

Water Quality on Bucca Bucca Creek and the potential impacts of intensive plant agriculture

Final Report - Coffs Harbour City Council Environmental Levy Program



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Executive summary

The blueberry industry is the fastest growing horticultural sector in the Coffs Harbour City Council Local Government Area. However, the influence of this intensive industry on water quality remains unknown. Coffs Harbour City Council engaged Southern Cross University to perform water quality investigations in creeks within the Bucca Bucca Creek catchment, a tributary of the Orara River.

Creek water sampling was conducted on 11 occasions between the 7th February and 7th May 2017, covering a wide range of hydrological conditions. Eight blueberry farms were paired to a nearby control site without any blueberry activity. In the 90 day sample period, there were three rain events $>90 \text{ mm day}^{-1}$ that produced runoff sufficient to create flooding in the sample sites.

Overall, the results revealed a clear link between blueberry farming and nitrogen runoff in headwater streams.

While NO_x (nitrate + nitrite) was the dominant nitrogen species downstream of blueberry farms, dissolved organic nitrogen [DON] was the dominant species in control sites. NO_x at both non-blueberry and blueberry site means were above the ANZECC maximum trigger value ($1.071 \mu\text{mol L}^{-1}$). However, there was a highly significant difference between non-blueberry ($6.3 \pm 2.0 \mu\text{mol L}^{-1}$) and blueberry ($56.9 \pm 14.2 \mu\text{mol L}^{-1}$) sites. 51% of blueberry samples and 56% of non-blueberry samples were below the ANZECC trigger values, yet 24% of NO_x samples at blueberry sites measured were between 50 and 800 fold higher than the ANZECC trigger value.

NO_x measurements were highest following rain events. Radon (a natural groundwater tracer) observations and low nitrogen concentration in groundwater samples imply groundwater discharge was not a major source of nitrogen to the creeks. We suggest that surface runoff dominates the delivery of nitrogen to the creeks investigated.

NO_x loads were on average >13 -fold higher at blueberry sites ($21.8 \text{ kg N-NO}_x \text{ ha yr}^{-1}$) than non-blueberry sites ($1.6 \text{ kg N-NO}_x \text{ ha yr}^{-1}$). NO_x concentrations and loads in creeks clearly increased with increasing blueberry density. At $<15\%$ of blueberry land use, there was no detectable influence in NO_x concentrations and loads in the headwater streams. We estimate that creeks within a catchment with 15% blueberry land use may have mean NO_x concentrations >25 fold higher than the ANZECC trigger value.

Assuming that our load estimates over 90 days of observations can be upscaled to annual nitrogen creek exports, and that local farmers use the recommended amount of fertiliser ($121 \text{ kg N ha yr}^{-1}$), between 18 and 25% of the used fertiliser was lost to the creeks. This implies that there are opportunities for decreasing the use of fertilisers in the Bucca Bucca catchment as well as managing any nitrogen that escapes to the creeks.

With the rapid growth of the blueberry industry and the established link between blueberry farming and nitrogen runoff, we strongly recommend site-specific management approaches to reduce farm nitrogen runoff, and the assessment of potential impacts of blueberry nitrogen runoff to downstream habitats such as estuaries and the Solitary Islands Marine Park.

1. Introduction

Coffs Harbour City Council engaged Southern Cross University to perform water quality investigations within the Bucca Bucca Creek catchment, a tributary of the Orara River. This project was motivated by community concerns over the impacts of intensive plant agriculture (primarily blueberries) on the water quality of many waterways within the Coffs Harbour Local Government Area ([LGA]. Blueberry farms are the fastest growing horticultural industry in the Coffs Harbour LGA, with many banana famers converting land use to blueberries (Bevan, 2006; Rural Lands Council, 2016).

Coffs Harbour City Council has an environmental and planning responsibility under the Coffs Harbour City Council Biodiversity Action Strategy 2012–2030 to know if any land use change is detrimentally affecting local waterways (Coffs Harbour City Council [CHCC], 2012c). To date, no work has been done to assess potential nutrient pollution from blueberry farms in the Coffs Harbour LGA into surrounding streams. With the growing sprawl of blueberry farming, scientific knowledge is required to manage any nutrient runoff that may be detrimental to valuable freshwater creeks and downstream estuaries.

As an intensive horticulture industry, blueberries require a vast array of nutrients, primarily nitrogen (N), phosphorus (P) and potassium (K). Therefore, fertilisers are used to supplement these nutrients in cultivated monocultures (Barker & Pilbeam, 2015). Some of the fertiliser may escape farms and enter nearby waterways. Waterway nutrient runoff may be difficult to quantify since pathways and sources are often complex and site specific. Possible nutrient sources to creeks include horticultural fertiliser runoff, groundwater seepage, geologic erosion, atmospheric deposition, detritus decomposition and other environmental factors (Conley, 1999; Galloway et al., 2004; Seitzinger et al., 2006; Vitousek et al., 1997).

In this report, we describe the findings of observations performed during various flows to establish baseline data and identify whether water quality may be linked to agricultural practices in the Bucca Bucca catchment. We specifically test whether runoff from blueberry farms may deliver excess nutrients to local streams. To assess this hypothesis, we performed detailed sampling of 16 sub-catchments. Our analysis includes:

- 1) A comparison to Australia and New Zealand Environment and Conservation Council [ANZECC] pollution trigger values for upland streams in NSW.
- 2) A comparison between creeks potentially influenced by blueberry and nearby creeks without any potential impacts.
- 3) An assessment of nutrient pathways into creeks, i.e., whether nutrients are delivered via surface runoff following rain events or by steady groundwater inflows.
- 4) An assessment of land use percentage contribution, i.e., if percentage of a watershed occupied by blueberry farms will determine the level of nutrient load in downstream creeks.

While we focus on dissolved nutrient runoff, we also report the results of a preliminary pesticide survey in creeks that can be used to inform future, more detailed investigations.

2. Methods

2.1. Study area

Bucca Bucca Creek is ideal for sampling as it does not have a history of land contamination or banana cultivation and has a rapidly increasing area under blueberry cultivation. The Bucca Bucca Creek catchment (lat. -30.12°S, long. 153.03°E) is 117.27 km² and lies about 15 km north-northwest of Coffs Harbour, in the NSW north coast bioregion on Gumbaynggirr Aboriginal Country (NSW Office of Water, 2014). The catchment is 72% forested, is dominantly owned by NSW forestry corporation for timber harvest, though contains freehold lands used for pasture, cropping and horticulture (CHCC, 2012d; NSW Office of Water, 2014). Within the catchment there are 15 blueberry farms, however horticulture is one of the smallest land uses. The catchment receives 1485.6 mm mean precipitation per year with an average of 71.3 days with >1 mm of rain (Australian Government Bureau of Meteorology [BOM], 2017a). Bucca Bucca Creek is 29.3 km long, with 77 smaller tributary sub-catchments, releasing >1.67 ML day⁻¹ of water to the Orara River (NSW Office of Water, 2014). Bucca Bucca Creek catchment drains from the south to the north west with an elevation profile of 557 m ASL to 67 m ASL. Water flows to the Pacific Ocean via the Orara and Clarence Rivers. Observed watercourse depths within the catchment range from <0.05 m to >3.2 m and observed widths from <0.1 m to >12 m, although these figures can triple in flood periods. Annual mean temperatures are 11.9 °C minimum and 24.3°C maximum (BOM, 2017a).

This catchment is considered a low hydrological stress (based on total stream flow) and a high environmental stress (based on land use, point source discharges, turbidity, salinity, pH, algal blooms, fish kills, erosion, riparian vegetation, fish barriers and macro invertebrates) (CHCC, 2012d). The Bucca Bucca Creek catchment forms part of the Great Eastern Ranges Corridor, a national strategy to protect biodiversity (Mackey, Watson, & Worboys, 2010).

The dominant soil type in the Australian Soil Classification (Isbell, 2016) is Kandosol, with five other major soil groups present along the creek sediment areas (NSW Office of Environment and Heritage, 1999). Kandosol soils are not calcareous, Kandosols are siliceous in composition, have a sandy to loamy upper horizon and porous subsoils that are sandy to light clay textured (Isbell, 2016; Schroeder, Panitz, Sullivan & Wood, 2014). These soils have low fertility, low water holding capacity and nutrients are easily leached from the subsoil (Isbell, 2016; Queensland Government, 2015; Schroeder, Panitz, Sullivan & Wood, 2014).

The catchment contains important stands of old growth rainforest and tall open forest dominated by Tallowwood (*Eucalyptus microcorys*), Grey Ironbark (*Eucalyptus paniculata*), Blackbutt (*Eucalyptus pilularis*) and Flooded Gum (*Eucalyptus grandis*) (CHCC, 2012b). The habitat within the catchment is home to twenty vulnerable or endangered species (Appendix 1; CHCC, 2012a; CHCC, 2012b). The main creek and associated tributaries contain freshwater habitat for the Eastern Freshwater Cod (*Maccullochella ikei*) listed as endangered under the Commonwealth *Environment Protection and Biodiversity Conservation Act 1999* [EPBC Act] and NSW *Fisheries Management Act 1994* (CHCC, 2012a; CHCC, 2012b). The catchment also provides riparian habitat for the Giant Barred Frog (*Mixophyes iteratus*), listed as endangered under the EPBC Act and NSW *Threatened Species Conservation Act 1995* (CHCC, 2012a; CHCC, 2012b; Murphy & Murphy, 2011).

