THE RUNOFF CARRYING CAPACITY OF COFFS COASTS ESTUARIES

Final Report - Coffs Harbour City Council Environmental Levy Grants Program

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Executive Summary

Land-use intensification on the Coffs Coast of NSW is expected to lead to the export of more nutrients to downstream coastal waters and estuaries. However, the nutrient carrying capacity of the streams and linkages to land use remain unknown. Here, we examined the spatial and temporal drivers of dissolved nutrient loads in 11 regional creeks from Corindi in the north to Pine Creek in the South covering a diverse land use gradient.

Samples were collected over contrasting hydrological conditions from dry to wet. Out of the 102 days of observations, 53 days were influenced by rainfall at rates of $\geq$1, $\geq$10 and $\geq$25mm day^{-1} for 47, 4 and 2 days, respectively (BOM, 2019b)

To establish the carrying capacity, we compare our observations to ANZECC guidelines. 65% and 66% of total samples collected from peri-urban and agricultural creeks were above nitrate + nitrite (NOx) ANZECC guidelines. The highest total dissolved nitrogen (TDN) concentration was observed in Woolgoolga Creek and Double Crossing Creek (3.3 mg N L^{-1}and 3.8 mg N L^{-1}). Most peri-urban and agricultural creeks carrying NOx runoff were above Southeast Australia, ANZECC lowland water quality guidelines, while pristine creeks were usually within the recommended values.

Following an 80 mm rain event, loads of dissolved inorganic nitrogen (DIN) from agricultural catchments reached 368 mg N m^{-2} catchment area day^{-1}. Forest and peri-urban catchments had total dissolved nitrogen (TDN) loads equivalent to 17.8 and 31.1% of agricultural catchments. Overall, nitrogen pollution followed this order: Double Crossing Creek>Woolgoolga Creek> Coffs Creek> Ferntree Creek>Pinebrush Creek>Arrawarra Creek>Cordwell Creek>Boambee Creek>Pine Creek>Upper Corindi Creek>Bonville Creek.

Isotopic tracers ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) in the forest and peri-urban catchments creeks indicated fertilisers and soil nitrogen as the main sources of nitrate. Double Crossing Creek received a mix of recirculated greywater and nitrogen fertilisers.

Overall, we showed that agricultural intensification and episodic rainfall events are the major drivers of nutrient loads in Coffs Coast Region. Better management of on-farm fertilizer use is necessary to improve creek water quality and ensure nutrients do not exceed ANZECC guidelines.

1. Introduction

Long term nitrogen (N) and phosphorus (P) loadings from anthropogenic activities have led to extensive nutrient enrichment and eutrophication in rivers, estuaries and the coastal ocean worldwide (Beman et al., 2005; Howarth and Marino, 2006; Vitousek et al., 1997). Total inorganic nitrogen (N) runoff export from global rivers is expected to increase from 0.1 teragram of N per day in 1850 to 0.3 teragram of N per day by 2050, mostly as a result of increasing fertiliser use (Jickells et al., 2017). The Coffs Coast region is experiencing rapid land-use change and increasing agricultural development, which is expected to increase nutrient losses to rivers and estuaries (Lee et al., 2019).

An understanding of the effects of hydrology and land use on aquatic nutrient fluxes is vital for effective pollution management in subtropical regions like the Coffs Coast Region (CCR) (Correll and Weller, 1989; Wong et al., 2018). In our previous investigations, we revealed 18-25% of added fertiliser was lost to the Bucca Bucca Creek with nitrate concentrations >25 fold higher than the Australia and New Zealand Environment and Conservation Council (ANZECC) trigger values (White, 2018). Here, we report new observations covering a much larger area extending from Corindi in the North to Pine Creek in the South.

Understanding the sources, fate and delivery pathways of nitrate (NO_3^-) is important to plan water management (Kaushal et al., 2011; Xue et al., 2009). Groundwater and surface water connectivity often control the surface discharge and act as the main pathways that deliver nitrogen to rivers. Radon (^{222}Rn) has been used as a tracer to assess groundwater flux in river/stream systems (Makings et al., 2014; Webb et al., 2019). High ^{222}Rn concentrations often correspond to high groundwater discharge. Furthermore, the dual isotopic composition of NO_3^- i.e., $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- can distinguish different sources of NO_3^- (Archana et al., 2018; Cho et al., 2019; Lohse et al., 2013) because those sources (e.g. atmospheric deposition, sewage and fertilizer) often exhibit distinctive isotopic signatures.

In this report, we quantify nutrient discharge into eleven streams at the head of their estuaries across a land-use gradient in the Coffs Coast Region. We specifically test whether the carrying capacity of the streams is exceeded by using ANZECC water quality guidelines. Our analysis includes

1) A quantification of catchment nutrient runoff in 11 catchments in the Coffs Coast Region.
2) An assessment of sources, pathways and drivers of catchment nutrient runoff.
3) A regional comparison of water quality indicators in these creeks to the ANZECC water quality guidelines for Lowland streams in NSW.

2 Material and Methods

2.1 Study site

This study was carried out in freshwater streams (3rd and 4th order) along the Coffs Harbour coastal region (CCR), Australia. We selected 11 catchments spanning a land-use gradient (Fig.1) with similar geomorphology and climate. Basaltic soils (e.g., Kandosol) are found in all catchments and are typically well-drained with podzolic horizon features (Isbell, 2016; Milford, 1999a; b). The area experiences a subtropical climate with an average annual rainfall of 1700 mm (mainly falling in January to May) and ambient temperatures ranging from 10ºC to 28ºC (BOM, 2017). Similar to many catchments on the east coast of Australia, the regional hydrology is strongly influenced by episodic rainfall (WBM, 2018). There are on average 141 days influenced by rainfall annually, with rates of ≥1, ≥10 and ≥25mm day^{-1} for 89, 34 and 15 days, respectively (BOM, 2019b).

Land uses ranged from pristine forest (Arrawara Creek) to residential (Coffs Creek) and intensive agriculture (Double Crossing Creek and Pine Brush Creek). Vegetation types in those catchment areas are dominated by remnant wet-sclerophyll and mixed rainforest (WBM, 2009). Some catchments such as Pine Brush Creek (42%) and Double Crossing Creek (35%) have a significant agricultural land cover (Fig 1). A large portion of many catchments is covered with urban, agricultural, and cleared land. This pattern of land use is named here as peri-urban (Alexander Wandl et al., 2014). For this study, we divided 11 catchments into three different categories (forest, peri-urban, and agriculture) based on the percentage of land use. The 11 catchments occupy 164.2 km^2 among which 69.1% (113.5 km^2) is forest, 24.2% (39.7 km^2) is peri-urban (which includes 5.3% urban and 18.8% cleared land) and 6.8% (11.1 km^2) is intensive agriculture.

The Coffs Coast Region is mostly modified mostly by agriculturally dominated catchments (e.g. Pine Brush Creek and Double Crossing Creek having ~35-42% of the total area covered by intensive horticulture). From the mid of 20th century, banana cultivation dominated in the region (Yeates, 1993). In the early 2000's, blueberry (*Cyanococcus*) farming and cucumber (*Cucumis sativus*) hothouses have expanded, replacing most banana farms. The resident population densities for these catchments range from 0.0 person km^{-2} in the forest catchment of Arrawara Creek to >200 persons km^{-2} in the urban Coffs Creek catchment (ABS, 2017).

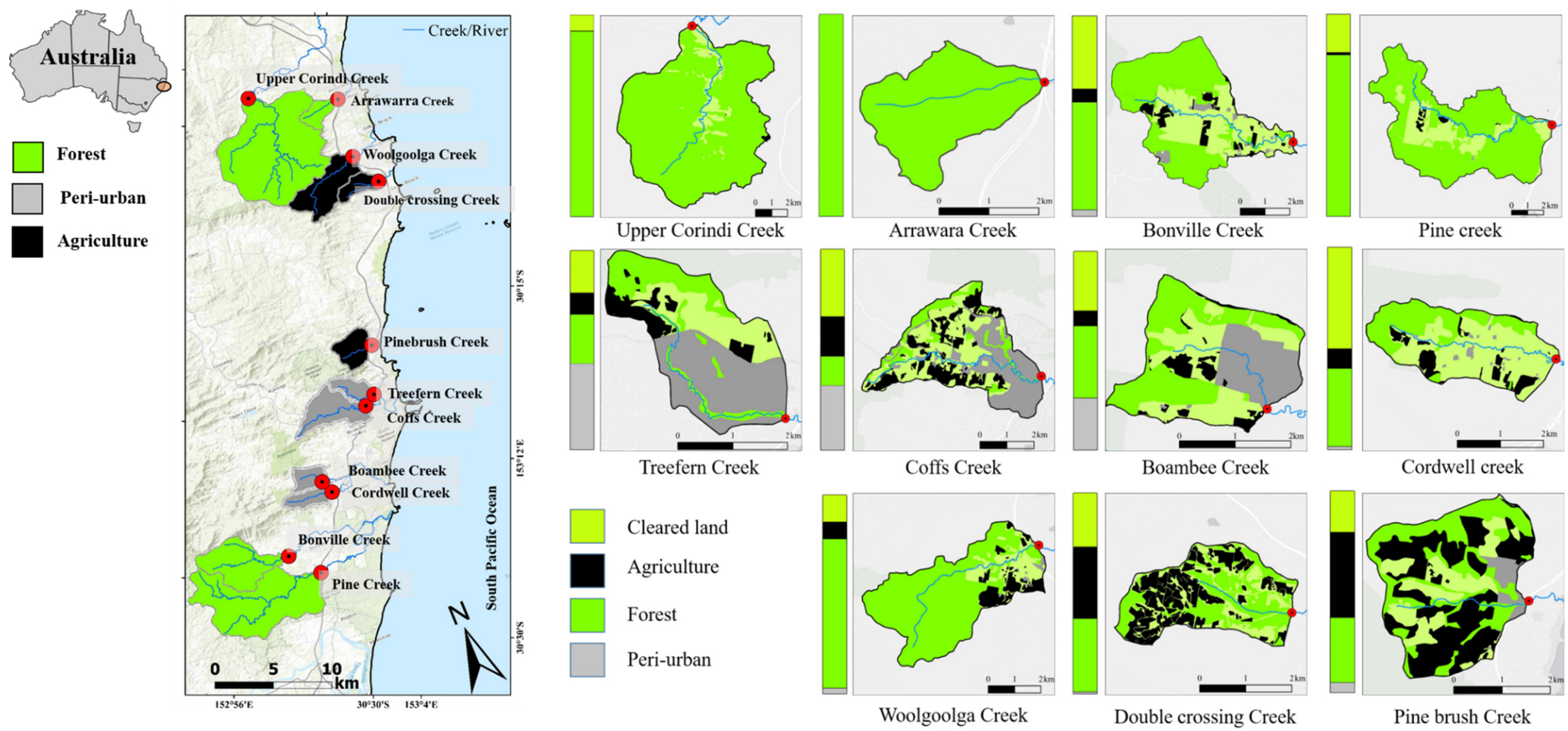

Figure 1 Study sites on the East Coast of Australia, classification of catchments (left) and land-use (right). Catchments were classified into three groups, i.e. Forest, peri-urban and agriculture. Individual catchment land-use classification on the right (north to south). Agriculture land use includes horticulture. Urban infrastructure, dwellings and cleared land are included in peri-urban land use. Red circles indicate sampling stations. Samples were collected in 3rd & 4th order streams just upstream of the estuarine interface. *Close proximity of agriculture to our sample site in Woolgoolga creek led us to classify as agriculturally influenced.

2.2 Sampling and analysis

Discrete samples were collected from the centre of the stream at weekly intervals (from 10th of January until the 2nd of May 2019) for 102 days covering a wide range of hydrological conditions (Fig.2). Surface water samples were collected for the analysis of dissolved inorganic nitrogen (DIN) (NH_4^+, NO_3^- and NO_2^-), dissolved organic carbon (DOC), and NO_3^- isotopes ($\delta^{15}N$-NO_3^- and $\delta^{18}O$ NO_3^-). Nutrient and stable isotope samples were filtered on-site using 0.45 µm disposable cellulose acetate syringe filters into 10 mL polyethylene vials, kept on ice for less than 4-hrs, then stored at -18 ºC until analysis. Analyses for ammonium (NH_4^+), NOx (nitrate plus nitrite), and total dissolved nitrogen (TDN) were carried out colorimetrically using a Flow Injection Analyser (Lachat Flow Injection Analyser).

