_4 upstream can produce N_2O as an intermediate, and therefore is likely to contribute to N_2O instream. Denitrification of NO_X is likely occurring instream and large losses of the inert gas, N_2, are expected. N_2O is a by-product of denitrification, not the primary result, therefore, as saturations above 5000 % N_2O are observed, the upstream NO_X concentrations are likely to be much higher than observed at this time series station. The concept of nutrient spiralling (Newbold, 1992) describes that as N moves via stream flow, loss pathways are limited to gaseous denitrification of NO_X, nitrification of NH_4, fractional gaseous losses and downstream export. Short term assimilation to biota will be ultimately cycled instream. Though the fraction of loss to N_2O is often small, the high surface area to volume ratios in headwater streams increase the probability of gaseous N exports (Alexander et al., 2000; Howarth et al., 1996). Therefore, nitrification of NH_4 and denitrification of NO_X, coupled with groundwater inflows and runoff from soils are likely the primary drivers of N_2O in Double Crossing Creek.

Table 4: Mean dissolved N_2O emission to the atmosphere calculated using equations derived from Raymond and Cole (2001) and Borges et al. (2004).

	N_2O emissions (R&C) (μmol m^2 day^{-1})	N_2O emissions (Borges 2004) (μmol m^2 day^{-1})
Overall	**450.07**	**490.74**
Std. error	59.87	56.43
Dry	**-9.41**	**-10.98**
Std. error	2.24	1.48
Rain	**1005.79**	**971.14**
Std. error	172.65	146.96
Wet	**478.93**	**573.76**
Std. error	68.22	66.88