2.2. Site Selection and experimental Strategy

Sampling was conducted on 11 occasions between the 7th February and 7th May 2017, covering a wide range of hydrological conditions. Environmental Systems Research Institute [ESRI] ArcGIS™ mapping software, field scouting, aerial imagery, consultation with CHCC staff and local

landholders were used to examine the study area and identify eight blueberry farms (n=16 sites) as suitable study sites (ESRI, 2016; Land and Property Information NSW, 2016).

Each blueberry farm was paired to a nearby control site without any blueberry activity. Sites downstream of a blueberry farm were labelled “treatment” (T), while sites adjacent or upstream of blueberry farms were labelled “control” (C) (Figure 1). Two control sites were used for farm B and one control site was used for two treatment sites at farm D. Farm G was not accessible twice during the sample period. Samples G_{C1} and G_{T1} were not collected due to access issues. Samples G_{C8} and G_{T8} were not collected due to road flooding. The selection of control sites depended on local morphology and access and followed two strategies:

- (1) For farms A, B, C, D and E, an adjacent creek was used as control,
- (2) For farms F, G and H, a sample from the same creek just upstream of the blueberry farm was used as control.

Catchments upstream of each site were identified by creating polygons following the upper limits of 1 m interval contours surrounding the waterways, then using light detection and ranging [LIDAR] elevation data to create an upstream watershed delineation in ArcGIS (CHCC, 2016; Geoscience Australia, 2015). Land use (m² and % catchment) was classified using field observations and remote sensing imagery (CHCC, 2016; Geoscience Australia, 2015; Land and Property Information NSW, 2016).

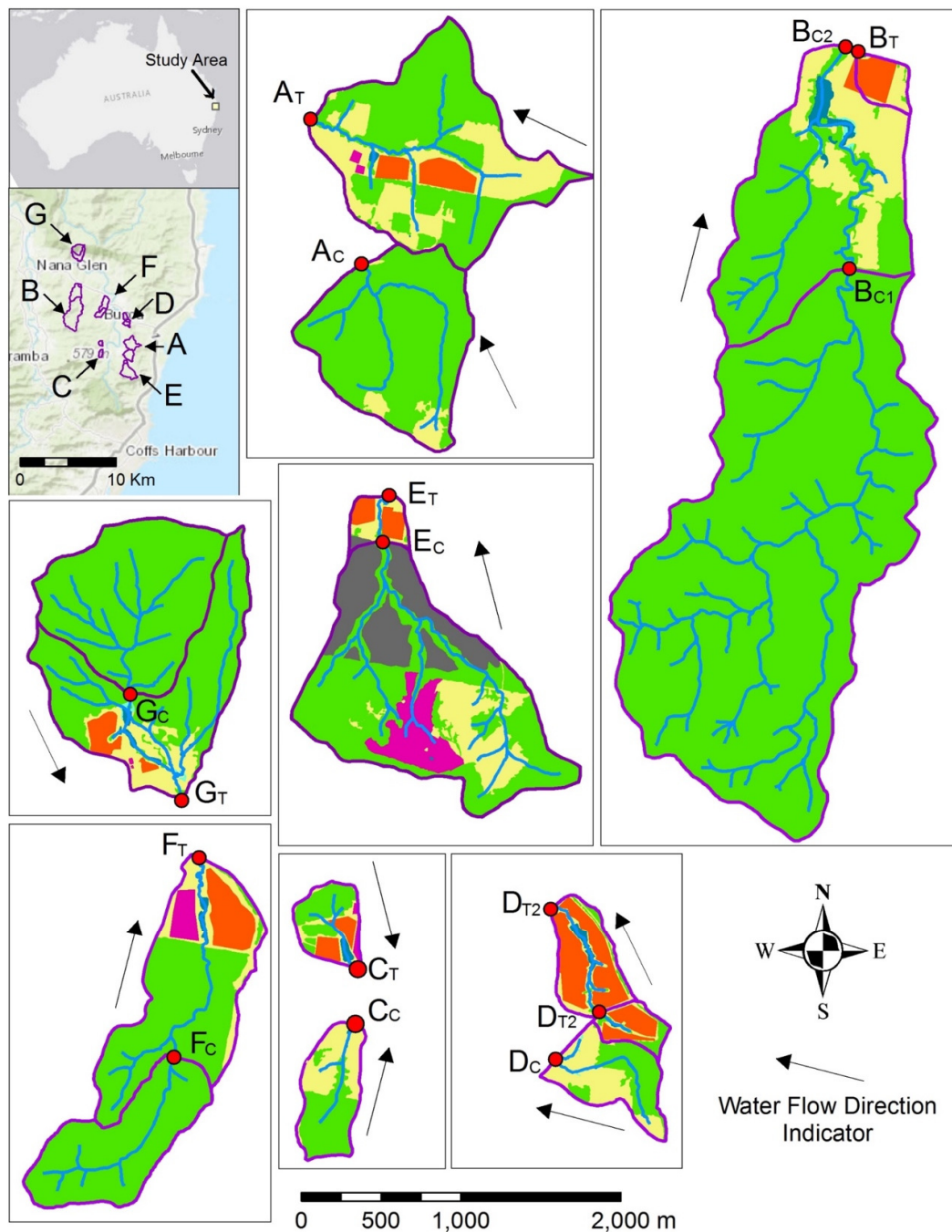


Figure 1: Classification of land uses upstream of sample sites in Bucca Bucca Creek catchments. Sites were chosen as treatment (X_T) or control (X_C) sites. Treatment sites are those that contain >1% blueberry farm land use upstream of a sample site. The classification Forest incorporates wet and dry sclerophyll, rainforest, introduced species and plantation forestry. The classification Horticulture incorporates banana, macadamia, raspberry and cucumber horticulture. Cleared land incorporates pasture, houses and roads.

Table 1: Locations, stream orders and upstream land uses of control (X_C) and treatment (X_T) sites in the Bucca Bucca Creek catchment, NSW.

Site	Coordinates	Stream Order	Forested Land Use (%catchment)	Cleared Land Use (%catchment)	Blueberry Land Use (%catchment)	Blueberry Farm Area (m ²)	Watershed Area (m ²)
A _C	-30.2117 153.1178	3	93	7	0	0	932606
A _T	-30.2008 153.1138	3	61	32	7	89708	1303466
B _{C1}	-30.1550 153.0559	4	100	0	0	0	4154927
B _{C2}	-30.1472 153.0620	4	92	6	0	2622	5555599
B _T	-30.1455 153.0640	1	6	35	59	54598	92343
C _C	-30.2068 153.0921	2	56	44	0	0	265610
C _T	-30.2064 153.0919	2	48	21	26	45574	175979
D _C	-30.1828 153.1128	2	44	53	0	0	280367
D _{T1}	-30.1804 153.1159	1	27	20	51	49844	96873
D _{T2}	-30.1744 153.1127	2	9	17	65	164997	254065
E _C	-30.2206 153.1157	3	51	38	0	0	1573939
E _T	-30.2182 153.1161	3	49	38	3	47536	1676872
F _C	-30.1693, 153.0919	2	100	0	0	0	552097
F _T	-30.1579, 153.0933	3	80	9	10	144609	1418434
G _C	-30.1185 153.0631	3	100	0	0	0	894515
G _T	-30.1260 153.0668	3	87	9	3	47061	1755389

2.3. *Sampling methods*

Nutrients (phosphate [PO₄], nitrate + nitrite [NO_x], ammonium [NH₄], dissolved organic nitrogen [DON], dissolved organic phosphorus [DOP]) and ancillary parameters (temperature, pH, dissolved oxygen [DO] and electrical conductivity [EC]) were sampled from surface creek water at each sample site. A calibrated EcoSense EC300a probe measured pH (± 0.02) and water temperature ($\pm 0.1^\circ\text{C}$). A HQ40D multi probe was used to measure EC ($\pm 0.02 \mu\text{S cm}^{-1}$ @ 25°C) and DO ($\pm 0.2 \text{ mg L}^{-1}$). Probes were recalibrated every two weeks using standard calibration solutions per the manufacturers specifications. Dissolved nutrients were sampled at each site using a sample rinsed 60 mL polyethylene syringe. Samples were immediately filtered through a $0.45 \mu\text{m}$ cellulose acetate syringe filter 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.

2.4. *Hydrology*

Rainfall and runoff data (30.15S, 153.10E) was acquired from the Australian Bureau of Meteorology's [BOM] Australian Landscape Water Balance model (BOM, 2017b). Rainfall data was produced as daily precipitation grids interpolated to a 5 km^2 national grid (Jones et al., 2009). Runoff was a modelled assessment calculated by estimating surface runoff, combining soil infiltration and soil saturation. Baseflow was factored based on groundwater stores and deep soil drainage (BOM, 2017b). The BOM uses the AWRA-L model calibrated by streamflow observations and remotely sensed soil moisture and evapotranspiration (BOM, 2017b).