The 50 samples for $\delta^{15}N$-NO_3^- and $\delta^{18}O$ NO_3^- were analysed using the chemical azide method. NOx was quantitatively converted to NO_2^- using cadmium reduction then to NO_2^- using sodium azide. The resultant N_2O was then analysed on a Hydra 20–22 continuous flow isotope ratio mass spectrometer (CFIRMS; Sercon Ltd., UK) interfaced to a cryoprep system (Sercon Ltd., UK). Nitrogen and oxygen isotope ratios are reported in per mil (‰) relative to atmospheric air (air) and Vienna Standard Mean Ocean Water (VSMOW), respectively. The initial NO_2^- concentrations were typically < 1% relative to NO_3^-. Hence, the measured of $\delta^{15}N$–N_2O represents the signature of $\delta^{15}N$– NO_3^-. The reproducibility of the isotopic analyses based on repeated analysis of internationally-recognized and laboratory internal standards (KNO_3^-) lies within ±0.3‰ for $\delta^{15}N$ and ±0.5‰ for $\delta^{18}O$.

DOC samples were filtered through pre-combusted 0.7µm GF/F filters (Whatman) into 40 ml borosilicate vials treated with 30µL of H_3PO_4 and then analysed using a total organic carbon analyser (Thermo Fisher Scientific, ConFLo IV). Discrete samples of radon were collected in ~2-liter gas-tight bottles and then measured using a radon-in-air monitor (RAD-7, Durridge Company) in a laboratory within 24 hours of collection (Lee and Kim, 2006). Calculations of ^{222}Rn (dpm L^{-1}) were done using polonium (^{218}Po; $T_{1/2}$ =3.10 min) counts inside the RAD-7 after accounting for air and water volumes, efficiency, sample time and time lag as described elsewhere (Lee and Kim, 2006). Physio-chemical parameters such as dissolved oxygen (DO %), salinity, temperature (ºC), and pH were measured using a Hach multimeter (40 HQd, Hach, USA). Discharge (Velocity x Cross-section area) of the water calculated using portable current meter (Global water company flow probe).

Nutrient loads from upper headwater catchments to the estuary were estimated by multiplying surface runoff by the nutrient concentrations in the surface water and normalizing it over the catchment area. Daily runoff data from 10th January to 2nd May 2019, based on an AWRA-L model and meteorological data (rainfall and temperature,) (30.30S, 153.10E) were acquired from the Australian Bureau of Meteorology (BOM, 2019a). The AWRA-L model is a grid-based distributed water balance model conceptualised for small catchments that is a function of streamflow observations, soil moisture, and evapotranspiration. Since only one rainfall station was available for hydrology comparisons, we assumed a homogenous parametrisation of daily runoff calculated from an average (mm m^{-2} day^{-1}) of all catchments.

Catchments were delineated by creating polygons following 1 m interval contours surrounding the waterways and with a digital elevation model (DEM) in ArcGIS 10.5.1, ESRI. Land use (m^2 and % catchment) was classified using field observations, Coffs Harbour Local Environmental Plan, and Google Earth 2019 imagery (Council, 2009). Catchments were classified into three groups, i.e. forest, peri-urban, and agriculture. Agriculture land use includes horticulture. Urban infrastructure such as roads, public buildings, dwellings, and cleared/transition land were included in Peri-urban land use.

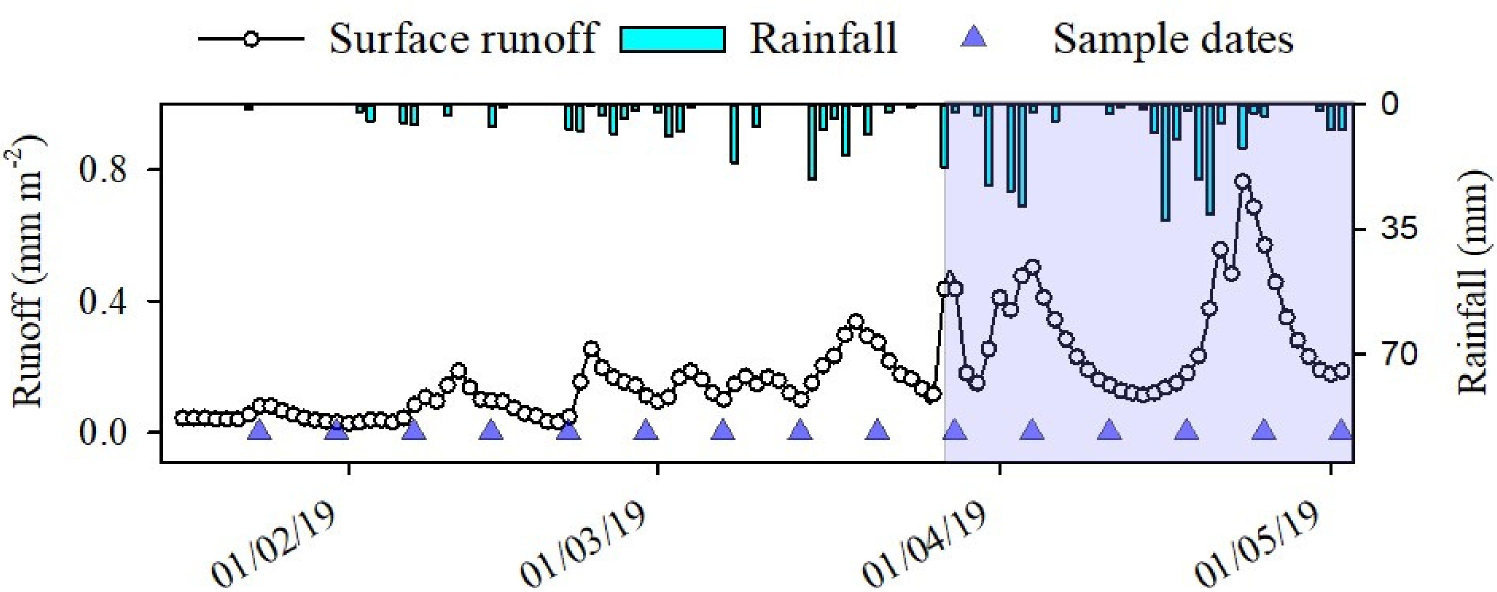

Figure 2 Rainfall and surface runoff (based on the AWRA-L) model over 102 days in the Coffs Coast region (CCR) catchments (BOM 2019). Sample dates are shown along the bottom as triangles and wet section marked in light blue shading.

3. Results

3.1 Hydrology

We captured diverse hydrological conditions from dry to wet over the 15 surveys. During dry conditions, runoff did not exceed 0.4 mm. The first rain event delivered ~17.6 mm on March 27th. Maximum weekly rainfall was 80 mm, which coincided with maximum catchment runoff of 0.8 mm day^{-1}. Out of the 102 days of observations, 53 days were influenced by rainfall at rates of ≥1, ≥10 and ≥25mm day^{-1} for 47, 4 and 2 days, respectively (BOM, 2019b). We classified hydrology into dry (17th January and 27th March 2019) and wet (28th March 2019 to 2nd May 2019) (Fig.2).

3.2 Nutrients

Dissolved inorganic nitrogen (DIN) concentrations ranged between 0.001 and 3.7 mg N L^{-1} with averages of 0.05 and 0.5 mg N L^{-1} for a dry and wet period, respectively. DIN and phosphate (PO_4) concentrations were generally higher during the wet period compared to the dry period in all sites except for the forest catchment of Arrawarra Creek (Fig. 3). The highest DIN concentration (3.2 mg N L^{-1}and 3.7 mg N L^{-1}) was observed in Woolgoolga Creek with 8.6% agricultural land use and Double Crossing Creek with 35.4% agriculture (fig. 3). Creeks with agricultural catchments and closest to non-point sources such as Woolgoolga and Double Crossing Creek exhibited high DIN, particularly during the wet periods, while forested catchments were generally higher in DOC concentrations (Fig 3). DON was the dominant form of nitrogen during the dry period (forest - 81.7 ±14.3%, peri-urban - 68.8±23.4%, agriculture - 69.1±25.8%) (Fig. 4) whereas during wet period NOx was foremost form of nitrogen in peri-urban and agriculture catchments (forest - 18.1±22.8%, peri-urban - 52.9±29.5%, agriculture - 71.5±24.0%).

3.3 Groundwater discharge tracer

Radon (^{222}Rn), a natural groundwater discharge tracer had higher concentration during the dry period than the wet period in all creeks. The highest concentrations of ^{222}Rn were measured in the peri-urban catchment of Boambee Creek (524.2 dpm L^{-1}). All peri-urban catchments had relatively higher ^{222}Rn concentration than agricultural and forest catchments (forest 63.0±18.8 dpm L^{-1}, peri-urban 105.5±62.2 dpm L^{-1}, agriculture 86.7±15.0 dpm L^{-1}) (Fig. 5).

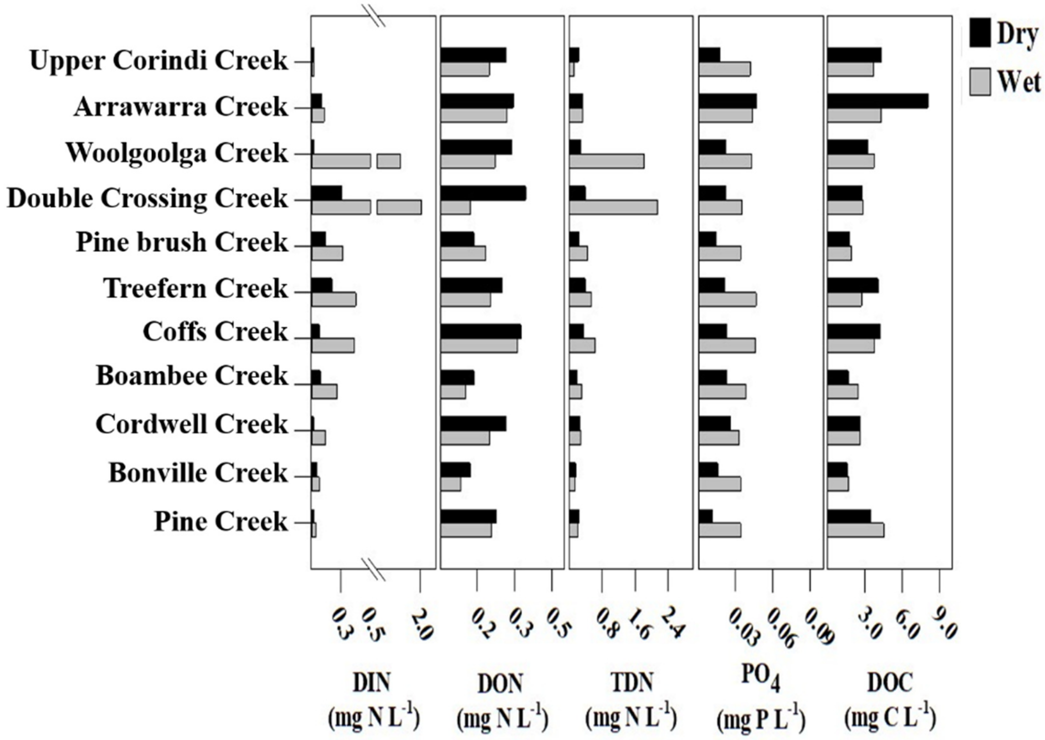

Figure 3 Average creek nutrient concentrations along the land-use gradient during dry and wet conditions. DIN, PO_4 were higher during the wet period in all creeks (except for PO_4 in Arrawarra Creek).