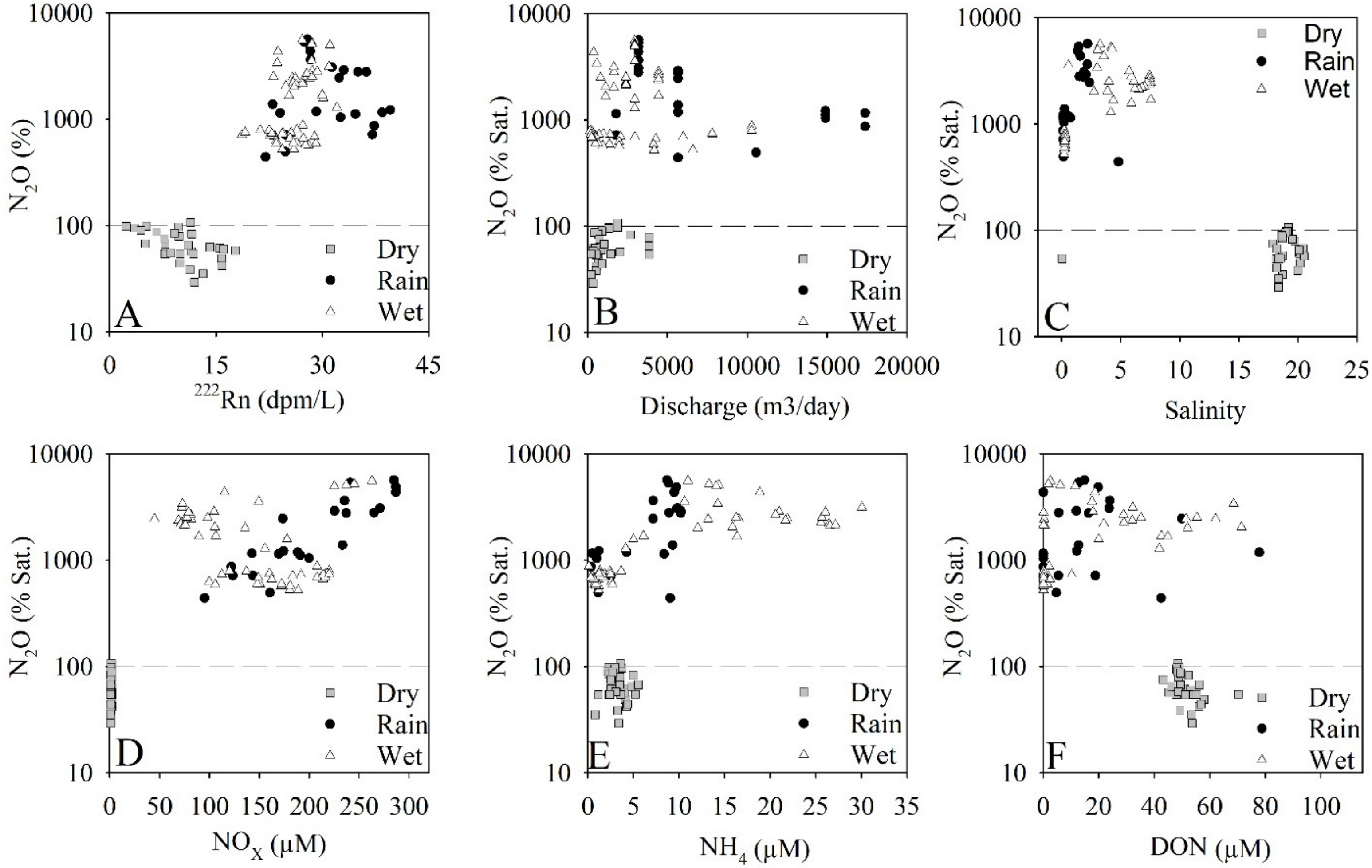

Figure 9: Scatter plots of N_2O versus potential drivers revealing population clusters during Dry, Rain and Wet conditions. Dotted line indicates 100% N_2O saturation: observations above the line are sources to the atmosphere and observations below the line are N_2O sinks.

4. Conclusions

1) NO_X was the dominant nitrogen [N] species accounting for 78.1 % of total N. The highest NO_X was 287.11 µM, 100 fold higher than the ANZECC trigger value. 55.1% of total NO_X samples were between 50 and 100 fold higher than the trigger values, demonstrating the need for effective action to reduce nitrogen runoff from this catchment.

2) Rainfall increased both concentrations and loads of nitrogen. NO_X concentrations and NO_X loads were 145 fold greater and 695 fold higher in rain than the dry period respectively. The results revealed the influence of upstream land use on water quality and phase shifting from nutrient deficient during dry conditions to hypernutrified following rainfall. The phase shift from very low NO_X to very high NO_X happened within one day.

3) Our N_2O emissions estimates are among the highest ever described, reaching 2859 µmol m^2 day^{-1} on 24 February. There was an apparent relationship between NO_X and N_2O as expected for waterways downstream of farmlands.

4) We calculate fertiliser loss from farms to waterways to be ~20 % of the recommended use. The dissolved nitrogen load estimates are 6 fold higher than the modelled Australian East Coast Average and similar to rivers in China, India and Europe with strong agricultural and urban influences.

As Hearnes Lake was open and draining in wet conditions when NOx loads were highest, it assumed that some of the water that passed the Double Crossing Creek time series site was exported to the coastal ocean and SIMP. As the marine environment is generally low in N and algal growth is limited by N, large NO_X loads may enable an increase in algal growth and drive shifts in coastal marine communities.

The results of this research suggest that there are opportunities for the agricultural activities in the catchment to decrease fertiliser use, alter land use practices, and capture N on farm before it escapes to creeks. We strongly recommend site-specific management to reduce N runoff and aquatic greenhouse gas emissions using the same techniques described in White and Santos (2018). Further estimates of greenhouse gas emissions from soils and dams are suggested. Ongoing or future impacts to habitats in Hearnes Lake and the SIMP may occur without effective management of nutrient runoff.

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6. Appendix

Results of water observations at Double Crossing Creek between 27 January and 3 April 2018.