2.5. *Groundwater tracing*

Groundwater inflow was assessed using the radiogenic isotope radon [^{222}Rn ; $T_{1/2}=3.83$ days] at Farm F only. ^{222}Rn is an excellent tracer for groundwater inflows (Burnett, 2006) and has been used extensively to assess groundwater and surface water interactions in rivers and streams (Cook, et al., 2003; Ellins et al., 1990; Hamada, et al., 1997). In addition to the regular sampling described above, Farm F was heavily sampled over a six day period following a rain event of 31 mm in a day. The farm (sites F_C and F_T) was sampled 5 times before the rain event, ≈ 3 hourly for the first 12 hours after the rain, ≈ 6 hourly the day following the rain, ≈ 12 hourly for the third day and ≈ 24 hourly for the following three days to establish a temporal scale and hydrological drivers (i.e., surface runoff vs groundwater seepage).

^{222}Rn sampling was conducted by collecting $\approx 6 \text{ L}$ of creek water in specialised HDPE plastic bottles with custom gas analysis tubing (Stringer & Burnett, 2004). Gas detection was done using a RAD7 (DurrIDGE Company) radon in air measurement device, connected in a closed loop via desiccant (Lee & Kim, 2006). Air was circulated through the closed loop for a minimum of 2 hours and a sample taken every 10 mins. Calculations of ^{222}Rn (dpm L^{-1}) were done using polonium [^{218}Po ; $T_{1/2}=3.10 \text{ min}$] counts inside the RAD7 and accounting for air and water volumes, efficiency, sample time and time lag between collection and sampling. The detection limits and further analytical approaches are described in detail elsewhere (Burnett, et al., 2001; Lee & Kim, 2006).

2.6. *Groundwater sampling*

In addition to the 16 surface water sites, 10 groundwater bores were sampled. Bores were purged for at least 10 minutes to replace standing groundwater. Groundwater was then pumped and sampled for nutrients, water quality and ^{222}Rn , consistent with the above methods. Bore depths were between 26 m and 108 m.

2.7. Pesticide sampling and analysis

Pesticides were sampled at each site once during spatial survey sample 11 on 7/5/17. Two unfiltered 750 mL acid washed brown glass bottles were sample rinsed from each site three times, then filled and capped underwater to eliminate any air in the samples. Bottles were kept on ice (<5 °C) for <5 hours, refrigerated overnight (<5 °C) and sent to EnviroLab Group (Chatswood, NSW) to be analysed within 9 days. Pesticide samples were extracted with dichloromethane and analysed with Gas Chromatography – Mass Spectrometry [GCMS] using methods from USEPA 8081 (organochlorides), USEPA 8141 (organophosphates) and USEPA 8270 (speciated carbamates). Table 2 shows the pesticides analysed and the detection limits using this methodology.

Table 2: Pesticide chemicals tested and minimum detection limits at control and treatment sites in the Bucca Bucca Creek catchment on 7/5/17.

Chemical Family	Chemical name	Minimum detection limit (ppb)	Chemical Family	Chemical name	Minimum detection limit (ppb)
Nitrile-organo-chloride	Chlorothalonil	5	Organo-phosphate	Azinphos-methyl	0.02
Organo-chloride	HCB	0.01	Organo-phosphate	Bromophos ethyl	0.2
Organo-chloride	Alpha-BHC	0.05	Organo-phosphate	Chlorpyrifos	0.01
Organo-chloride	Gamma-BHC	0.05	Organo-phosphate	Chlorpyrifos-methyl	0.2
Organo-chloride	Beta-BHC	0.05	Organo-phosphate	Diazinon	0.01
Organo-chloride	Delta-BHC	0.05	Organo-phosphate	Dichlorovos	0.2
Organo-chloride	Aldrin	0.01	Organo-phosphate	Dimetholate	0.15
Organo-chloride	Heptachlor	0.01	Organo-phosphate	Ethion	0.2
Organo-chloride	Heptachlor Epoxide	0.01	Organo-phosphate	Fenitrothion	0.2
Organo-chloride	Gamma-Chlordane	0.01	Organo-phosphate	Malathion	0.05
Organo-chloride	Alpha-Chlordane	0.01	Organo-phosphate	Ronnel	0.2
Organo-chloride	Endosulfan I	0.02	Organo-phosphate	Parathion-ethyl	0.01
Organo-chloride	Endosulfan II	0.02	Organo-phosphate	Parathion-methyl	0.2
Organo-chloride	Endosulfan sulphate	0.02	Polychlorinated Biphenyl (PCB)	Arochlor 1016	0.01
Organo-chloride	pp-DDE	0.01	Polychlorinated Biphenyl (PCB)	Arochlor 1221	0.01
Organo-chloride	pp-DDD	0.01	Polychlorinated Biphenyl (PCB)	Arochlor 1232	0.01
Organo-chloride	DDT	0.006	Polychlorinated Biphenyl (PCB)	Arochlor 1242	0.01
Organo-chloride	Dieldrin	0.01	Polychlorinated Biphenyl (PCB)	Arochlor 1248	0.01
Organo-chloride	Endrin	0.01	Polychlorinated Biphenyl (PCB)	Arochlor 1254	0.01
Organo-chloride	Methoxychlor	0.02	Polychlorinated Biphenyl (PCB)	Arochlor 1260	0.01
Triazole	Propiconazole	4	Speciated carbamate	Methomyl	3
Triazole	Tebuconazole	2			

2.8. Nutrient analysis

Laboratory analysis of dissolved nutrients (NO_x, NH₄, PO₄) was carried out colourimetrically using a Lachat Flow Injection Analyser [FIA]. Levels of total dissolved N [TDN] and total dissolved P [TDP] were determined colourimetrically using an FIA. Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were determined as the difference between the total dissolved nutrients (TDP and TDN) and dissolved inorganic nutrients (PO₄ and (NO_x + NH₄)). The analytical approach and detection limits are described in detail elsewhere (Eyre and Ferguson, 2005).

2.9. Interpretation

Ancillary water parameters (EC, pH and DO%) and nutrient concentrations (TDN, NO_x, NH₄, TDP and PO₄) of surface water from control (n=86) and treatment (n=86) sites were analysed using a t-test (two tailed independent samples t-test assuming equal variances) to determine significant differences in control and treatment sample means. Histograms were used to compare against ANZECC trigger values for upland streams (south eastern NSW) in slightly disturbed ecosystems (ANZECC, 2000). All values are summarised using means and standard deviations unless otherwise noted.

The load (flux per area, per time) of nutrients were calculated for each sample by the equation after:

$$F = \frac{M(RA)}{A}$$

where F is the flux of nutrients ($\mu\text{mol ha day}^{-1}$), M is the concentration of nutrient ($\mu\text{mol L}^{-1}$), R is surface runoff (mm day^{-1}) and A is catchment area (ha). Appropriate unit conversion were applied to data. Fertiliser loss was calculated as the recommended fertiliser added per year (Doughty, et al., 1988) divided by the mean creek flux of nitrogen.

The ratio between surface water and groundwater radon concentrations were used to estimate groundwater contribution to streams using the equation:

$$\text{GW}_{\%SW} = \frac{\text{SW}_{\text{Rn}}}{\bar{x}\text{GW}_{\text{Rn}}}$$

where $\text{GW}_{\%SW}$ is an estimation of groundwater contribution to each surface water sample, SW_{Rn} is the ^{222}Rn (dpm L^{-1}) in each creek water sample and GW_{Rn} is the average ^{222}Rn (dpm L^{-1}) of the ten groundwater samples taken across the Bucca Bucca Creek catchment. This approach provides the minimum groundwater contribution to stream runoff and is semi-quantitative (Peterson et al., 2010; Santos and Eyre, 2011).

3. Results and discussion

3.1. Hydrological conditions

Overall, the sampling captured contrasting hydrological conditions from baseflow to flooding. In the 90 day sample period (Table 3) there were three rain events $>90 \text{ mm day}^{-1}$ (16/3/17, 119 mm; 18/3/17, 92.2 mm; and 31/3/17, 90.3 mm) that produced runoff ($>12.3 \text{ mm day}^{-1}$) sufficient to create flooding in the sample sites (Figure 2). The maximum runoff observed was 35.9 mm day^{-1} on 19/3/17, following 318 mm of rain in the previous 7 days. Prior to these large rainfall events (31/1/17 to 14/3/17), rainfall did not exceed 31.3 mm day^{-1} and runoff did not exceed 0.53 mm day^{-1} . After the 31/3/17, there were no rain events greater than 12.4 mm day^{-1} and runoff fell from 12.3 mm day^{-1} on the 1/4/17 to 0.2 mm day^{-1} on 16/4/17 and stayed below 0.15 mm day^{-1} for the remainder of the sampling period.

Table 3: Sample dates and hydrology for the 16 selected sites in the Bucca Bucca Creek catchment (BOM, 2017b).