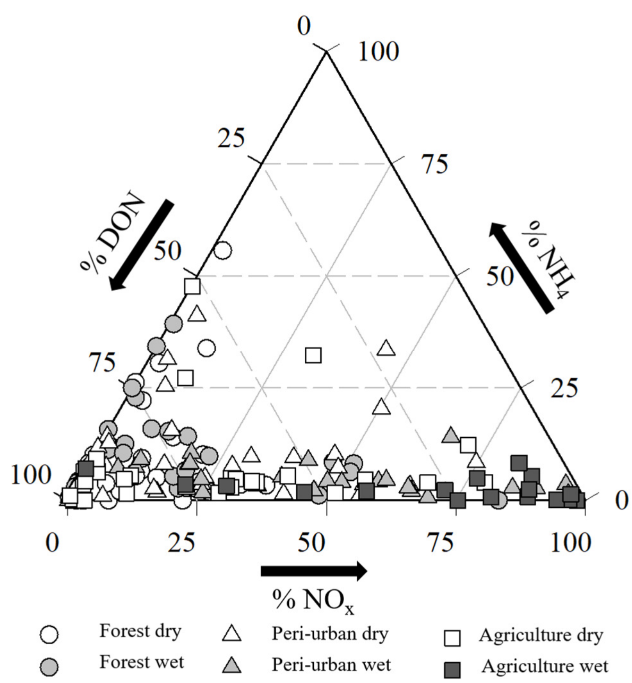

Figure 4 The relative contribution of the different nitrogen species in forest, peri-urban and agricultural catchment during the dry and wet season

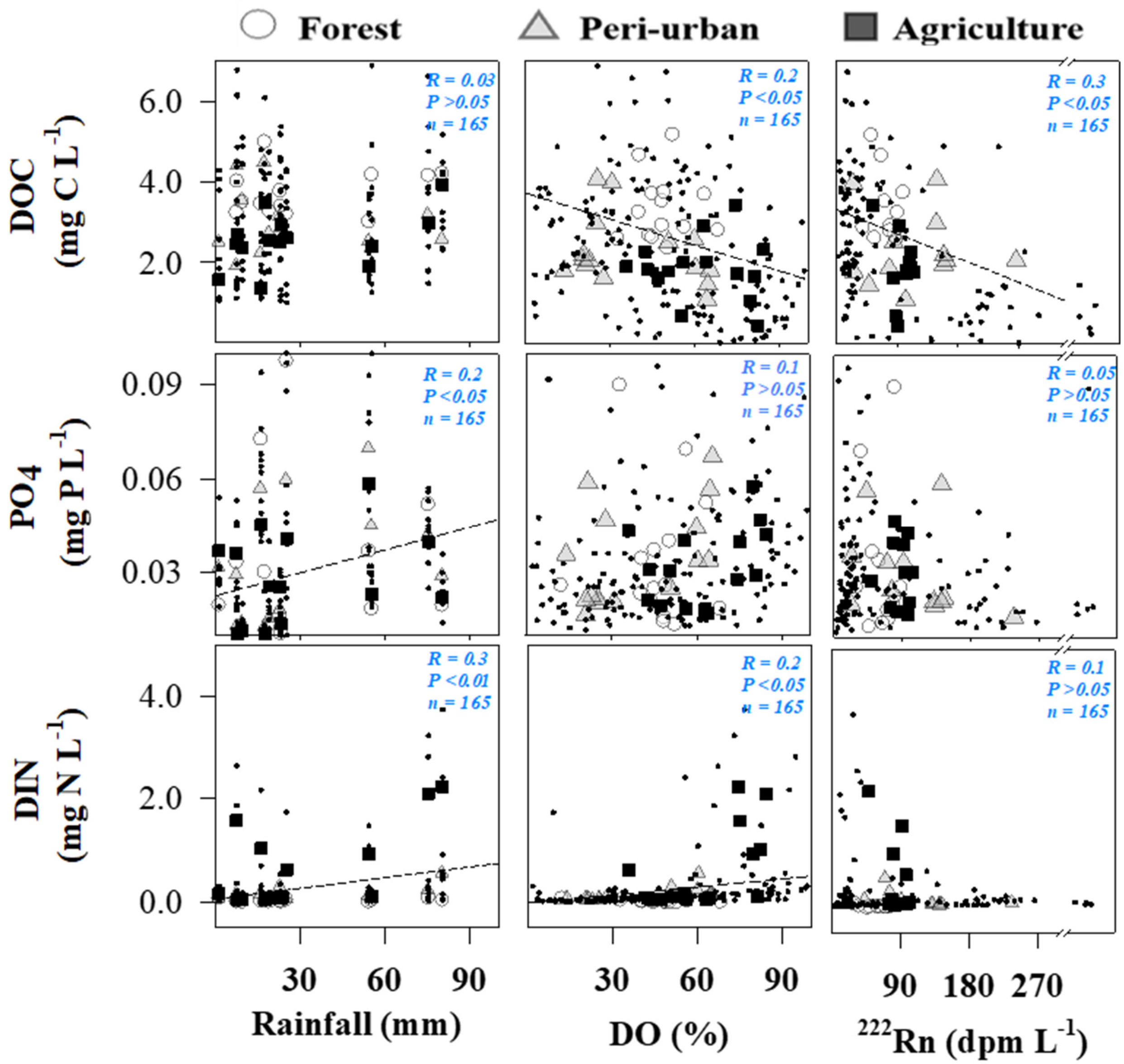

Figure 5 Scatter plots of rainfall, DO (%), and radon (^{222}Rn) versus nutrients concentrations. Forest creeks appear as white circles, peri-urban catchments appear as grey triangles, and agricultural creeks appear as black squares. Small black dots represent individual observations, while larger symbols represent averages. Dotted line shows co-relationship between rainfall, DO (%) and nutrients.

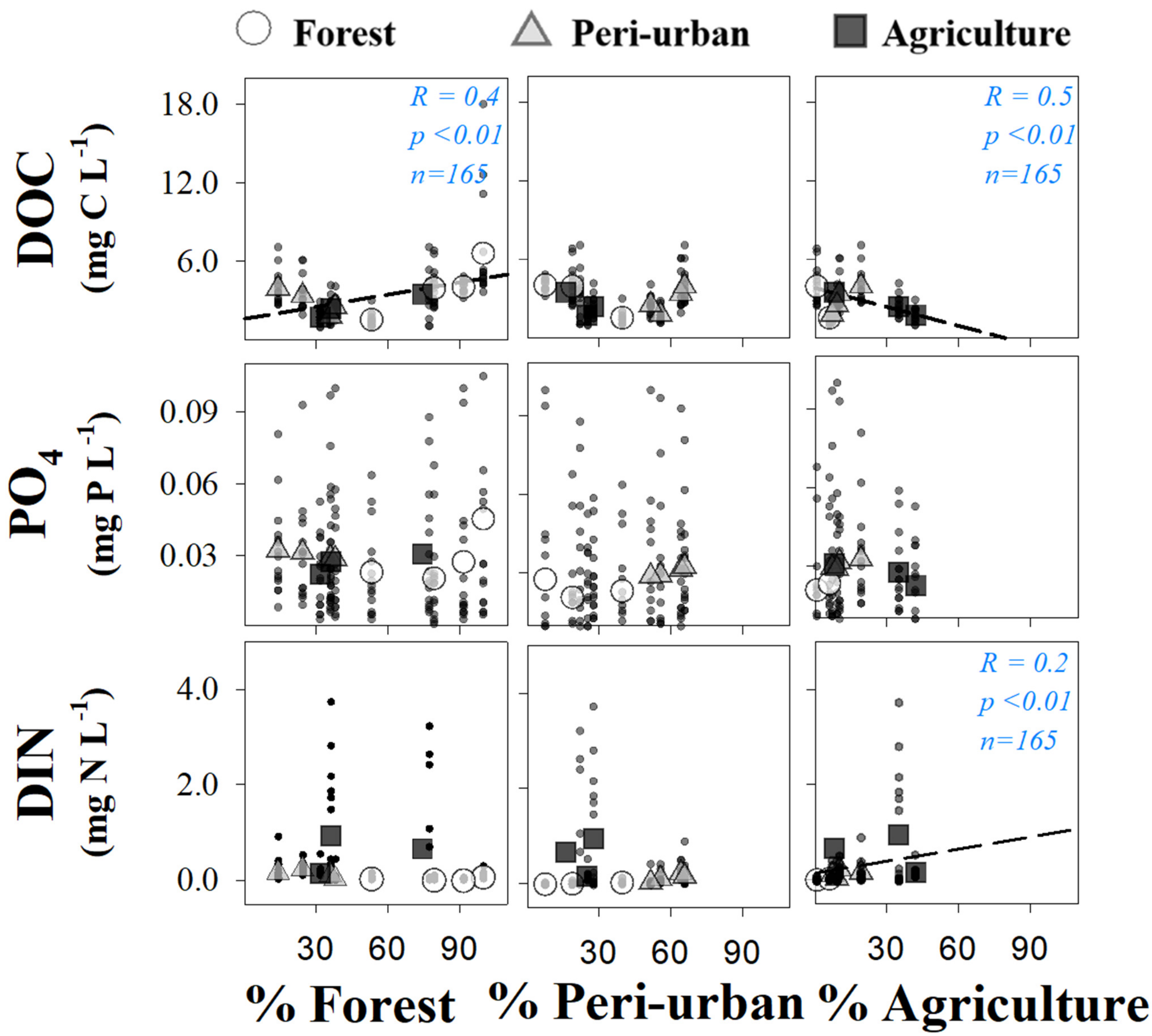

Figure 6 Scatter plot of % land use (forest, peri-urban and agriculture) versus nutrients concentration. Each white circle represents survey observations (165) in different catchments (11). Average of forest creeks appear as white circles, peri-urban catchments appear as grey triangles, and agricultural creeks appear as black squares.

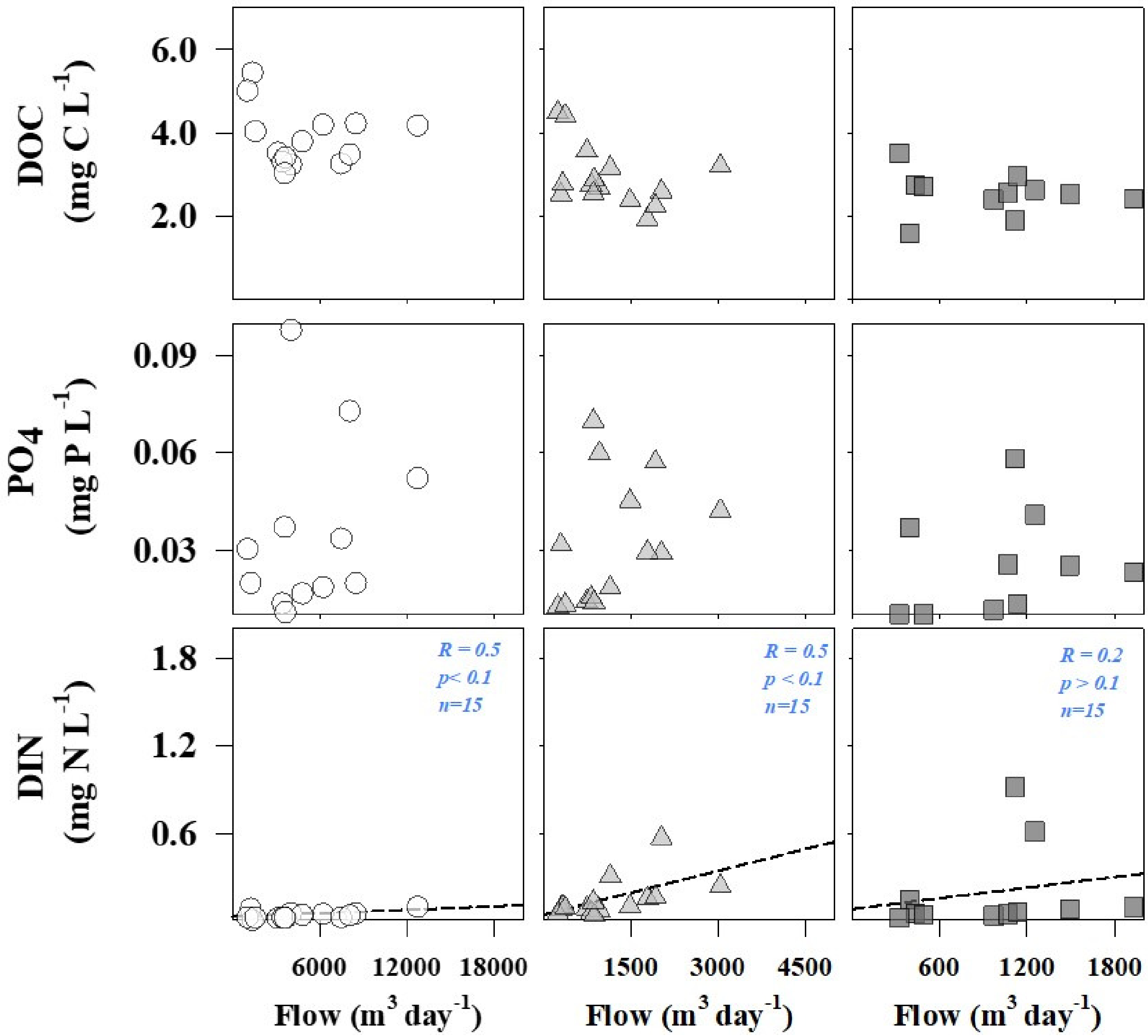

Figure 7 Scatter plot of surface water flow versus nutrient concentration at Coffs coast catchments. Group of forest catchments nutrient concentrations (Avg) are marked in the white circle, peri-urban catchments in the grey triangle and agriculture dominated catchments group in black Square.