Date	Sample	Rain (mm)	N_2O (nM)	N_2O (% Sat.)	NO_X (µM)	NH_4 (µM)	DON (µM)	TDN (µM)	PO4 (µM)	Salinity (ppt)	Depth (mm)	^{222}Rn in water (dpm L^{-1})
27/01/2018 18:19	**1**	0			1.44	1.72	48.94	52.10	0.13	20.1	1281	12.98
28/01/2018 9:40	**2**	0	3.8	61.9	1.46	2.57	50.77	54.80	0.15	20.1	1280	15.54
29/01/2018 10:40	**3**	10	3.7	60.0	1.76	3.18	53.56	58.50	0.07	20.1	1285	16.03
30/01/2018 9:55	**4**	0	3.0	49.2	1.81	4.09	58.00	63.90	0.08	20.2	1281	15.73
31/01/2018 10:35	**5**	0	3.8	62.5	1.81	3.98	50.21	56.00	0.09	20.2	1274	14.12
1/02/2018 11:48	**6**	0	2.8	42.3	1.82	4.27	56.01	62.10	0.10	20.0	1289	15.84
2/02/2018 12:01	**7**	7	4.7	67.5	1.37	3.51	49.52	54.40	0.09	20.4	1296	7.82
3/02/2018 10:01	**8**	19	4.0	57.2	1.93	4.08	45.19	51.20	0.10	20.5	1322	11.48
4/02/2018 11:55	**9**	31	4.2	54.5	1.83	3.63	47.94	53.40	1.82	20.2	1362	11.83
5/02/2018 8:24	**10**	16	4.5	65.2	1.66	4.83	46.11	52.60	0.35	20.1	1391	11.03
5/02/2018 17:29	**11**	5	5.4	79.5	1.65	3.53	48.72	53.90	0.08	19.7	1394	9.76
6/02/2018 9:40	**12**	3	5.6	83.2	1.73	4.98	52.39	59.10	0.10	19.5	1397	11.54
6/02/2018 17:06	**13**	0	6.4	97.4	1.79	3.77	48.24	53.80	0.07	19.2	1397	9.65
7/02/2018 9:40	**14**	0	7.1	107.3	1.59	3.59	48.52	53.70	0.19	19.2	1396	11.39
7/02/2018 17:23	**15**	0	6.4	98.8	1.54	2.98	48.28	52.80	0.12	19.0	1394	5.19
8/02/2018 10:10	**16**	0	6.4	98.2	1.45	2.29	48.96	52.70	0.23	19.1	1394	2.32
8/02/2018 17:55	**17**	0	6.1	95.5	1.40	2.95	48.05	52.40	0.18	19.0	1392	3.50
9/02/2018 17:26	**18**	0	5.7	90.4	1.30	2.15	48.35	51.80	0.14	18.6	1388	4.37
10/02/2018 12:35	**19**	0	5.3	84.5	1.26	2.29	49.95	53.50	0.21	18.7	1385	9.11
11/02/2018 14:40	**20**	0	5.5	87.5	1.47	2.73	49.40	53.60	0.18	18.7	1378	6.60
12/02/2018 8:01	**21**	0	3.7	58.2	1.24	3.04	48.72	53.00	0.21	18.7	1376	17.74
13/02/2018 14:02	**22**	0	2.4	38.5	1.30	3.28	49.32	53.90	0.27	18.7	1371	11.30
14/02/2018 15:36	**23**	0	4.5	75.3	1.28	2.55	43.27	47.10	0.24	17.8	1365	7.70
15/02/2018 14:30	**24**	12	3.3	54.4	1.25	2.34	53.11	56.70	0.19	18.4	1368	9.92
17/02/2018 11:40	**25**	0	3.3	54.2	1.19	1.18	51.23	53.60	0.10	18.2	1360	7.78
18/02/2018 11:05	**26**	0	1.8	29.3	0.88	3.39	53.73	58.00	0.20	18.4	1352	11.95
19/02/2018 13:05	**27**	0	2.2	35.2	0.83	0.80	53.47	55.10	0.10	18.4	1349	13.15
20/02/2018 11:10	**28**	4	3.6	54.7	0.86	2.45	55.29	58.60	0.10	18.5	1349	7.99
21/02/2018 9:35	**29**	22	3.6	54.8	0.80	5.21	70.29	76.30	0.16	18.4	1378	8.64
22/02/2018 10:20	**30**	0	4.6	67.8	0.83	5.57	56.20	62.60	0.16	18.2	1378	4.97
23/02/2018 12:21	**31**	8	3.0	44.3	0.85	4.36	56.89	62.10	0.15	18.2	1386	9.90
24/02/2018 7:40	**32**	51	35.9	441.8	95.16	9.04	42.49	146.69	0.50	4.8	1498	21.96
24/02/2018 10:55	**33**	42	117.6	1383.9	233.55	9.32	12.81	255.69	1.81	0.3	1574	22.98
24/02/2018 14:04	**34**	8	99.0	1184.4	188.55	4.26	77.87	270.69	2.09	0.6	1550	29.13
24/02/2018 17:15	**35**	6	202.0	2450.2	173.55	7.16	49.97	230.69	0.90	2.4	1420	32.39