Sample Number	Sample date	Rain on sample day (mm)	Rain within 48hrs prior to sample (mm)	Rain within 7 days prior to sample (mm)	Runoff on sample day (mm day^{-1})	Runoff within 3 days prior to sample (mm day^{-1})
1*	7/2/17	1.5	1.5	1.5	0.01	0.03
2	14/2/17	7	7	22.5	0.09	0.19
3	21/2/17	0	28.1	47.4	0.29	0.8
4	28/2/17	31.3	47.9	48.2	0.52	0.76
5	4/3/17	1	3.4	64.3	0.2	0.88
6	15/3/17	119	166.3	166.3	0.53	0.74
7	22/3/17	1.8	35.1	306.4	18.18	77.41
8*	31/3/17	90.3	95.7	96.3	13.8	16.22
9	9/4/17	0.1	13.2	39.8	1.64	7.35
10	21/4/17	1	4.8	6.2	0.05	0.19
11	7/5/17	0.1	1.6	10.5	0.04	0.18

* samples were not able to be taken at farm G

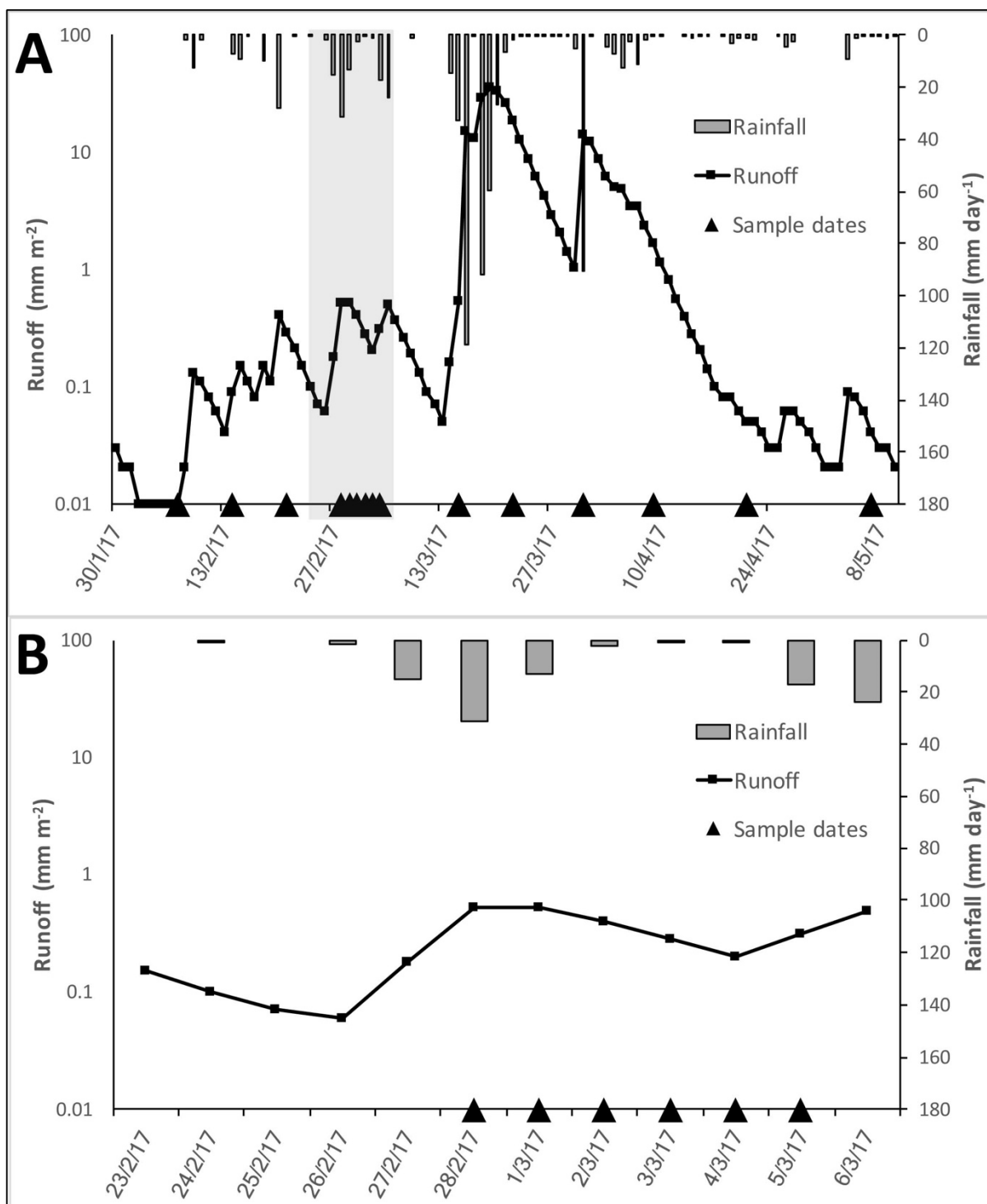


Figure 2: A) Hydrograph of rainfall and runoff in the Bucca Bucca Creek catchment. Sample dates are shown along the bottom as triangles. Greyed area indicates intensive sampling period at farm F (BOM, 2017b). B) Intensive sampling period at farm F from 28/2/17 to 5/3/17 during a rain event of 79.7 mm in 7 days. (BOM, 2017b). This rain event was not significant enough to produce runoff $>0.52 \text{ mm day}^{-1}$.

3.2. Pesticides

All results of dissolved pesticides were below the measurable limits listed in Table 2. Because these samples were taken in baseflow conditions only, they are inconclusive as to whether blueberry farms are contributing pesticides to creeks. It is recommended that further pesticide sampling be undertaken following rain events in the creeks. Pesticide in sediment sampling would build confidence in the fate of any pesticides used in blueberry farms and the possible export pathways of these pesticides.

3.3. Surface water quality

Below we compare water quality observations to ANZECC guidelines. Raw data are reported in Appendix 2.

pH - Sample means for both control sites and treatment sites were below the minimum pH of the ANZECC trigger values (pH 6.5 to pH 7.5) (ANZECC, 2000; Figure 3A). There were 22% of treatment samples and 19% of control samples within the trigger values (Figure 4A). Only 1 sample (DT21, pH 8.1) was >pH 7.5, however there were 4 control samples and 5 treatment samples between pH 5 and pH 5.5. The control samples were sample Dc4 with pH 5.2, Gc4 with pH 5.5, Ac4 with pH 5.2 and Ac6 with pH 5.5. The treatment samples were sample CT4 with pH 5.1, CT5 with pH 5.4, CT6 with pH 5.3, AT6 with pH 5.4 and AT7 with pH 6.5. There was no significant difference ($t_{(170)}=1.84$, $p=0.068$) between control (pH 6.1 ± 0.04) and treatment (pH 6.3 ± 0.05) sites.

Electrical conductivity [EC] - The means of both control and treatment sites were within the maximum and minimum ANZECC trigger values ($30 - 350 \mu\text{S cm}^{-1}$ @ 25°C) for electrical conductivity (ANZECC, 2000; Figure 3B). There was no significant difference ($t_{(170)}=0.65$, $p=0.516$) between control ($229.0\pm17.5 \mu\text{S cm}^{-1}$ @ 25°C) and treatment ($214.9\pm12.7 \mu\text{S cm}^{-1}$ @ 25°C) sites. Only 8% of treatment sites were above $350 \mu\text{S cm}^{-1}$ @ 25°C , these were all at site FT (maximum sample FT1, $630 \mu\text{S cm}^{-1}$ @ 25°C) (Figure 4B). These high conductivity results correlate with baseflow periods in the creek. When creek flow increased with rain events, the lowest sample here was FT9 ($93.6 \mu\text{S cm}^{-1}$ @ 25°C). There was 17% of control sites above $350 \mu\text{S cm}^{-1}$ @ 25°C . Seven of these samples were at site Dc (maximum Dc2, $867 \mu\text{S cm}^{-1}$ @ 25°C), two samples were at site AC (maximum AC1, $535 \mu\text{S cm}^{-1}$ @ 25°C), one sample at site EC (EC1, $397.6 \mu\text{S cm}^{-1}$ @ 25°C) and three samples at site CC (maximum CC11, $534 \mu\text{S cm}^{-1}$ @ 25°C). All high EC samples were in baseflow conditions, likely due to groundwater inflow through the riparian sediments (Schuetz & Weiler, 2011).

Dissolved oxygen [DO] - DO was generally low at the sites sampled and the means of both control and treatment sites were below the maximum and minimum ANZECC trigger values (90 DO % sat. to 110 DO % sat.) (ANZECC, 2000; Figure 3C). There was a significant difference ($t_{(170)}=2.3$, $p=0.022$) between control (50.4 ± 2.6 DO % sat.) and treatment (59.7 ± 3.0 DO % sat.) sites. Only 3% of treatment sites were within the ANZECC trigger values, these were samples BT7 (94.1 DO % sat.), ET6 (91.2 DO % sat.) and ET8 (91.8 DO % sat.) (Figure 4C). Similarly, only 5% of control sites were within the ANZECC trigger values, these were samples BC18 (91.4 DO % sat.), BC27 (97.0 DO % sat.), BC28 (98.6 DO % sat.), GC5 (94.6 DO % sat.) and CC4 (90.3 DO % sat.). The highest result was from sample DT21 (198.6 DO % sat.) and the lowest result was from sample BT2 (3.5 DO % sat.).