Table 1 Catchment classification, Population density, Land-use, TDN concentrations, and fluxes at Coffs coast catchments.

Creek	Classification	Population density	% Forest	% Urban	% Agriculture	% Grazing /cleared land	Average TDN conc.	Average TDN fluxes
							(mg L^{-1} N)	(mg N m^{-2} yr^{-1})
Upper Corindi	Forest	3.0	91.8	0.0	0.2	7.9	0.2 ± 0.1	10.9 ± 5.6
Arrawarra	Forest	0.7	100.0	0.0	0.0	0.0	0.3 ± 0.1	21.5 ± 15.2
Woolgoolga	Agriculture*	20.0	74.7	3.0	8.6	13.6	0.9± 1.1	99.0 ± 166.7
Double-crossing	Agriculture	4.0	36.4	1.1	35.4	27.0	1.3 ± 1.3	122.2 ± 167.9
Pine brush	Agriculture	4.7	31.8	5.2	42.7	20.3	0.3 ± 0.2	25.2 ± 23.2
Ferntree	Peri-urban	174.0	24.7	43.3	10.7	21.4	0.5 ± 0.1	32.4 ± 25.3
Coffs	Peri-urban	219.0	14.4	32.2	19.7	34.0	0.5 ± 0.3	33.4 ± 31.7
Boambee	Peri-urban	18.9	36.3	26.2	7.6	29.8	0.2 ± 0.1	18.0 ± 16.5
Cordwell	Peri-urban	19.6	38.3	1.8	9.6	50.2	0.3 ± 0.1	18.4 ± 14.7
Bonville	Forest	2.0	53.5	3.5	6.5	36.6	0.2 ± 0.1	11.2 ± 9.9
Pine	Forest	1.0	79.5	0.3	1.2	18.9	0.2 ± 0.1	14.9 ± 11.9
	Forest	0.9					0.2 ± 0.1	14.6 ± 10.6
	Peri-Urban	93.6					0.4 ± 0.2	25.5 ± 22.0
	Agriculture	9.5					0.9 ± 0.9	82.1 ± 119.3

*Close proximity of horticulture to our sample site led us to classify the creek as agriculturally influenced although the percentage forest is the highest land use compared to others.

During the dry period, agriculture catchment exports of DIN normalized over the catchment area were similar to peri-urban and pristine catchment exports. In contrast, during the wet period, agriculture DIN catchments exports were ~6 fold higher than other peri-urban catchments (Fig. 9, Table 1). DIN exports from agriculture catchments were higher in the wet period (159.7 ± 136.1 mg m^{-2} yr^{-1}) than during the dry period (6.4 ± 10.9 mg m^{-2} yr^{-1}). Spikes in DIN loads were observed after 80 mm of rainfall. Forest catchments released ~ 3 fold more DON and 4.5 fold more DOC to downstream catchments compared to other land uses.

3.4 Nitrogen Isotopes

A dual-isotope approach ($\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$) was adopted to identify the dominant NO_3^- sources (Fig 10). The main fertilisers used by local farmers are ammonium nitrate, ammonium phosphate, ammonium sulfate, anhydrous ammonia, urea, or a mixture of those (White et al., 2018a). The fertilisers endmembers were light in $\delta^{15}N$ (-8.0 to -0.1 ‰). The Double Crossing Creek catchment farms receive treated greywater from the local waste water treatment plant at rates of ~100 $m^3\ hr^{-1}$. Two samples collected from the farm greywater outlet had concentrations of 1.8 mg N L^{-1} NO_3^- and heavy $\delta^{15}N-NO_3^-$ (21.9 and 20.9 ‰). The measured $\delta^{15}N$ values in the NH_4 fertilisers and greywater fell within the ranges reported in the literature (Accoe et al., 2008; Kendall and Caldwell, 1998; Nestler et al., 2011).

The $\delta^{15}N-NO_3^-$ of forest, peri-urban and agriculture catchment was in the range from 1.2 to 8.0 ‰ (n: 10 average: 4.8±2.6 ‰), 1.9-9.4 (n: 18 average: 7.0±2.2 ‰), 6.1 to 16.9 (n: 21 Average: 10.1±3.1 ‰) respectively. Double-Crossing Creek has relatively high $\delta^{15}N-NO_3^-$ (n: 9 Average: 14.0±2.0 ‰), which most likely results from in-catchment transformation processes such as denitrification using nitrogen derived from artificial fertilizer (White, 2020), indicates sewage and manure as sources of NO_3^- in this catchment. The $\delta^{18}O–NO_3^-$ in all types of catchment varied between 2.5-31.9 ‰. Agricultural catchments like Woolgoolga Creek have $\delta^{18}O–NO_3^-$ in the range of 25.5-32.2 ‰. Considering the mixing model and sources comparison ranges (Kendall and Caldwell, 1998; Nestler et al., 2011), these indicate that NO_3^- fertiliser applications from intensive farming areas are a significant source. Forest and peri-urban catchments isotopic values imply soil stored nitrogen or fertilized soil is the source of NO_3^- (Fig. 10). The positive strong correlation between $\delta^{15}N-NO_3^-$ and % agriculture during both wet and dry period indicates agriculture activities were the main control of $\delta^{15}N-NO_3^-$ in the catchments (Fig. 11).

4 Discussion

4.1 Creek carrying capacity with respect to ANZECC guidelines.

ANZECC guideline values provide default trigger values above which there is a risk of ecosystem degradation. When the trigger value is exceeded, further research and remediation of the risk identified should be conducted. This report builds on previous work revealing nitrogen concentrations exceeding ANZECC values in the Bucca Bucca (White, 2018) and Hearnes Lake (White et al., 2018b) catchments. The Australian and New Zealand Environment Conservation Council (ANZECC) Guidelines (2000 and

2006) provide threshold values for freshwater for pH, dissolved oxygen (DO), and nutrients such as nitrogen (N) and phosphorus (P).

PO_4/FRP (Filterable reactive Phosphorous)

80% of the samples collected from Coffs Coast streams during the wet period were above the ANZECC FRP trigger values. The highest number of samples collected above the ANZECC guideline was in the urban Coffs Creek (73.3%). Double Crossing Creek and Ferntree Creek carry more nutrients runoff than its capacity during the wet period (100% samples are above the ANZECC guideline) whereas during dry conditions ~30% samples were above guidelines. We suspect PO_4 in the Coffs Coast Region is associated with disturbed soil strata flushed by heavy rainfall. In addition to that phosphorous is used heavily on coastal berry farms to combat plant damaging molds (*Phytophthora*).Therefore, relatively more disturbed peri-urban and agriculture catchments carry more PO_4.

NH_4 (ammonium)

41.7, 38.3 and 17.8% of the samples collected from the forest, peri-urban and agricultural streams were above the ANZECC guidelines. The highest number of samples above ANZECC guideline was in 100% forested Arrawarra Creek (73.3%) whereas another forested stream Bonville Creek, and an agriculture stream Pine brush Creek contained samples which all fell within guidelines. In agricultural streams, 17.8% of samples were above ANZECC guidelines. This unexpected low percentage can be associated with nitrification of ammonium-based fertilisers used on farms converting NH_4^+ to NO_3^-.

NO_x

25.0, 65.0 and 66.7% of the samples collected from the forest, peri-urban and agricultural streams were above desired runoff carrying capacity with reference to ANZECC guidelines. As per many previous studies, NOx is always a predominant form of nitrogen in semi-urban and agricultural catchments. All samples collected in peri-urban Ferntree Creek and agricultural Pine Brush Creek were above desired nutrient carrying capacity whereas for forested streams such as Corindi Creek, all samples were within ANZECC guidelines.

Table 2 Australian and New Zealand Environment Conservation Council (ANZECC) trigger value for lowland streams.

Freshwater (Lowland)	pH	DO (%)	NOx mg N L^{-1}	NH_4 mg N L^{-1}	PO_4 mg P L^{-1}	TDN mg N L^{-1}
	6.5-8	80-110%	0.04	0.02	0.02	0.5

Table 3 Observations in the Coffs Coast region creeks above the ANZECC guidelines. Average of forest, peri-urban and agriculture catchments stated in the last.

Creek	Classification	PO_4 (%)	NH_4 (%)	NO_x (%)	TDN (%)
Upper Corindi Creek	Forest	40.0	53.3	0.0	0.0
Arrawarra Creek	Forest	46.7	73.3	46.7	6.7
Woolgoolga Creek	Agriculture*	40.0	40.0	33.3	46.7
Double-crossing Creek	Agriculture	60.0	13.3	66.7	53.3
Pine brush Creek	Agriculture	46.7	0.0	100.0	13.3
Ferntree Creek	Peri-urban	53.3	60.0	100.0	40.0
Coffs Creek	Peri-urban	73.3	53.3	66.7	40.0
Boambee Creek	Peri-urban	40.0	13.3	80.0	0.0
Cordwell Creek	Peri-urban	40.0	26.7	13.3	6.7
Bonville Creek	Forest	33.3	0.0	46.7	0.0
Pine Creek	Forest	40.0	40.0	6.7	0.0
	Forest	40.0	41.7	25.0	1.7
	Peri-urban	51.7	38.3	65.0	21.7
	Agriculture	48.9	17.8	66.7	37.8

PO_4 – Phosphorus, NH_4 – Ammonia, NOx-Nitrogen oxides, TDN – Total dissolved nitrogen etc. for above table.

4.2 Catchment nutrient runoff across the land-use gradient

Estimates of catchment nutrient loads are useful for the development of catchment management plans (Liu et al., 2019). Land-use can be a predictor of nutrient loads (Hooke et al., 2012; Mithra-Christin Hajati, 2019; Young et al., 1996). Here, we found a significant relationships between dissolved DIN concentrations or loads and % agricultural land-use (R: 0.2 $p<0.01$ n: 165) (Fig. 6). The average agriculture catchment TDN exports were ~six-fold higher than those from the forest and three-fold higher than peri-urban catchments (Table 1, Figure 8). In a south-eastern Australian subtropical catchment, ~5 fold greater TDN export was observed in agriculture catchments than forest catchments (19.0 mg N m^{-2} yr^{-1} and 61.0 mg N m^{-2} yr^{-1} in the forest and agricultural catchment, respectively) (Vink et al., 2007). The higher TDN export from the agricultural catchment is consistent with intensive agricultural land-use and fertiliser applications at rates of 5 g N m^{-2} yr^{-1} (Lu and Tian, 2017).