Date	Sample	Rain (mm)	N_2O (nM)	N_2O (% Sat.)	NO_X (µM)	NH_4 (µM)	DON (µM)	TDN (µM)	PO4 (µM)	Salinity (ppt)	Depth (mm)	^{222}Rn in water (dpm L^{-1})
24/02/2018 20:00	**36**	2	240.1	2902.9	225.55	10.20	11.93	247.69	0.50	2.1	1263	33.01
24/02/2018 23:00	**37**	0	231.0	2776.7	237.11	10.20	16.38	263.69	0.47	1.8	1096	36.17
25/02/2018 4:58	**38**	2	234.4	2794.1	265.11	8.92	5.66	279.69	0.14	1.5	911	35.01
25/02/2018 8:05	**39**	0	254.2	3075.5	271.11	9.81	23.77	304.69	0.13	1.9	862	31.34
25/02/2018 11:03	**40**	0	286.6	3634.0	235.51	7.17	24.01	266.69	0.05	2.2	831	28.33
25/02/2018 13:57	**41**	0	342.6	4354.8	287.11	9.47	0.11	296.69	0.03	1.6	806	28.30
25/02/2018 16:57	**42**	0	389.3	4848.2	287.11	9.72	19.86	316.69	0.14	1.4	791	28.22
25/02/2018 20:00	**43**	0	434.7	5332.5	241.11	8.86	12.72	262.69	0.05	1.5	770	27.44
25/02/2018 22:55	**44**	0	458.8	5655.7	285.11	8.69	14.89	308.69	0.09	2.2	760	27.88
26/02/2018 5:12	**45**	0	450.1	5580.8	263.11	11.00	2.58	276.69	0.14	3.2	743	27.12
26/02/2018 8:04	**46**	0	412.9	5205.5	245.11	13.30	1.79	260.20	0.37	4.2	736	28.55
26/02/2018 10:55	**47**	0	403.3	5098.6	237.11	14.40	6.18	257.69	0.16	4.3	732	28.47
26/02/2018 13:55	**48**	6	405.6	4971.5	225.11	14.10	11.48	250.69	0.41	3.0	731	31.05
26/02/2018 17:00	**49**	26	313.3	3572.7	149.51	10.60	17.58	177.69	0.05	0.6	787	28.48
26/02/2018 20:00	**50**	2	107.6	1289.6	155.71	4.15	41.83	201.69	0.85	4.2	821	32.01
26/02/2018 22:55	**51**	0	126.1	1576.8	177.71	5.01	19.97	202.69	1.52	5.9	819	30.10
27/02/2018 5:01	**52**	0	131.7	1699.4	106.51	6.10	42.59	155.20	0.31	7.6	790	29.97
27/02/2018 8:00	**53**	0	190.7	2437.7	81.51	13.20	0.39	95.10	0.19	7.5	782	28.21
27/02/2018 11:00	**54**	0	225.0	2863.0	104.71	21.00	17.98	143.69	0.29	7.4	773	28.57
27/02/2018 14:06	**55**	0	211.9	2689.8	81.11	20.60	28.98	130.69	0.28	7.5	763	27.78
27/02/2018 16:57	**56**	0	193.8	2457.1	75.31	21.90	51.48	148.69	0.21	7.5	754	25.73
27/02/2018 19:57	**57**	0	186.4	2366.6	68.91	21.70	32.08	122.69	0.16	7.4	746	26.25
27/02/2018 10:55	**58**	0	188.5	2446.9	45.00	16.58	62.11	123.69	0.01	7.2	740	26.15
28/02/2018 5:08	**59**	0	173.6	2271.3	72.00	25.58	29.11	126.69	0.04	7.0	730	27.14
28/02/2018 7:56	**60**	0	169.8	2210.4	71.40	26.48	21.81	119.69	0.16	6.8	728	25.83
28/02/2018 10:57	**61**	0	159.6	2116.8	74.10	26.58	0.62	101.30	0.05	6.6	727	26.27
28/02/2018 16:54	**62**	0	164.4	2152.3	75.80	27.18	0.10	103.08	0.06	6.2	720	27.19
28/02/2018 10:55	**63**	0	198.4	2525.2	77.60	25.68	55.41	158.69	0.04	6.1	711	28.56
1/03/2018 4:58	**64**	0	221.2	2828.2	79.00	26.08	0.10	105.18	0.10	5.9	706	29.27
1/03/2018 11:02	**65**	0	238.5	3139.9	72.40	30.08	32.21	134.69	0.10	5.7	704	30.93
1/03/2018 20:00	**66**	0	161.3	2015.0	135.60	12.08	52.01	199.69	0.11	2.7	677	25.99
2/03/2018 8:07	**67**	0	162.0	2053.6	105.40	15.88	71.41	192.69	0.05	3.9	669	24.82
2/03/2018 19:57	**68**	0	131.1	1668.6	89.40	16.38	44.91	150.69	0.15	4.4	667	25.28
3/03/2018 10:00	**69**	0	197.3	2514.0	98.20	16.28	35.21	149.69	0.04	4.0	664	23.10
4/03/2018 10:40	**70**	0	259.2	3401.4	72.80	14.28	68.61	155.69	0.01	3.0	658	23.61
5/03/2018 9:50	**71**	0	336.5	4352.6	115.20	18.88	18.61	152.69	0.18	3.6	651	23.71
6/03/2018 9:33	**72**	28	97.2	1142.4	169.40	8.39	0.10	177.89	0.25	0.8	685	24.04
6/03/2018 13:20	**73**	53	62.5	716.7	123.60	2.55	5.54	131.69	1.81	0.2	821	24.77
6/03/2018 17:05	**74**	2	62.4	716.9	143.40	1.47	18.82	163.69	1.90	0.2	1021	37.05
7/03/2018 6:50	**75**	20	107.9	1221.4	174.40	1.22	12.07	187.69	1.04	0.2	885	39.57