Phosphate [PO₄] - There was no significant difference ($t_{(170)}=1.08$, $p=0.282$) between control ($0.2\pm0.01 \mu\text{mol L}^{-1}$) and treatment ($0.4\pm0.1 \mu\text{mol L}^{-1}$) sites in PO₄ measurements, and the mean of both control and treatment samples were below the ANZECC maximum trigger value ($0.5 \mu\text{mol L}^{-1}$) (ANZECC, 2000; Figure 3D). There was a greater mean and variability at the treatment sites.

Only 8% of treatment samples were above the ANZECC trigger value, though 3 of these samples were at site D_{T2}. These were samples D_{T2}1 (0.6 µmol L⁻¹), D_{T2}7 (0.7 µmol L⁻¹) and D_{T2}9 (10.8 µmol L⁻¹) (Figure 4D). D_{T2}9 was the highest observed sample in both control and treatment sites. Samples 7 and 9 were in high flow periods and sample 1 was in a baseflow period. Only 4.6% of control samples were above the ANZECC trigger value. These were F_T1 (0.6 µmol L⁻¹), F_T2 (0.8 µmol L⁻¹), D_C1 (0.6 µmol L⁻¹) and A_C2 (0.6 µmol L⁻¹), these samples were all in baseflow periods. These results are not surprising, in that most P is stable when applied as an inorganic fertiliser, dominantly in the form of orthophosphates [PO₄]. PO₄ adsorbs to soils quickly and is relatively insoluble, therefore unable to leach through groundwater (Vimpany & Lines-Kelly, 2004). It is however mobile when eroded as part of a soil. Hence, when continuous erosion occurs, PO₄ is a pollution issue to streams (Vimpany & Lines-Kelly, 2004).

Total dissolved phosphorus [TDP] - Similar to PO₄, the mean of TDP in both control and treatment sites were below the maximum ANZECC trigger value (0.67 µmol L⁻¹) (ANZECC, 2000; Figure 3E) and there was no significant difference ($t_{(170)}=0.6$, $p=0.549$) between control (0.5 ± 0.1 µmol L⁻¹) and treatment (0.6 ± 0.1 µmol L⁻¹) sites. There were 17% of treatment sites above the ANZECC trigger value, dominantly at sites D_{T1} (maximum D_{T1}2, 1.1 µmol L⁻¹) and D_{T2} (maximum D_{T2}9, 13.5 µmol L⁻¹) (Figure 4E). Sample D_{T2}9 was the highest overall sample and was in a high flow period. In control samples, 22% were above the ANZECC trigger value, dominantly at sites D_C (maximum D_C1, 2.4 µmol L⁻¹) and C_C (maximum C_C4, 1.1 µmol L⁻¹).

Ammonium [NH₄] - Ammonium had a significantly higher ($t_{(170)}=2.39$, $p=0.018$) mean in control sites (20.5 ± 6.2 µmol L⁻¹) than treatment (5.6 ± 0.7 µmol L⁻¹) sites. The means of control and treatment sites were above the ANZECC maximum trigger value (0.929 µmol L⁻¹) (ANZECC, 2000; Figure 3F). Mean and variability was higher in control sites, driven by baseflow at sites A_C, B_C, D_C and F_C. These samples may be driven by groundwater inputs or bacterial breakdown of organic material. There were 24% of treatment samples and 31% of control samples within the ANZECC trigger value (Figure 4F). The maximum value at a treatment site was 31.6 µmol L⁻¹ in sample D_{T1}2. The maximum value at a control site was 322.7 µmol L⁻¹ in sample D_C2. Both of these samples were in baseflow conditions.

Nitrate + nitrite [NO_x] - Both control and treatment site means were above the ANZECC maximum trigger value (1.071 µmol L⁻¹) and there was a highly significant difference ($t_{(170)}=3.52$, $p=0.00055$) between control (6.3 ± 2.0 µmol L⁻¹) and treatment (56.9 ± 14.2 µmol L⁻¹) sites (ANZECC, 2000; Figure 3G). Treatment sites showed a high variability within each site, this was driven by hydrology. There were 51% of treatment samples and 56% of control samples below the ANZECC trigger value (Figure 4G). The highest samples measured were between 50 and 812 µmol L⁻¹. During baseflow conditions (<25 mm rain in 48 hrs), all treatment sites had ≥2 samples below the ANZECC trigger value. When rainfall and runoff increased in rain events (>25 mm rain in 48 hrs), NO_x measurements were highest. The highest and lowest measurement for each site is given in Table 4.

Total dissolved nitrogen [TDN] - There was no significant difference ($t_{(170)}=1.62$, $p=0.107$) between control (61.6 ± 10.1 µmol L⁻¹) and treatment (93.2 ± 16.6 µmol L⁻¹) sites, though the mean of treatment samples was >30 µmol L⁻¹ greater than the mean of control samples. Both treatment and control sample means were >40 µmol L⁻¹ greater than the ANZECC maximum trigger value (17.86 µmol L⁻¹) (ANZECC, 2000; Figure 3H). This is driven by the above NO_x and NH₄ measurements, combined with dissolved organic nitrogen. There were 28% of treatment samples and 23% of control samples within the ANZECC trigger values (Figure 4H). The highest treatment sample was 855.7 µmol L⁻¹ in samples D_{T2}6 and the highest control sample was 551.9 µmol L⁻¹ in sample D_C1.

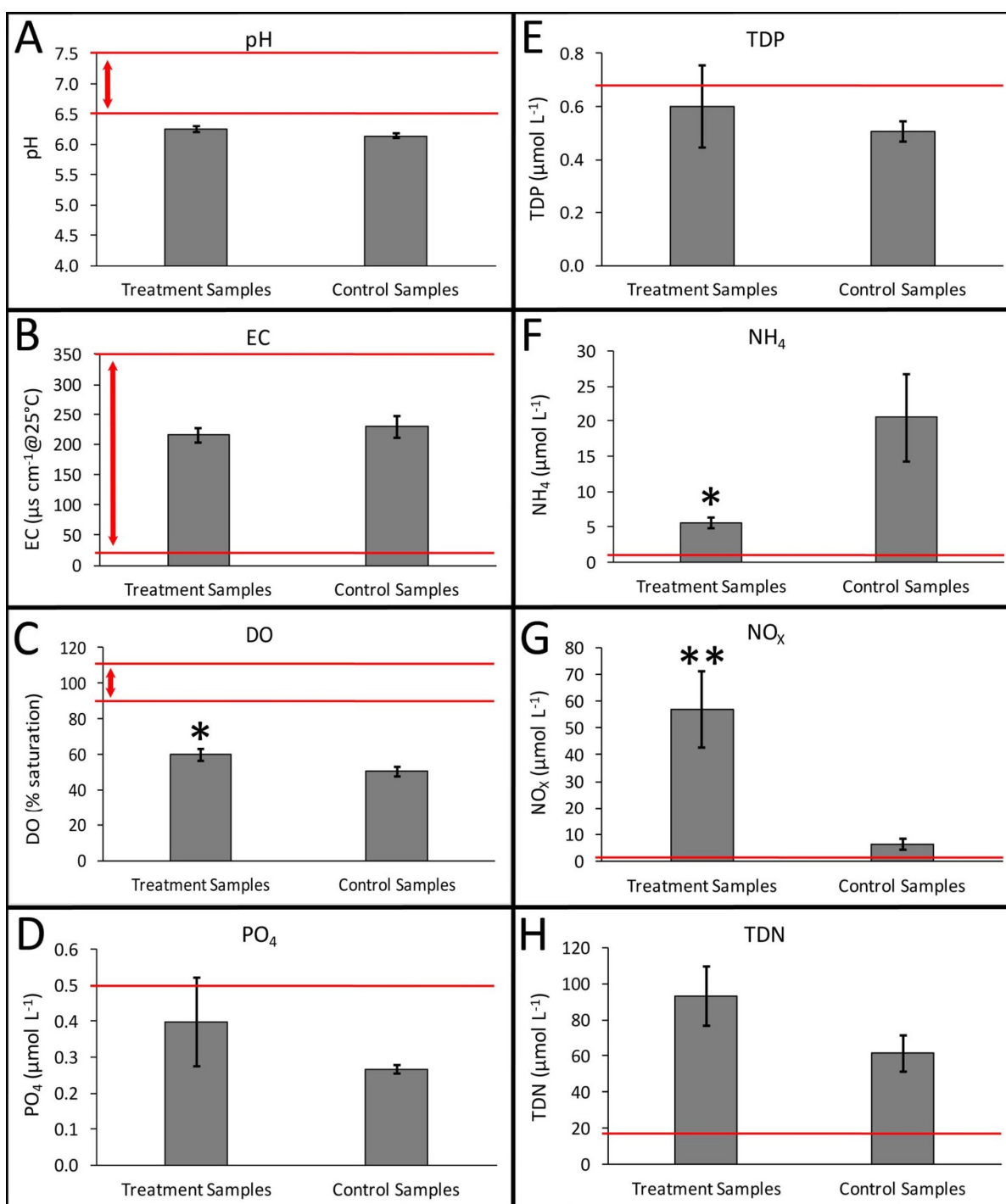


Figure 3: Plots of mean ancillary water parameters (EC, pH and DO) and nutrients (TDN, NO_x, NH₄, TDP and PO₄) in surface water from control (n=86) and treatment (n=86) samples in the Bucca Bucca Creek catchment, NSW. Error bars are standard error, * indicates significant (p<0.05) statistical difference, ** indicates highly significant (p<0.001) statistical difference. Single red bars (Boxes D, E, F, G and H) and dual red bars with arrows (Boxes A, B and C) indicate ANZECC threshold trigger values for slightly disturbed upland streams in NSW (ANZECC, 2000).