Table 4: Comparison of stream order and TDN export from subtropical freshwater Australian streams from prior studies

River/Creek	Drainage area (km2)	Stream order	Annual rainfall (mm)	Main land use (%)	TDN export (mg N m-2 y-1)	Reference
Bucca Creek	117	1-2	1486	Agriculture (59%)	2970	(White et al., 2018c)
Canning Creek	147	3-4	400	Forest (84%)	50	(Petrone, 2010)
Jane Brook Creek	135	3-4	1200	Forest (54%)	60	(Petrone, 2010)
Helena Brook Creek	161	3-4	1200	Forest (82%)	55	(Petrone, 2010)
Burnett Brook Creek	99	3-4	800-1200	Peri-urban (42%)	52	(Petrone, 2010)
Yule Brook creek	53	3-4	800-1200	Peri-urban (36%)	180	(Petrone, 2010)
South Belmont drain	27	3-4	800-1200	Urban (100%)	90	(Petrone, 2010)
Sussanah Brook Creek	55	3-4	800-1200	Agriculture (95%)	130	(Petrone, 2010)
Ellen Brook Creek	664	3-4	800-1200	Agriculture (85%)	52	(Petrone, 2010)
Bickley Brook Creek	72	3-4	800-1200	Agriculture (35%)	52	(Petrone, 2010)
Southern Creek	149	3-4	800-1200	Agriculture (53%)	150	(Petrone, 2010)
Red Hill Creek	1.9	3-4	853	Forest	19	(Vink et al., 2007)
Kileys Run Creek	1.3	3-4	70	Pasture	61	(Vink et al., 2007)
Coffs forest Creeks	112	3-4	1700	Forest (82%)	14	This study
Coffs peri-urban Creeks	26.5	3-4	1700	Peri-urban (61%)	25	This study
Coffs agriculture Creeks	25.7	3-4	1700	Agriculture (40%)	82	This study

In subtropical Australian forest catchments, total nitrogen and total phosphorus exports were 110 mg N m^{-2} yr^{-1} and 6 mg P m^{-2} yr^{-1}; respectively (Young et al., 1996). These values are seven fold and three fold higher than the forest catchments we observed in CCR (14.6±10.6 mg N m^{-2} yr^{-1} and 2.4±2.9 mg P m^{-2} yr^{-1}). We suspect the lower concentrations in our study are due to the relatively higher order of the streams (3rd and 4th). Rapid uptake and transformation of inorganic nitrogen often occurs in 1 to 3rd order streams. For example, ammonium entering 1st order streams was removed within 10-100 meters, and nitrate was removed within 50-1000 meters of the source (Peterson et al., 2001). In temperate USA streams, the upper 1 km of 1st order streams retained 64% of dissolved inorganic nitrogen inputs and exported the remaining 36% downstream. We suspect that the lower exports in our study are due to the relatively higher order of the streams (3rd and 4th).

DON export from forest catchments (10.7±6.04 mg N m^{-2} yr^{-1}) in our study was consistent with fluxes reported in subtropical forested catchments such as Jane Brook Creek and Helena Brook Creek (15.0 mg N m^{-2} yr^{-1}) (Petrone, 2010). We found an average NOx export rate from 3 agriculture catchments in CCR were 63.9±112.6 mg N m^{-2} yr^{-1}. Those fluxes were 2.5 fold smaller than earlier observations in nearby 1st and 2nd order creeks draining an intensive agriculture catchment (218±80 mg m^{-2} yr^{-1})(White et al., 2018c). In the temperate agricultural catchment (95% of total catchment) of Western Australia, higher NOx fluxes (170 mg N m^{-2} yr^{-1}) compared to the CCR agriculture catchments were found. This might be due to a difference in farming intensities (Petrone, 2010). Double-Crossing Creek catchment (35.4% intensive agriculture land use) has ~24.5 fold higher NOx export than 100% pristine forest catchment, i.e., Arrawara (97.6±167.8 mg N m^{-2} yr^{-1} and 4.3±6.0 mg N m^{-2} yr^{-1}). This supports our initial hypothesis that intensive agricultural land-use maximizes nutrient inputs to creeks and estuaries.

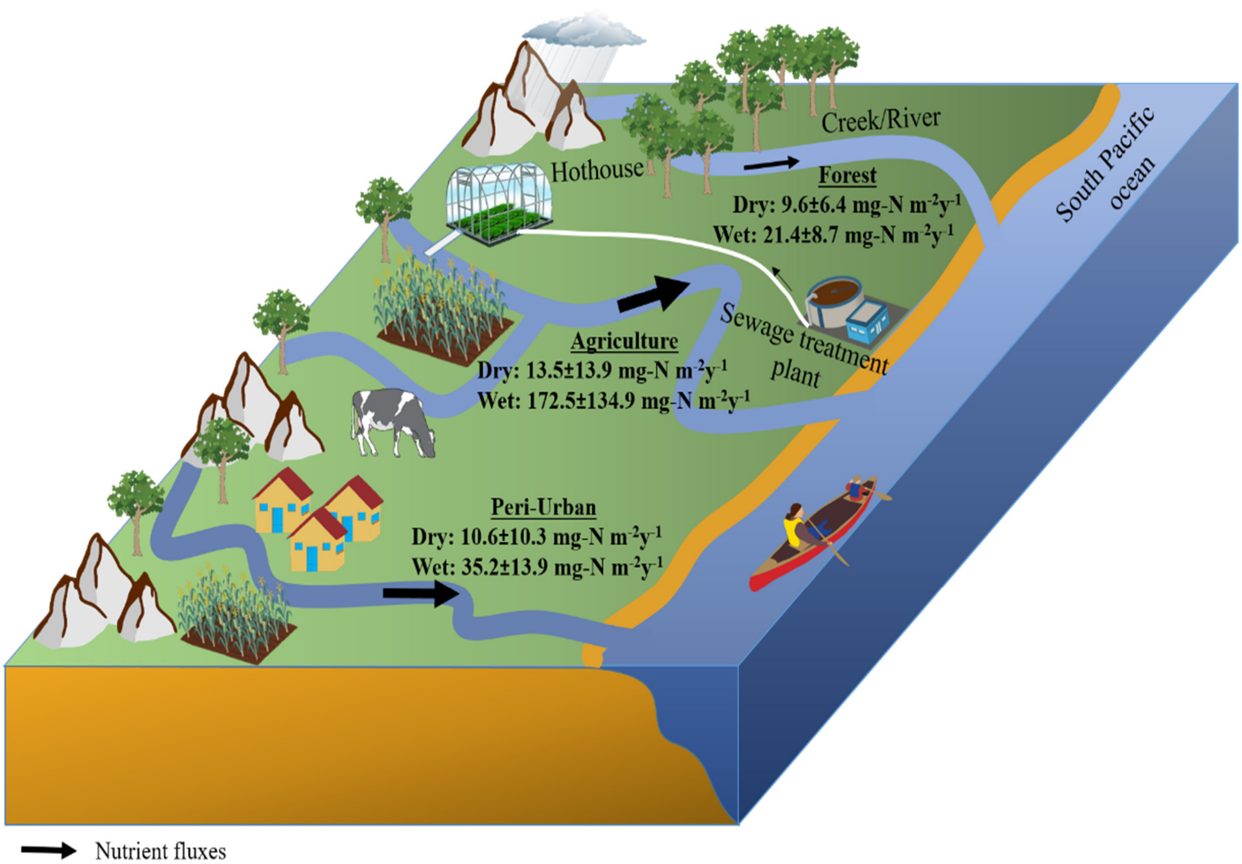

Figure 8. Conceptual model of Coffs Coast Creeks catchment TDN export during dry and wet conditions.

4.3 Nitrogen pathways: Groundwater or surface runoff?

^{222}Rn had a non-significant ($r<0.1$, $P> 0.05$) correlation with DIN concentrations within individual creeks and across the multiple catchments (Fig. 5). This implies that groundwater discharge was not a likely source of DIN. These results are similar to what was found in a nearby agriculture catchment, Bucca Bucca, where groundwater was determined not to be a significant nutrient source to creeks (White, 2018). The groundwater concentration of NOx (0.01 mg N L^{-1}) were 2 orders of magnitude lower than surface water concentrations in this study. During dry periods ^{222}Rn concentrations were almost double the ^{222}Rn during wet periods in the significantly modified peri-urban catchments (dry: 122.7 dpm L^{-1} & wet: 71.0 dpm L^{-1}). This suggests that during the wet periods, rainfall infiltrates and recharges the shallow aquifer and discharges during dry periods via disturbed soil strata and river banks. In south-eastern Australia, runoff due to precipitation can vertically infiltrate up to 0.5 to 2 m into the shallow groundwater during the wet period (Akeroyd et al., 1998).

In contrast to European and North American temperate systems, where the seasonal pattern of elevated nutrient concentrations in stream water is often related to the spring snowmelt, our results and other studies in Australia (Adame et al., 2019; McNamara et al., 2005; Wadnerkar et al., 2019) indicate that nitrogen exported from subtropical coastal catchments is greatly influenced by episodic rain events. DIN and PO_4 had a strong positive correlation with rainfall and flow (Fig 5, 7) implying that the flushing of nutrient-rich soils via surface runoff is the most likely N pathway to the creeks.

During the wet period in CCR, NO_3^- accounts for 18.1%, 52.9% and 71.0% (forest, peri-urban and agricultural catchments respectively) of total dissolved nitrogen (Fig.4). NO_3^- is often the main form of nitrogen during the wet period in agriculture and peri-urban catchments (Bhumbla, 2012; Kaushal et al., 2011; Nestler et al., 2011). In subtropical NSW, Australia, flood periods lasted for 14% of the 4 months experiment, and accounted for 32% of NO_X catchment export (Santos et al., 2013). For instance, the catchment export of total dissolved nitrogen following a rain event in the same catchment was 73-109.5 mg N m^{-2} d^{-1} (Santos et al., 2013). Here, 51% (53 days) of the experiment were influenced by rain. Average catchment TDN export during the wet periods were two fold, three fold and thirteen-fold (9.6±6.4 mg N m^{-2} d^{-1}, 10.6±10.3 mg N m^{-2} d^{-1}, 172.5±134.9 mg N m^{-2} d^{-1} in the forest, peri-urban and agriculture resp.) higher than dry period (21.4±8.7 mg N m^{-2} d^{-1}, 35.2±13.9 mg N m^{-2} d^{-1} and 172.5±134.9 mg N m^{-2} d^{-1} in forest, peri-urban and agriculture catchments.). These wet period export rates further demonstrate that nitrogen exports to waterways were controlled by surface runoff rather than groundwater discharge (fig.9).

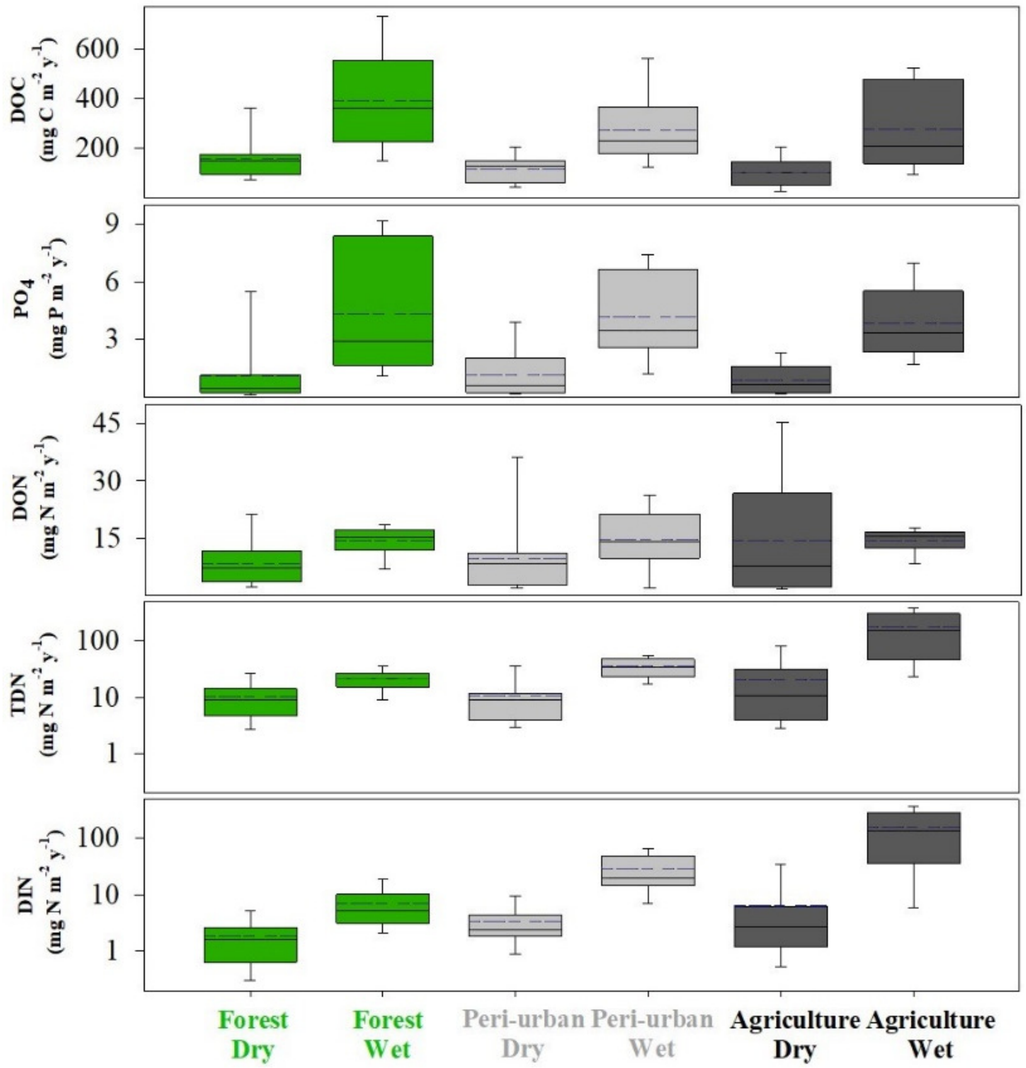

Figure 9. Box plot of water nutrients and dissolved organic carbon loads measured over 105 days. Forest catchments loads during dry and wet periods are marked in the green box, peri-urban catchments in grey and agriculture dominated catchments in the black box. The dotted blue line represents the median value.