Date	Sample	Rain (mm)	N_2O (nM)	N_2O (% Sat.)	NO_x (µM)	NH_4 (µM)	DON (µM)	TDN (µM)	PO4 (µM)	Salinity (ppt)	Depth (mm)	^{222}Rn in water (dpm L^{-1})
7/03/2018 11:30	**76**	0	95.9	1113.3	191.00	0.90	0.10	192.00	0.79	0.2	811	34.64
7/03/2018 17:00	**77**	0	89.9	1039.4	200.00	0.98	0.10	201.08	0.63	0.2	758	32.55
8/03/2018 7:15	**78**	0	77.7	876.5	208.00	0.10	2.10	210.20	0.39	0.2	691	27.22
8/03/2018 18:27	**79**	0	70.2	797.0	220.00	1.35	0.10	221.45	0.28	0.2	669	26.38
9/03/2018 8:22	**80**	0	65.8	735.9	216.00	1.24	0.10	217.34	0.21	0.2	650	25.50
9/03/2018 16:45	**81**	4	65.4	748.1	218.00	1.44	1.25	220.69	0.22	0.2	646	25.56
10/03/2018 13:20	**82**	6	59.9	693.5	212.00	0.64	0.10	212.74	0.28	0.2	641	23.30
11/03/2018 18:09	**83**	10	59.0	665.1	214.00	1.16	0.14	215.30	0.21	0.3	632	25.40
12/03/2018 10:01	**84**	0	61.0	690.1	208.00	1.01	0.10	209.11	0.13	0.3	623	23.22
13/03/2018 11:45	**85**	0	59.6	699.1	216.00	1.67	0.10	217.77	0.19	0.3	614	22.64
14/03/2018 11:02	**86**	0	62.5	729.6	214.00	1.56	0.10	215.66	0.12	0.3	607	22.69
15/03/2018 9:22	**87**	0	65.7	742.4	220.00	1.87	0.10	221.97	0.18	0.3	602	24.44
16/03/2018 10:20	**88**	0	63.9	728.9	191.80	1.60	10.29	203.69	0.14	0.3	597	24.30
17/03/2018 14:40	**89**	0	57.7	713.1	183.40	1.36	0.93	185.69	0.19	0.3	592	18.63
18/03/2018 14:30	**90**	0	59.2	753.2	160.20	1.23	0.10	161.53	0.20	0.3	587	19.07
19/03/2018 12:10	**91**	0	64.5	785.6	137.00	2.46	0.10	139.56	0.27	0.3	585	22.48
20/03/2018 13:10	**92**	0	63.9	792.2	120.00	3.66	0.10	123.76	0.21	0.3	583	21.22
21/03/2018 11:40	**93**	4	60.8	732.8	112.40	2.51	0.10	115.01	0.20	0.3	585	22.86
22/03/2018 11:31	**94**	8	52.8	627.2	99.80	2.59	0.10	102.49	0.27	0.3	590	23.47
23/03/2018 10:11	**95**	16	51.8	591.8	106.00	2.74	0.10	108.84	0.28	0.3	621	23.48
24/03/2018 11:07	**96**	149	101.7	1158.4	142.60	0.49	0.10	143.19	1.26	0.1	821	38.43
24/03/2018 16:02	**97**	12	74.8	866.4	121.80	0.36	0.10	122.26	1.46	0.1	783	37.29
25/03/2018 13:40	**98**	0	42.4	494.1	160.80	1.15	4.74	166.69	0.58	0.2	516	24.78
26/03/2018 15:40	**99**	0	44.6	525.3	180.60	1.16	0.10	181.86	0.59	0.2	453	25.95
27/03/2018 10:13	**100**	0	45.0	522.2	188.80	1.22	0.10	190.12	0.45	0.2	435	24.34
28/03/2018 13:45	**101**	0	48.1	573.5	172.20	1.23	0.10	173.53	0.35	0.2	384	28.02
29/03/2018 10:20	**102**	0	51.4	593.5	150.80	0.88	1.52	153.20	0.37	0.2	384	29.10
30/03/2018 11:14	**103**	0	48.8	575.3	180.80	0.86	0.10	181.76	0.33	0.2	395	27.60
31/03/2018 11:32	**104**	0	51.8	600.1	172.40	0.70	0.10	173.20	0.33	0.2	368	26.35
1/04/2018 12:01	**105**	0	50.8	600.6	148.00	0.86	0.10	148.96	0.44	0.2	361	25.90
2/04/2018 10:16	**106**	0	58.0	664.0	162.60	0.67	2.42	165.69	0.29	0.3	354	27.29
3/04/2018 11:01	**107**	0	59.9	686.7	149.20	0.33	0.10	149.63	0.24	0.3	349	28.89