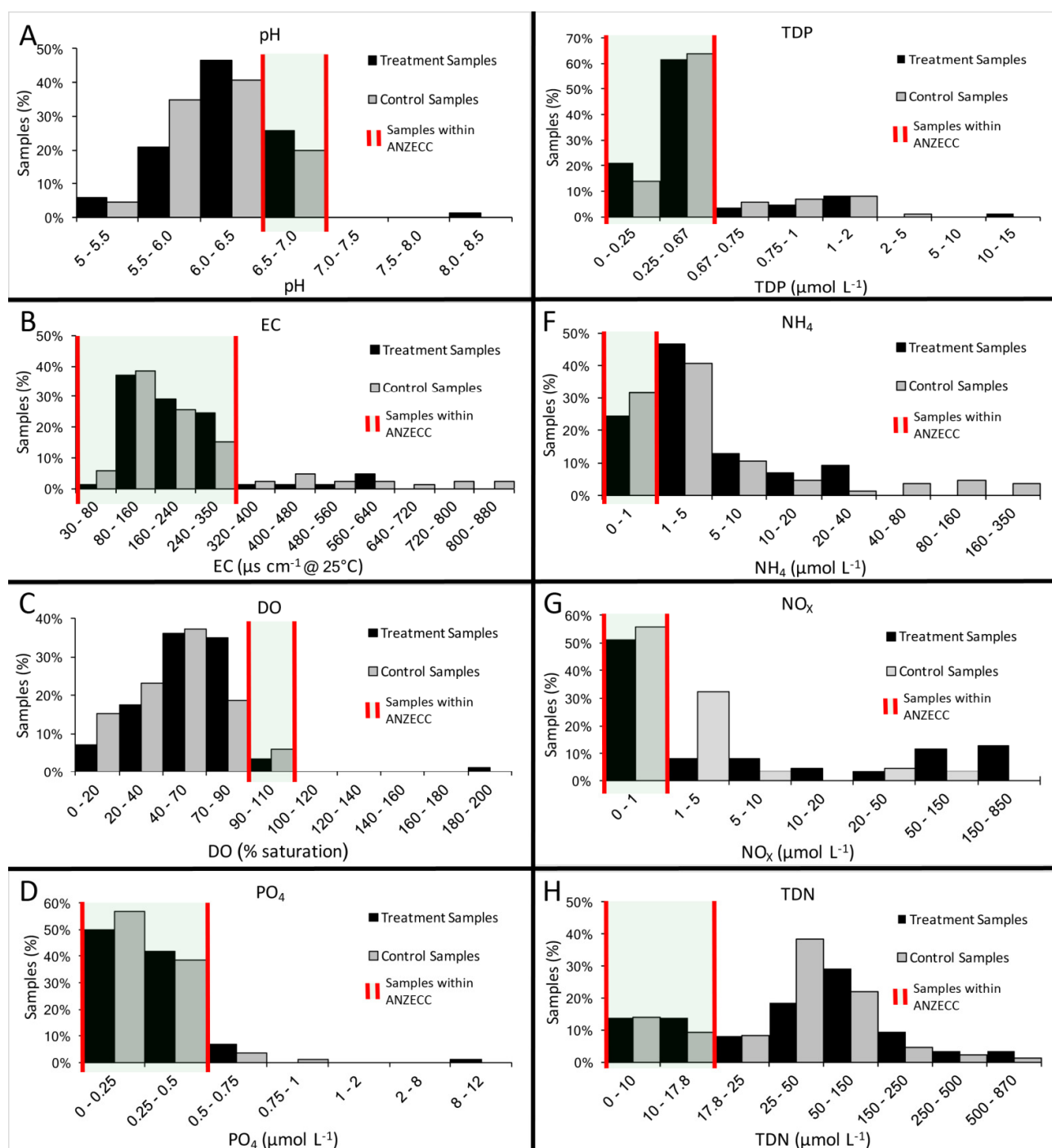


Figure 4: Histograms of mean ancillary water parameters (EC, pH and DO) and nutrient concentrations (TDN, NO_x, NH₄, TDP and PO₄) of surface water from control (n=86) and treatment (n=86) samples in the Bucca Bucca Creek catchment, NSW. Dual red bars indicate maximum and minimum ANZECC threshold trigger values for slightly disturbed upland streams in NSW.

Table 4: Maximum and minimum NO_x concentrations in samples taken at control (n=86) and treatment (n=86) sites in the Bucca Bucca Creek catchment, NSW.

Site	Maximum Sample		Minimum sample	
	Date sampled	NO _x (μmol L ⁻¹)	Date sampled	NO _x (μmol L ⁻¹)
A _C	15/3/17	9.2	9/4/17	0.4
A _T	15/3/17	16.3	21/2/17	0.5
B _{C1}	15/3/17	49.1	7/5/17	0.4
B _{C2}	7/5/17	9.9	7/2/17	0.1
B _T	22/3/17	293.3	21/2/17	0.1
C _C	28/2/17	4.2	14/2/17	0.1
C _T	4/3/17	215.1	21/2/17	0.1
D _C	21/2/17	4.5	28/2/17	0.3
D _{T1}	15/3/17	811.1	14/2/17	0.6
D _{T2}	15/3/17	549.8	7/5/17	0.1
E _C	15/3/17	131.9	28/2/17	0.1
E _T	15/3/17	149.0	14/2/17	0.1
F _C	4/3/17	1.6	22/3/17	0.4
F _T	15/3/17	24.6	14/2/17	0.1
G _C	28/2/17	22.6	4/3/17	0.4
G _T	15/3/17	78.5	21/4/17	0.3

3.4. Groundwater quality

Groundwater samples were taken between 2/5/17 and 4/5/17 from an average depth of 57.2 m (Table 5). Groundwater constituents are compared to ANZECC guidelines (ANZECC, 2000) for slightly disturbed upland streams in NSW rather than drinking water, irrigation or livestock guidelines. ²²²Rn in water varied from 5544 ± 36 dpm L⁻¹ to 150 ± 6 dpm L⁻¹ with an average of 2852 ± 24 dpm L⁻¹. PO₄ was above the ANZECC trigger value (0.5 μmol L⁻¹) in 80% of samples. The maximum PO₄ sample was 1.9 μmol L⁻¹ and minimum was 0.3 μmol L⁻¹. The average PO₄ in the 10 groundwater samples was 0.9 μmol L⁻¹. NO_x results were above the ANZECC trigger value (1.07 μmol L⁻¹) in 70% of samples with an average of 21.4 μmol L⁻¹ (Figure 5). The maximum NO_x was 104.9 μmol L⁻¹ and the minimum 0.2 μmol L⁻¹. NH₄ varied between <0.01 μmol L⁻¹ and 0.8 μmol L⁻¹ with an average of 0.2 μmol L⁻¹. All NH₄ samples were below the ANZECC trigger value (0.929 μmol L⁻¹). pH of samples was between pH 5.81 and pH 6.73, only 40% of samples were within the ANZECC trigger values (pH 6.5 to pH 7.5)

Groundwater is often high in dissolved nutrients and can deliver these nutrients to surface waters through seepage (Burnett et al., 2006; Su et al., 2014). Pollution of groundwater through leaching of soluble nutrients may be a serious long term issue (Li & Zhang, 1999; Spalding & Exner, 1993) and many previous studies have found groundwater pollution and agricultural landscapes (Eckhardt & Stackelberg, 1995; Helena et al., 2000; Zhang, et al., 1996). Surprisingly, groundwaters in the Bucca Bucca Creek catchment had nitrogen concentrations that were usually lower than surface waters, implying that any contamination may not have reached the aquifers yet. Groundwater recharge and therefore contamination, often occurs over long time scales (years to centuries; Santos et al., 2017). Since the blueberry industry is recent in this catchment, our observations may serve as a baseline for future assessments of any impacts brought about by the new industry.