4.4 Stable isotopes to interpret nitrogen sources.

4.4.1 Forest catchments

In forested catchments, NO_3^- sources can be soil nitrate and precipitation (Nestler et al., 2011). In the southern hemisphere (Southeast Australia) NO_3^- and $\delta^{18}O\text{-}NO_3^-$ in precipitation was 0.1±0.02 mg N L^{-1} and 62±5‰ (Wong et al., 2015). Our lower $\delta^{18}O\text{-}NO_3^-$ (2.5-23.5‰) values during the dry and wet period in surface water, indicate precipitation is unlikely to be a significant source of NO_3^-. We found

$\delta^{15}N$-NO_3 in the range of 1.2-8.0‰ isotope values from the forest catchments (such as Arrawara Creek, Pine Creek and Bonville Creek) overlap to a great extent and are indistinguishable from soil nitrate (with earlier documented 4.8‰ and 9.2‰), suggesting soil nitrogen as the likely source (Fig. 10)(Kendall et al., 2007; Nestler et al., 2011). Nitrogen from organic matter gets transformed to NH_4 via ammonification and then into NO_3^- by nitrification (Accoe et al., 2008). Subsequent reduction of nitrate to N_2O and N_2 which occurs under anaerobic conditions on riparian areas can modify the signature of residual NO_3^- along the flow pathway in a 1:1 and 2:1 pattern ($\delta^{18}O$: $\delta^{15}N$; see lines in Fig. 10).

4.4.2 Peri-urban catchments

The four investigated peri-urban catchments contain a mixture of urban, forest, agriculture, and cleared land. Isotopic data in such peri-urban catchments ($\delta^{15}N$-NO_3^- 1.9 – 9.4‰ and $\delta^{18}O$–NO_3^- 2.6-11.5‰) mostly lie within the isotopic range of soil nitrogen but could also be affected by manure or organic fertilisers (Kendall et al., 2007). Nitrogen is commonly found in residential areas, including fertilisers applied to backyards, leaky sewer lines, and waste from pets (Paul and Meyer, 2001). All residential and commercial buildings are well connected to the wastewater treatment plants within catchments and sewage overflows are unusual (Council, 2009), which is consistent with an isotopic signature different than expected for sewage i.e. 7 to 25‰(Kendall and Caldwell, 1998; Xue et al., 2009). The two most urbanised catchments (Coffs Creek and Ferntree Creek) in one sample of each creek, $\delta^{18}O$-NO_3^- values were 31.9‰ and 23.4‰, respectively. Here, the relatively higher $\delta^{18}O$-NO_3^- values suggests a direct contribution of NO_3^- from precipitation to the stream.

4.4.3 Agricultural catchments

Samples collected from agricultural catchment streams such as Pine Brush Creek and Woolgoolga Creek suggest a large NO_3^- source from nitrogen fertilisers or fertilized soil. Heavier $\delta^{15}N$-NO_3^- values (4.6-10.3‰) compared to the forest catchments can be associated with denitrification of nitrified-NH_4 fertilisers for Pine Brush Creek. Similarly, heavier $\delta^{15}N$-NO_3^- with heavier $\delta^{18}O$–NO_3^- (25.4-32.2‰) observed in Woolgoolga Creek are also potentially associated with denitrification of NO_3^- fertilisers. The $\delta^{15}N$-NO_3^- of almost 40% of the samples in Pine Brush Creek and 70% samples in Woolgoolga Creek are above 9‰, outside the range previously reported for NO_3^- derived by the nitrification of soil organic matter, further suggesting manure as source of nitrate or denitrification of NO_3^- (Kendall et al., 2007). The low NO_3^- concentrations and the relationship between $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- which progress in a 2:1 pattern in Pine Brush Creek during the dry period, indicate the presence of denitrification as an important process controlling the fate of fertiliser derived NO_3^- in the agricultural catchments.

Higher NO_3^- concentration (1.0-3.2 mg N L^{-1}) and $\delta^{15}N$-NO_3^- (7.5-10.3 ‰) were observed during the wet period in Woolgoolga Creek, suggesting direct flushing of nutrients and/or already denitrified inorganic fertiliser bypassing further transformations such as denitrification (Burns et al., 2009). In-stream processing of NO_3^- was limited during wet period as a result of lower residence time and hence higher NO_3^- concentrations were observed (Billy et al., 2010; Burns et al., 2009).More denitrification during high flow is counter intuitive as residence times in the system are lower and hence less processing will occur. Increased soil moisture, will however create conditions more conducive to denitrification, and this has previously been invoked as an explanation for higher $\delta^{15}N$ in agricultural streams during wet periods (Wong et al 2018).

Isotopic data in Double Crossing Creek ($\delta^{15}N$-NO_3^- 11.6–16.9‰ and $\delta^{18}O$-NO_3^- 6.7-15.2‰) were heavier compared to Woolgoolga and Pine Brush Creeks, indicating a contribution of a NO_3^- source with heavy $\delta^{15}N$ and/or denitrification. This source is a likely mix of recirculated greywater and nitrogen fertilisers. The dominant agricultural land use in this catchment is blueberries, bananas and cucumbers, all of which rely on large amounts of fertilisers (Blueberry -1200 mg N m^{-2} yr^{-1}, Banana -1000-9000 mg N m^{-2} yr^{-1} and Cucumber - searching) (Ireland and Wilk, 2006; Newley et al., 2008). The local farms supplement synthetic fertilisers and greywater for irrigation.

Treated wastewater is widely used in agriculture because it is a rich source of nutrients (Pedrero et al., 2010; Shahalam et al., 1998). In Australia, ~2% of the water used for irrigation comes from sewage water effluent (ABS, 2017). Crops such as cucumber, corn, zucchini, wheat, beans and tomato give higher yields with wastewater irrigation (El Hamouri et al., 1996; Marten et al., 1980), reducing the need for chemical fertilisers (Pedrero et al., 2010) and irrigation water (Ali, 1987; Gurjar et al., 2017; Shahalam et al., 1998). In the Double Crossing Creek catchment, blueberry, cucumber and tomato farms receive treated wastewater from the nearby wastewater treatment plant. The use of this treated water results in a net saving to farmers (Hussain et al., 2002). The NO_3 input to the streams may have originated from two or more distinct sources such as atmospheric NO_3^- and fertilized soil in the peri-urban catchment of Ferntree Creek, and greywater and NH_4 fertiliser in Double Crossing Creek. This possibility could not be fully evaluated with these data and would require additional tracer data (Burns et al., 2009).

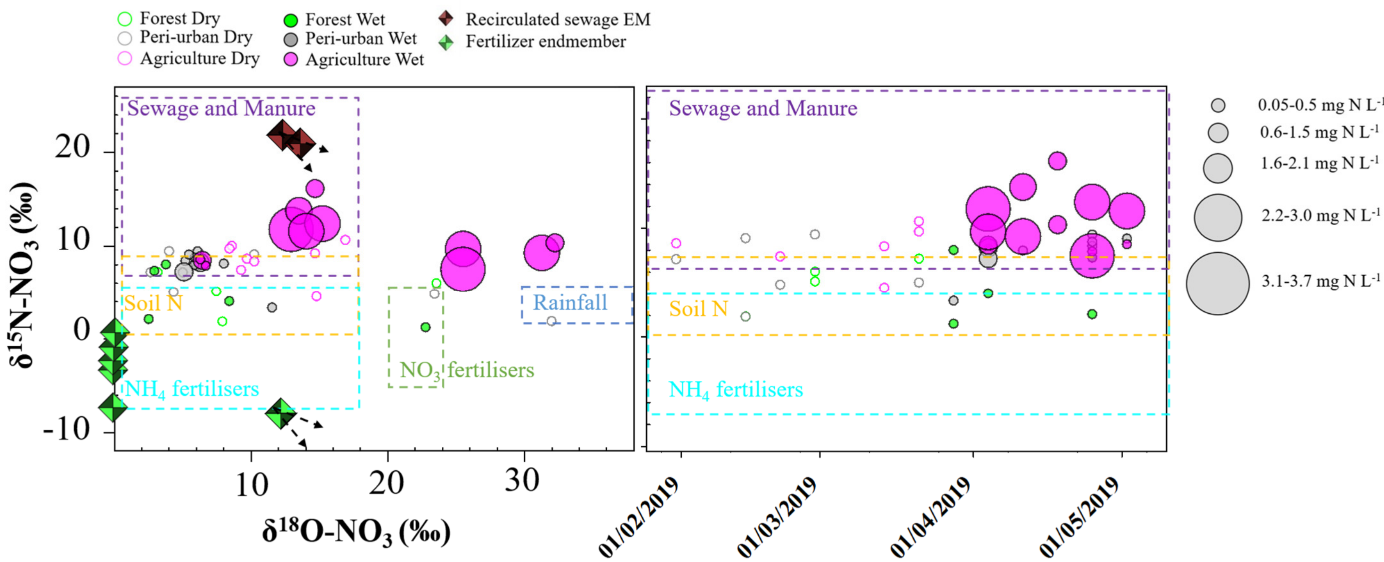

Figure 10 Right: $\delta^{18}O\text{-}NO_3^-$ versus $\delta^{15}N\text{-}NO_3^-$ values from forest, peri-urban and agriculture catchments embedded with the range of values reported in the literature, as indicated by the coloured dotted boxes representing atmospheric precipitation, NH_4 and NO_3 fertiliser, soil nitrogen, and manure and sewage end members. The brown box represents samples taken from the recirculated greywater for irrigation in the catchment. The green boxes represent NH_4 fertiliser obtained from farmers in the catchment. Black arrows show the theoretical 1:1 and 2:1 relationship of denitrification between $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$. We have only $\delta^{15}N\text{-}NO_3^-$ values of inorganic solid fertilizer endmembers which are plotted on Y axis. Left: Time-series of $\delta^{15}N\text{-}NO_3^-$ over 102 days in the Coffs Coast Region (CCR) catchments.

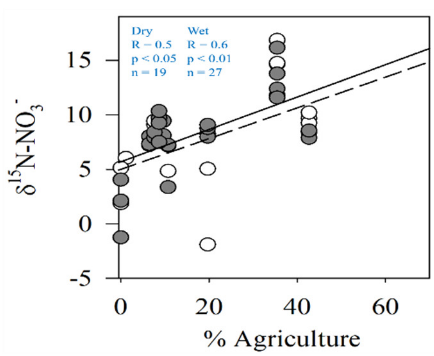

Figure 11 Relationship between $\delta^{15}N\text{-}NO_3^-$ and the percentage of agricultural land use during dry and wet periods. The solid line represents dry period, and a dotted line represents wet periods.

5. Conclusions

We examined spatial and temporal drivers of Coffs Coast streams across a land-use gradient, building on our earlier work focusing on Double Crossing Creek. The observations reveal that most creeks are unable to remove catchment nutrient inputs to a level below recommended ANZECC guidelines as summarized in Figure 12 and below:

1) The highest NO_X concentrations and loads were measured during the wet period in agriculture dominated creeks.

2) Relationships between radon, rainfall and nitrogen imply that nutrient loads were not driven by groundwater discharge.

3) Stable isotopes ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) indicate that the likely source of NO_3^- is fertiliser in the agricultural catchments and soil nitrogen in the agriculture and peri-urban catchments. In Double Crossing Creek, a mix of recirculated greywater and nitrogen fertilisers contributed to high nitrate levels.

4) In wet conditions, TDN loads were highest in agricultural creeks such as Double Crossing Creek and Woolgoolga Creek. Overall, the nitrogen pollution and loads normalized by catchment area follow this order: Double Crossing Creek>Woolgoolga Creek> Coffs Creek> Ferntree Creek>Pinebrush Creek>Arrawarra Creek>Cordwell Creek>Boambee Creek>Pine Creek>Upper Corindi Creek>Bonville Creek.

5) We found 51% and 18.8% of the total samples were above (NOx and TDN) ANZECC guidelines over a wider region than previously observed. We classified creeks into three groups, i.e. Surveillance mode (Green; <10% of samples are above ANZECC water quality guidelines), Alert mode (Orange; 11-50% of samples above ANZECC) and Action mode (Red zone; >50% of samples above ANZECC). Figure 12 summarizes this classification and represents a tool to prioritize areas for management.

6) Nutrient enrichment seems to be an issue affecting most streams in urban and agricultural catchments. Our previous recommendation of managing nutrient runoff in Bucca Bucca Creek (White, 2018) applies to several regional catchments.

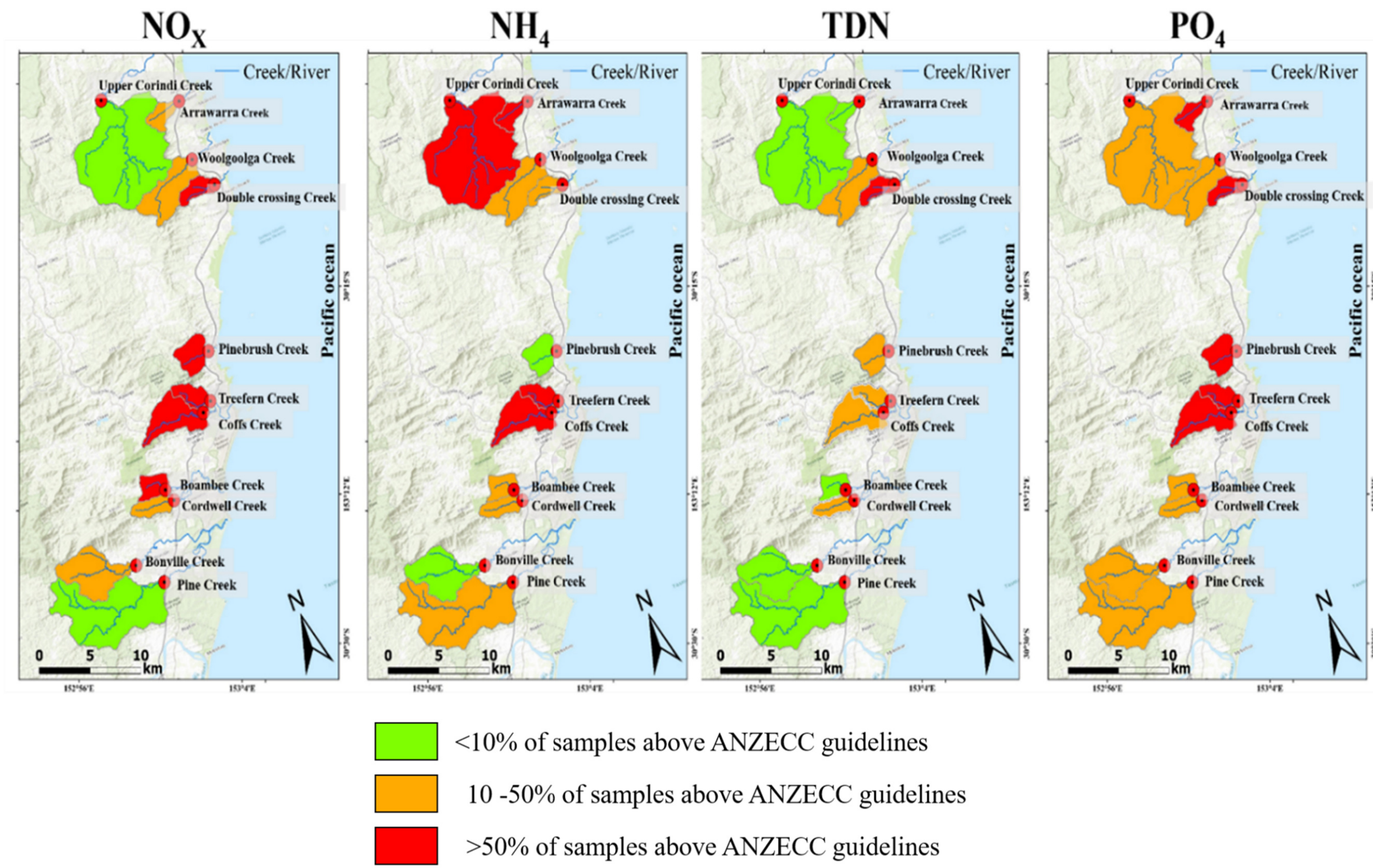

Figure 12 Catchments were classified into three colour codes based on % of samples above ANZECC nutrients guidelines, i.e Green, orange and red.

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Appendix – Forested Catchments

Upper Corindi Creek (-30.039160°, 153.119669°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	25.3	6.8	28.4	0.35	2570.2	0.01	0.04	0.0	0.1	0.1
31/1/19	30.5	6.9	55.8	177.8	2838.4	0.00	0.00	0.0	0.3	0.3
7/2/19	28.7	7.0	43.4	186.3	2123.2	0.004	0.05	0.0	0.1	0.2
14/2/19	27	6.9	57.5	157.3	6347.3	0.01	0.00	0.0	0.3	0.3
21/2/19	27.4	7.1	53.6	176.1	3218.3	0.01	0.04	0.0	0.3	0.3
28/2/19	23.3	6.8	7.3	171.6	8202.3	0.00	0.02	0.1	0.2	0.3
7/3/19	24.5	7.0	30.7	169.8	6995.4	0.00	0.01	0.0	0.2	0.2
14/3/19	26	6.9	167.8	167.8	7420.1	0.00	0.01	0.0	0.2	0.2
21/3/19	26.3	6.9	23	165.9	12649.9	0.00	0.01	0.0	0.2	0.2
28/3/19	24.8	7.0	30.7	157.4	9766.8	0.00	0.01	0.0	0.2	0.2
4/4/19	23	6.8	8.4	155.7	17231.5	0.00	0.02	0.0	0.1	0.1
11/4/19	22.7	6.4	23.7	142.5	15175.4	0.00	0.03	0.0	0.1	0.1
18/4/19	21.5	7.3	18.5	143	7308.3	0.00	0.03	0.0	0.1	0.1
25/4/19	26.8	7.5	55.4	153.3	25813.8	0.00	0.02	0.0	0.1	0.1
2/5/19	20.6	6.9	65.8	147.2	16359.9	0.01	0.02	0.1	0.2	0.2

Arrawarra Creek (-30.066162°, 153.183187°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	22.4	7.0	1.8	48.7	199.5	0.01	0.29	0.0	0.2	0.5
31/1/19	28.3	7.3	69.2	282.5	220.4	0.02	0.01	0.0	0.3	0.3
7/2/19	30.6	7.1	45.9	308.9	164.8	0.03	0.02	0.1	0.3	0.3
14/2/19	28.7	6.7	54.7	361.5	492.8	0.06	0.01	0.0	0.2	0.3
21/2/19	25	7.0	49.9	287	249.9	0.02	0.01	0.0	0.2	0.2
28/2/19	21.9	6.7	39.7	280	636.8	0.06	0.06	0.2	0.3	0.4
7/3/19	22.8	6.8	56.7	276	543.1	0.02	0.02	0.0	0.2	0.2
14/3/19	24.6	7.0	27.8	278	576.1	0.01	0.06	0.0	0.2	0.3
21/3/19	25.8	6.9	45.3	246	982.1	0.03	0.02	0.0	0.3	0.3
28/3/19	23.3	6.9	37.4	246	758.2	0.07	0.02	0.0	0.3	0.4
4/4/19	22.3	7.0	64.7	199	1337.8	0.10	0.04	0.0	0.3	0.4
11/4/19	27.5	7.1	50.8	296	1178.1	0.04	0.05	0.1	0.2	0.3
18/4/19	21.8	7.7	57.9	238	567.4	0.06	0.02	0.1	0.2	0.3
25/4/19	23.3	8.1	72.2	252	2004.1	0.13	0.02	0.1	0.1	0.3
2/5/19	20.8	7.1	41.3	257	1270.1	0.05	0.05	0.1	0.2	0.3

Bonville Creek (-30.376457°, 153.013245°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	24.7	6.8	12.9	29.4	511.7	0.00	0.01	0.0	0.3	0.3
31/1/19	25.5	6.5	63.3	84.5	565.1	0.02	0.00	0.0	0.1	0.1
7/2/19	23.8	6.7	57.4	84.60	422.7	0.03	0.00	0.0	0.1	0.2
14/2/19	23.2	6.6	61.2	86.6	1263.8	0.04	0.00	0.0	0.1	0.1
21/2/19	23.8	6.6	61.1	132.8	640.8	0.04	0.00	0.0	0.1	0.2
28/2/19	21.5	6.7	65.5	75.2	1633.1	0.03	0.01	0.0	0.1	0.1
7/3/19	22.7	6.5	63.0	77.9	1392.8	0.03	0.00	0.0	0.1	0.1
14/3/19	22.9	6.6	64.0	78.6	1477.3	0.03	0.01	0.0	0.3	0.3
21/3/19	22.0	6.7	86.1	72.5	2518.6	0.15	0.01	0.0	0.2	0.3
28/3/19	21.4	6.8	81.3	72.7	1944.6	0.06	0.01	0.0	0.1	0.1
4/4/19	19.9	7.0	85.2	66.9	3430.8	0.04	0.01	0.0	0.0	0.1
11/4/19	20.7	6.9	84.0	70.0	3021.4	0.04	0.00	0.0	0.0	0.1
18/4/19	19.9	7.7	88.4	67.5	1455.1	0.04	0.01	0.0	0.1	0.2
25/4/19	20.6	7.7	88.4	66.8	5139.6	0.15	0.00	0.1	0.0	0.2
2/5/19	20.3	7.0	85.2	75.7	3257.3	0.05	0.01	0.1	0.2	0.2

Pine Creek (-30.397856°, 153.031347°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	24.6	6.2	5.0	0.100	1793.7	0.01	0.00	0.0	0.2	0.2
31/1/19	26.8	6.1	20.7	0.170	1980.8	0.00	0.00	0.0	0.2	0.2
7/2/19	24.5	6.5	15.1	109.3	1481.7	0.00	0.00	0.0	0.1	0.1
14/2/19	23.3	6.3	20.7	115.5	4429.6	0.01	0.00	0.0	0.2	0.2
21/2/19	24.0	6.5	29.1	246.0	2246.0	0.01	0.01	0.0	0.3	0.3
28/2/19	21.8	6.6	18.7	98.80	5724.2	0.06	0.02	0.0	0.3	0.4
7/3/19	23.2	6.2	25.1	102.3	4881.9	0.00	0.05	0.0	0.1	0.2
14/3/19	24.1	6.4	13.1	104.4	5178.3	0.00	0.01	0.0	0.1	0.1
21/3/19	22.0	6.4	25.6	69.40	8828.0	0.00	0.03	0.0	0.4	0.4
28/3/19	21.3	6.4	11.4	82.60	6816.0	0.00	0.04	0.0	0.3	0.4
4/4/19	19.5	6.6	38.2	77.50	12025.4	0.01	0.03	0.0	0.1	0.2
11/4/19	19.8	7.1	21.5	77.00	10590.5	0.00	0.02	0.0	0.2	0.2
18/4/19	19.3	7.1	36.6	75.80	5100.3	0.00	0.01	0.0	0.1	0.2
25/4/19	20.6	6.9	37.9	707.2	18014.8	0.00	0.10	0.1	0.1	0.2
2/5/19	19.7	6.3	33.0	85.40	11417.2	0.01	0.02	0.1	0.1	0.1