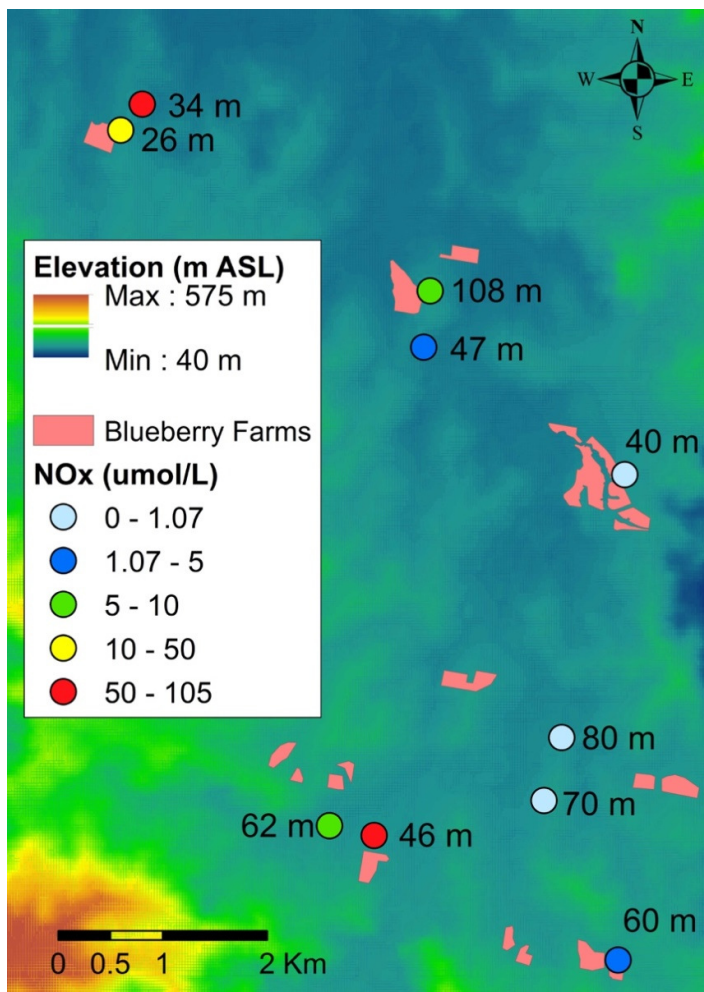


Figure 5: NO_x ($\mu\text{mol L}^{-1}$) in groundwater samples overlying an elevation map. Bore depths are shown near each sample. Depths were given by the landowner at each bore and are assumed to be correct. Elevation data source: CHCC, 2016.

Table 5: Results and coordinates of 10 groundwater samples in the Bucca Bucca Creek catchment, NSW. Bore depths were given by the landowner at each bore and are assumed to be correct.

Site	Coordinates	Date Sampled	Depth (m)	pH	EC (μS @25°C)	DO (%sat.)	^{222}Rn in water (dpm L ⁻¹)	NO _x ($\mu\text{mol L}^{-1}$)	NH ₄ ($\mu\text{mol L}^{-1}$)	DON ($\mu\text{mol L}^{-1}$)	TDN ($\mu\text{mol L}^{-1}$)	PO ₄ ($\mu\text{mol L}^{-1}$)	DOP ($\mu\text{mol L}^{-1}$)	TDP ($\mu\text{mol L}^{-1}$)
1	-30.199, 153.110	2/5/17 7:42	80	6.73	1022	16.1	1334.7 \pm 14.7	0.4	0.8	0.0	1.1	0.6	0.3	0.9
2	-30.205, 153.109	2/5/17 9:33	70	6.48	1345	15.2	2320.7 \pm 22.3	0.3	0.4	0.0	0.6	0.8	1.1	1.9
3	-30.219, 153.116	2/5/17 12:55	60	6.51	721	18.7	4952.8 \pm 33.6	1.7	0.0	2.6	4.3	1.0	0.4	1.4
4	-30.207, 153.087	2/5/17 14:23	62	6.17	567	42.2	1450.0 \pm 5.8	9.8	0.6	3.6	14.0	1.1	0.4	1.4
5	-30.208, 153.092	2/5/17 14:49	45	6.64	233.3	87	3874.8 \pm 32.8	57.3	0.0	2.7	60.0	0.4	0.0	0.4
6	-30.177, 153.117	3/5/17 11:54	40	6.66	391.3	12.8	1163.3 \pm 19.3	0.2	0.4	0.0	0.6	1.9	7.8	9.8
7	-30.161, 153.098	3/5/17 13:32	108	5.92	707	65.7	3911.2 \pm 29.3	5.3	0.0	0.3	5.6	0.7	0.3	1.0
8	-30.166, 153.096	3/5/17 14:26	47	5.95	118.9	13.6	1818.5 \pm 20.0	2.9	0.0	3.3	6.1	1.2	0.3	1.5
9	-30.144, 153.069	4/5/17 11:36	34	5.81	238.1	31.5	3455.5 \pm 25.1	104.9	0.0	2.2	107.2	0.3	0.3	0.6
10	-30.147, 153.067	4/5/17 12:54	26	6.01	174.4	63.8	5544.2 \pm 35.9	31.8	0.1	0.0	31.8	1.1	0.3	1.5
Mean			57.2	6.3	551.8	36.7	2852.6 \pm 23.9	21.4	0.2	1.5	23.1	0.9	1.1	2.0
St dev			24.4	0.4	402.6	26.8	1764.0	34.7	0.3	1.5	35.0	0.5	2.4	2.7

3.5. Nutrient speciation

While NO_x was the dominant nitrogen species in treatment sites, DON was the dominant species in control sites (Figure 6). This clear separation in nitrogen speciation is consistent with our suggestion that blueberry farms modify the composition of nearby creeks. The exception was farm E downstream of a banana farm with a dam between the control site and the treatment site. We suspect that the dam influences the N species composition by increasing residence time and allowing for denitrification to remove NO_x from solution. Groundwater nitrogen was 93% NO_x .

Nitrogen is environmentally available in aqueous, gaseous and solid forms, bound in organic material or in inorganic elemental compounds (De Boer & Kowalchuk, 2001). Limiting nutrients for primary production have been well studied: P is often limiting in freshwater and N is often limiting in coastal seawater and estuaries, based on the Redfield Ratio of 1P:16N (Fabricius, 2005; Smith et al., 2006; Redfield, 1934). Therefore, large N increases in freshwater systems that drain to estuaries can quickly cause eutrophication or algal blooms downstream (Howarth, 1988; Howarth et al., 1996; Nixon et al., 1996). Eutrophication is caused by the rapid growth of aquatic algae and can cause habitat loss, marine and freshwater plant death, coral death and the forfeiture of aquatic biodiversity (Jeppesen et al., 1998; Seehausen et al., 1997). While we have no data on the downstream impacts, we speculate that nitrate may travel from the headwater streams to estuaries.

Inorganic ammonium [NH_4] based fertiliser is the most common fertiliser applied to blueberry crops (Krewer & NeSmith, 1999). When NH_4 is applied to soils, small losses of gaseous N occur through volatilisation, whilst most of the NH_4 is converted to nitrates + nitrites [NO_x], within a few days (De Boer & Kowalchuk, 2001). The two step process of converting NH_4 to NO_x is dominantly carried out by autotrophic bacteria in the soil. Ammonia-oxidising bacteria convert NH_4 to NO_2^- , followed by nitrite-oxidising bacteria converting NO_2^- to NO_3^- (De Boer & Kowalchuk, 2001). Heterotrophic nitrification is also possible through a phylogenetic array of bacteria and fungi, transforming both inorganic and organic nitrogen compounds to NO_x , or gaseous N_2O and N_2 (De Boer & Kowalchuk, 2001; Knowles, 1982; Shoun et al., 1992). NH_4 is relatively insoluble, when compared to the highly soluble NO_x , resulting in significant NO_x losses through leaching (Puckett, 1994). As a result of the conversion of NH_4 to NO_x and the mobility of NO_x , farmers must factor these losses of NO_x when applying NH_4 based fertilisers to combat N deficiencies and leaching losses in the root zone (Krewer & NeSmith, 1999; Puckett, 1994). Thus, due to leaching and solubility, inorganic N in waterways and groundwater from the application of fertiliser is most evident as NO_x (De Boer & Kowalchuk, 2001; Puckett, 1994; Vimpany & Lines-Kelly, 2004).

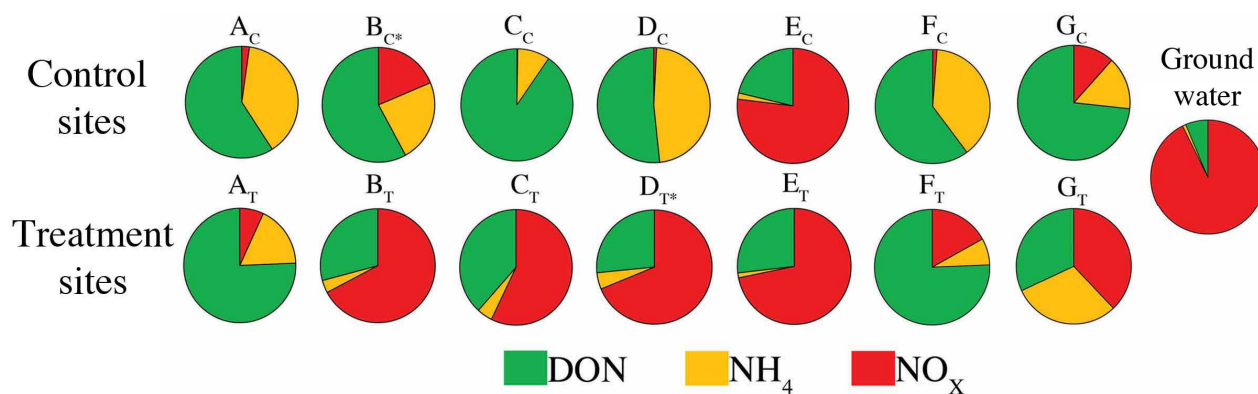


Figure 6: Mean ratio of N species ($\text{NO}_x:\text{NH}_4:\text{DON}$) as a percentage of TDN at control and treatment sites in the Bucca Bucca Creek catchment, NSW, showing that in all farms except farm E, NO_x (% TDN) increased from control sites to treatment sites. Groundwater is a mean of all groundwater bore sites sampled. * indicates the mean of two sites ($\text{B}_{\text{C}1}$ and $\text{B}_{\text{C}2}$; $\text{D}_{\text{T}1}$ and $\text{D}_{\text{T}2}$).