Appendix – Peri-urban Catchments

Treefern Creek (-30.282657°, 153.124678°)										
Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	25.9	7.0	28.6	0.25	192.4	0.19	0.03	0.0	0.2	0.4
31/1/19	28.3	6.8	30.8	263.8	212.4	0.23	0.03	0.0	0.1	0.3
7/2/19	27.9	7.0	30	214.4	158.9	0.09	0.01	0.0	0.3	0.4
14/2/19	23.4	6.9	42.8	196.5	475.0	0.10	0.02	0.0	0.3	0.4
21/2/19	27.9	6.9	50.6	211.2	240.9	0.20	0.01	0.0	0.1	0.3
28/2/19	23.6	6.9	4.07	212	613.9	0.14	0.03	0.0	0.2	0.4
7/3/19	23.1	7.0	33.7	187.4	523.5	0.13	0.05	0.0	0.1	0.3
14/3/19	23.9	6.9	33.5	184	555.3	0.07	0.03	0.0	0.3	0.4
21/3/19	25.6	6.7	34.6	127.6	946.7	0.17	0.03	0.0	0.5	0.7
28/3/19	22.1	7.0	59.2	173.6	731.0	0.44	0.09	0.0	0.1	0.7
4/4/19	20.6	7.3	79.2	127.7	1289.6	0.50	0.02	0.0	0.0	0.6
11/4/19	21	7.0	92.11	209	1135.7	0.35	0.01	0.0	0.2	0.5
18/4/19	22.9	7.9	97.9	196	547.0	0.26	0.01	0.1	0.3	0.6
25/4/19	21.2	8.1	86.4	166.3	1931.9	0.27	0.01	0.0	0.1	0.4
2/5/19	22	7.5	98.8	164.1	1224.4	0.28	0.03	0.0	0.3	0.6

Coffs Creek (-30.293236°, 153.110124°)										
Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	27	7.0	23.8	0.216	587.5	0.02	0.03	0.0	0.1	0.2
31/1/19	27.9	6.8	12.7	237.4	648.8	0.00	0.02	0.0	0.5	0.5
7/2/19	27.5	6.9	27	192.7	485.3	0.05	0.01	0.0	0.7	0.7
14/2/19	22.7	6.7	30.2	79.0	1450.9	0.15	0.01	0.0	0.3	0.4
21/2/19	25.9	6.7	38.9	176.8	735.7	0.06	0.02	0.0	0.1	0.2
28/2/19	23.2	6.8	35.4	180.1	1874.9	0.01	0.05	0.0	0.1	0.2
7/3/19	23.2	6.7	9.8	172.3	1599.1	0.00	0.03	0.0	0.2	0.2
14/3/19	25	6.8	17.3	700.7	1696.1	0.00	0.03	0.0	0.2	0.3
21/3/19	23.8	6.9	36.8	125.9	2891.6	0.08	0.04	0.0	0.4	0.5
28/3/19	22.3	6.9	60.8	170.7	2232.5	0.27	0.06	0.0	0.8	1.2
4/4/19	21.2	7.1	76.2	163.3	3938.9	0.9	0.04	0.0	0.0	0.9
11/4/19	21.7	6.8	86.0	253	3468.9	0.13	0.02	0.0	0.2	0.3
18/4/19	22.5	7.9	85.0	157.9	1670.6	0.12	0.05	0.1	0.4	0.6
25/4/19	21.2	8.0	67.7	205	5900.7	0.39	0.02	0.0	0.0	0.4
2/5/19	21.3	7.2	80.9	188.4	3739.6	0.20	0.02	0.1	0.2	0.4

Boambee Creek (-30.333426°, 153.058953°)										
Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	28.7	7.0	3.80	44.5	212.1	0.01	0.04	0.0	0.2	0.1
31/1/19	22.6	6.5	39.7	170.06	234.2	0.07	0.05	0.0	0.1	0.2
7/2/19	25.4	6.8	46.2	178	175.2	0.07	0.02	0.0	0.3	0.2
14/2/19	22.8	6.7	28.5	154.9	523.8	0.09	0.00	0.0	0.3	0.2
21/2/19	24.1	6.6	34.5	167.6	265.6	0.08	0.01	0.0	0.1	0.1
28/2/19	22.7	6.7	47.5	163.3	676.9	0.08	0.00	0.1	0.2	0.2
7/3/19	22.3	6.7	48.8	168.2	577.3	0.04	0.01	0.0	0.1	0.1
14/3/19	24.1	6.6	33.2	171.7	612.3	0.04	0.00	0.0	0.3	0.2
21/3/19	22.8	6.6	40.6	153.6	1043.9	0.07	0.01	0.0	0.5	0.5
28/3/19	22.0	6.9	83.9	144.5	806.0	0.33	0.00	0.0	0.1	0.5
4/4/19	21.0	7.1	86.7	134.7	1422.0	0.43	0.01	0.0	0.0	0.4
11/4/19	22.5	7.0	80.0	140	1252.3	0.10	0.01	0.0	0.2	0.2
18/4/19	21.5	7.4	80.0	157.2	603.1	0.09	0.01	0.1	0.3	0.3
25/4/19	21.8	8.1	86.4	265	2130.2	0.21	0.01	0.0	0.1	0.3
2/5/19	21.2	7.0	79.7	182.6	1350.0	0.12	0.01	0.1	0.3	0.2

Cordwell Creek (-30.343592°, 153.063006°)										
Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	25.0	6.8	3.30	0.15	219.9	0.01	0.05	0.0	0.1	0.1
31/1/19	25.9	6.5	3.50	147.8	242.8	0.00	0.03	0.0	0.2	0.2
7/2/19	24.3	6.8	9.50	147.0	181.6	0.00	0.00	0.0	0.5	0.5
14/2/19	24.8	6.8	13.4	265.5	543.0	0.00	0.00	0.0	0.1	0.1
21/2/19	23.5	6.6	56.3	268.5	275.3	0.01	0.01	0.0	0.1	0.2
28/2/19	21.4	6.7	27.2	143.3	701.7	0.00	0.01	0.1	0.2	0.2
7/3/19	22.4	6.9	44.6	147.2	598.5	0.00	0.01	0.0	0.3	0.3
14/3/19	23.3	6.5	5.30	157.8	634.8	0.01	0.01	0.0	0.4	0.4
21/3/19	22.0	6.6	7.80	141.7	1082.2	0.00	0.04	0.1	0.4	0.4
28/3/19	21.1	6.6	30.9	123.6	835.5	0.03	0.04	0.0	0.5	0.6
4/4/19	20.9	6.8	57.6	122.45	1474.1	0.43	0.02	0.0	0.0	0.5
11/4/19	20.8	6.9	91.0	127.0	1298.2	0.03	0.02	0.0	0.1	0.2
18/4/19	20.5	8.0	39.2	127.8	625.2	0.02	0.02	0.1	0.2	0.2
25/4/19	21.4	7.3	67.7	264.0	2208.3	0.07	0.01	0.0	0.1	0.2
2/5/19	21.3	6.9	37.4	138.8	1399.6	0.02	0.02	0.0	0.2	0.2

Appendix – Agriculture Catchments

Woolgoolga Creek (-30.111442°, 153.176808°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	27.2	7.3	46	0.5	657.3	0.02	0.05	0.0	0.1	0.2
31/1/19	28.1	6.8	73.1	382	725.8	0.02	0.01	0.0	0.2	0.2
7/2/19	30.0	7.1	51	260.5	542.9	0.00	0.01	0.0	0.2	0.2
14/2/19	27.4	7.1	37.1	173.7	1623.1	0.01	0.01	0.0	0.2	0.2
21/2/19	28.7	7.1	54.2	278	823.0	0.00	0.02	0.0	0.2	0.2
28/2/19	26.5	7.1	29.4	256	2097.5	0.00	0.03	0.1	0.5	0.5
7/3/19	24.0	7.0	23.5	247	1788.9	0.00	0.01	0.0	0.2	0.2
14/3/19	25.8	6.8	21.8	284	1897.5	0.01	0.00	0.0	0.2	0.2
21/3/19	27.0	7.0	119.9	251	3234.8	0.00	0.01	0.0	0.7	0.7
28/3/19	26.3	6.8	33.1	279	2497.6	0.00	0.02	0.0	0.2	0.2
4/4/19	22.5	6.9	55.5	284	4406.5	2.28	0.14	0.0	0.2	2.6
11/4/19	22.3	6.8	67.2	317	3880.7	2.40	0.24	0.0	0.3	2.9
18/4/19	22.6	7.6	60.1	282	1868.9	1.01	0.07	0.1	0.2	1.3
25/4/19	22.2	7.7	72.9	370	6601.1	3.18	0.05	0.1	0.1	3.3
2/5/19	21.1	6.9	76.3	271	4183.6	0.67	0.02	0.0	0.1	0.8

Double Crossing Creek (-30.136700°, 153.187851°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	23.9	7.2	46.3	0.270	206.1	0.13	0.13	0.1	0.2	0.4
31/1/19	27.3	7.0	44.5	510.0	227.6	0.02	0.01	0.0	0.2	0.2
7/2/19	28.7	7.1	55.7	499.0	170.3	0.00	0.00	0.0	0.2	0.2
14/2/19	26.1	7.1	54.1	159.5	509.0	0.02	0.00	0.0	0.2	0.2
21/2/19	25.6	7.1	52.7	487.0	258.1	0.02	0.01	0.0	1.8	1.8
28/2/19	24.1	6.5	9.07	46.20	657.8	0.01	1.72	0.0	1.9	3.6
7/3/19	23.4	7.1	47.5	459.0	561.0	0.05	0.01	0.0	0.1	0.1
14/3/19	24.2	7.0	49.2	472.0	595.1	0.06	0.01	0.0	0.1	0.2
21/3/19	22.4	7.0	53.8	485.0	1014.5	0.15	0.01	0.0	0.4	0.5
28/3/19	22.6	7.0	52.4	462.0	783.3	0.05	0.01	0.0	0.2	0.2
4/4/19	20.9	7.2	76.5	476.0	1381.9	3.74	0.00	0.0	0.1	3.8
11/4/19	27.2	7.2	65.8	453.0	1217.0	1.86	0.00	0.0	0.0	1.9
18/4/19	22.3	8.1	82.5	465.0	586.1	1.46	0.01	0.1	0.2	1.7
25/4/19	22.4	8.1	94.6	199.0	2070.2	2.82	0.01	0.0	0.1	2.9
2/5/19	20.6	7.2	92.3	198.1	1312.0	2.17	0.00	0.0	0.1	2.3

Pinebrush Creek (-30.251039°, 153.132683°)

Date	Temp	pH	DO (%)	EC (µS/cm)	Water flow (m^3/day)	NOx (mg/L N)	Ammonia (mg/L N)	Phosphate (mg/L P)	DON (mg/L N)	TDN (mg/L N)
24/1/19	25	7.1	73.8	0.25	318.1	0.14	0.01	0.0	0.0	0.2
31/1/19	30.1	6.7	74.1	262.7	351.2	0.12	0.01	0.0	0.1	0.2
7/2/19	30.9	6.9	82.1	269.6	262.7	0.09	0.00	0.0	0.1	0.2
14/2/19	26.3	6.9	50.4	128.3	785.5	0.09	0.02	0.0	0.2	0.3
21/2/19	26.1	6.8	61.3	265	398.3	0.10	0.02	0.0	0.0	0.1
28/2/19	22.1	6.9	68.9	252	1015.0	0.10	0.01	0.0	0.1	0.2
7/3/19	22.3	6.8	59	240	865.7	0.09	0.01	0.0	0.2	0.3
14/3/19	24.6	6.8	56.8	148	918.2	0.12	0.02	0.0	0.2	0.3
21/3/19	23.1	6.8	69.1	231	1565.4	0.14	0.01	0.0	0.3	0.5
28/3/19	22	6.9	66.4	210.9	1208.6	0.17	0.02	0.0	0.4	0.6
4/4/19	20.5	7.3	90.9	162.6	2132.4	0.54	0.01	0.0	0.1	0.7
11/4/19	20.9	7.1	91.9	206.2	1877.9	0.19	0.01	0.0	0.1	0.3
18/4/19	23.7	8.3	96.6	158.2	904.4	0.22	0.01	0.0	0.1	0.3
25/4/19	20.9	8.1	85.4	573	3194.4	0.24	0.00	0.0	0.1	0.3
2/5/19	21.4	7.3	78.3	534	2024.5	0.20	0.01	0.1	0.2	0.5