3.6. Nitrate pathways: Groundwater versus surface runoff

Radon (^{222}Rn), a natural groundwater discharge tracer, was measured in Farm F only. Overall, radon changed from $113.2 \pm 4.2 \text{ dpm L}^{-1}$ to $0.8 \pm 0.4 \text{ dpm L}^{-1}$, with higher values during baseflow as expected. There was an inverse relationship between ^{222}Rn and runoff, and a positive relationship between NO_x and runoff (Figure 7). This shows that groundwater discharge was not a likely source of NO_x to the creek. The intensive time series on a weekly scale failed to show any increase in NO_x as rainfall was not sufficient to flush the catchment. The estimation of groundwater in surface water (GW%) was done based on the average groundwater ^{222}Rn in the groundwater bore samples. The GW% in samples at Farm F_T are shown in Figure 8 and indicate that groundwater contributes <4% of water flow to the creek. When the highest NO_x results were measured (sample F_{T6}, $24.6 \mu\text{mol L}^{-1}$ and sample F_{T7}, $20.5 \mu\text{mol L}^{-1}$), the GW% in the creek was <0.1%, further indicating that groundwater is not likely to be a major source of NO_x to surface waters.

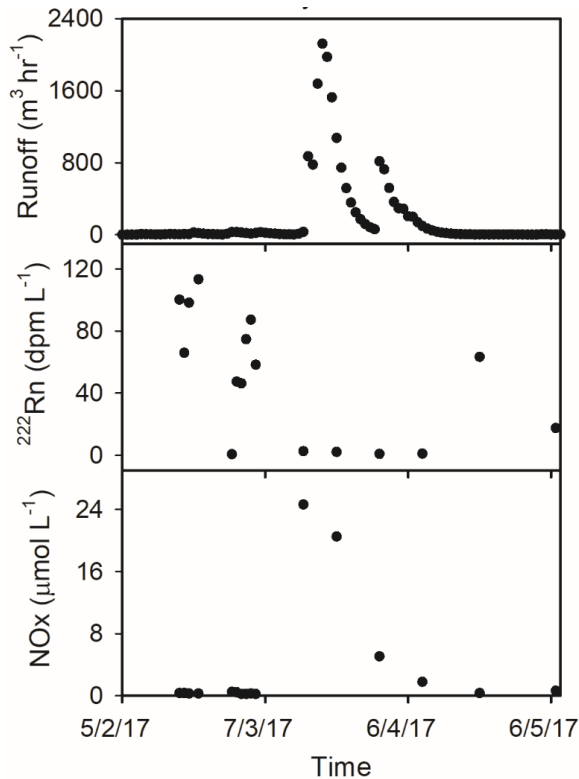


Figure 7: Time series of surface runoff, ^{222}Rn and NO_x at site F_T over the 90 day sampling period, highlighting that NO_x is not driven by groundwater as traced by ^{222}Rn .

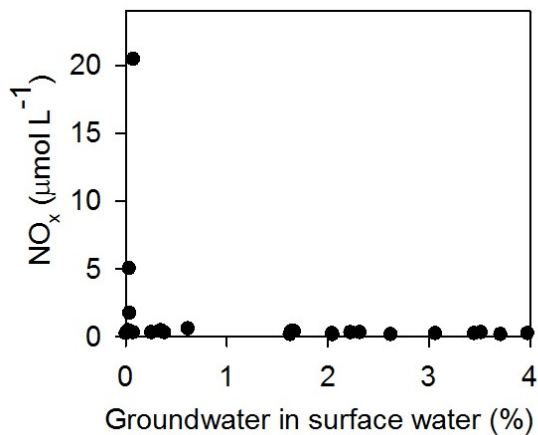


Figure 8: NO_x versus the minimum groundwater contribution to surface water runoff at site F_T . The highest NO_x were seen when groundwater was not a contributor ($<0.1\%$).

Since groundwater does not seem to be a major contributor to NO_x concentrations at site F_T , flushing events may be the primary driver of NO_x concentrations in the creeks sampled. Headwater stream nutrient concentrations are often driven by storm events, creating overland runoff and flushing the nutrients accumulated in the soils during dry periods (Vink, et al., 2007). Indeed, our observations revealed that NO_x follows a similar pattern to runoff in treatment samples (Figure 9). This same pattern was seen in the control samples, though concentrations of NO_x were significantly lower. Therefore, we suggest that surface runoff dominates the delivery of nitrogen to the creeks investigated regardless of the presence of blueberries.

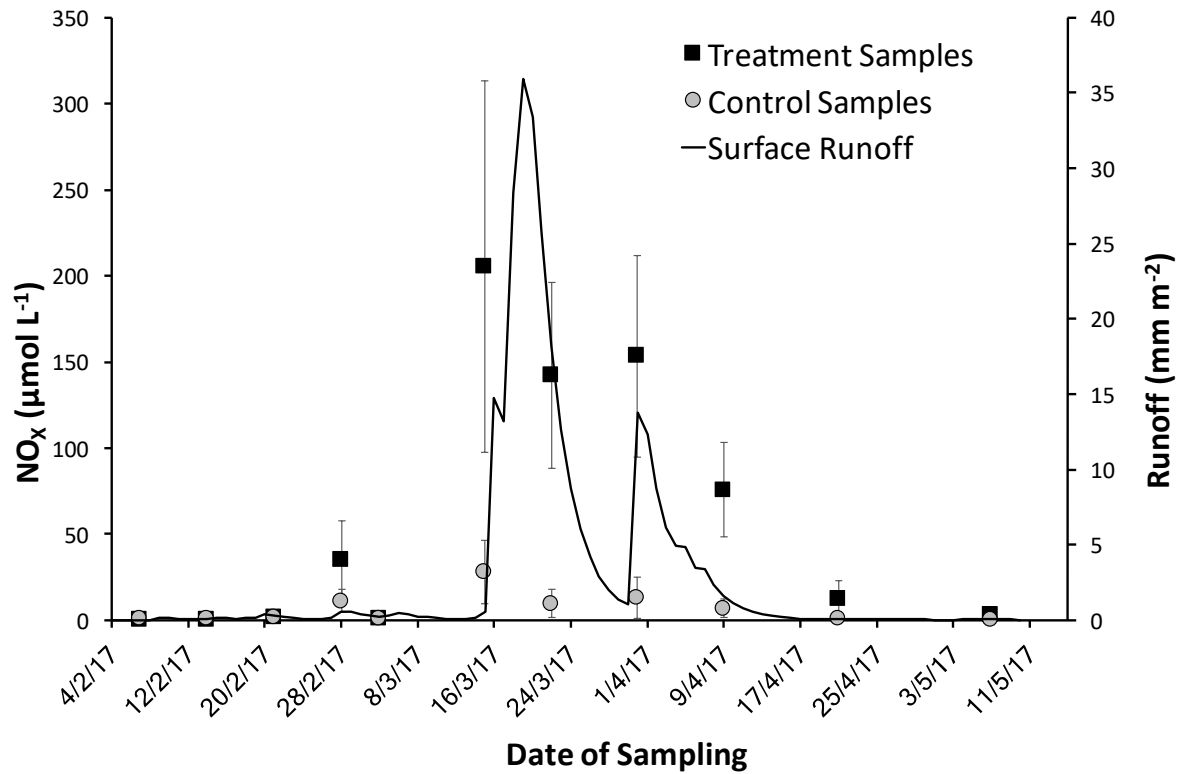


Figure 9: Plot of mean NO_x at control and treatment sites against runoff, showing that NO_x follows runoff strongly at treatment sites and weakly at control sites.

To further obtain insights into the importance of surface runoff, results were separated into rain event (>25mm rain in 48 hrs prior to sample) and baseflow (<25mm rain in 48 hrs prior to sample). The means at all sites following rain events were higher than baseflow (Figure 10). The highest NO_x concentrations during rain event conditions were found at farms B, C and D. These farms have the highest upstream land use dedicated to blueberries (farm B, 59% of catchment; farm C, 26% of catchment; and farm D, up to 65% of catchment), implying they would be priority areas for managing nitrogen runoff.

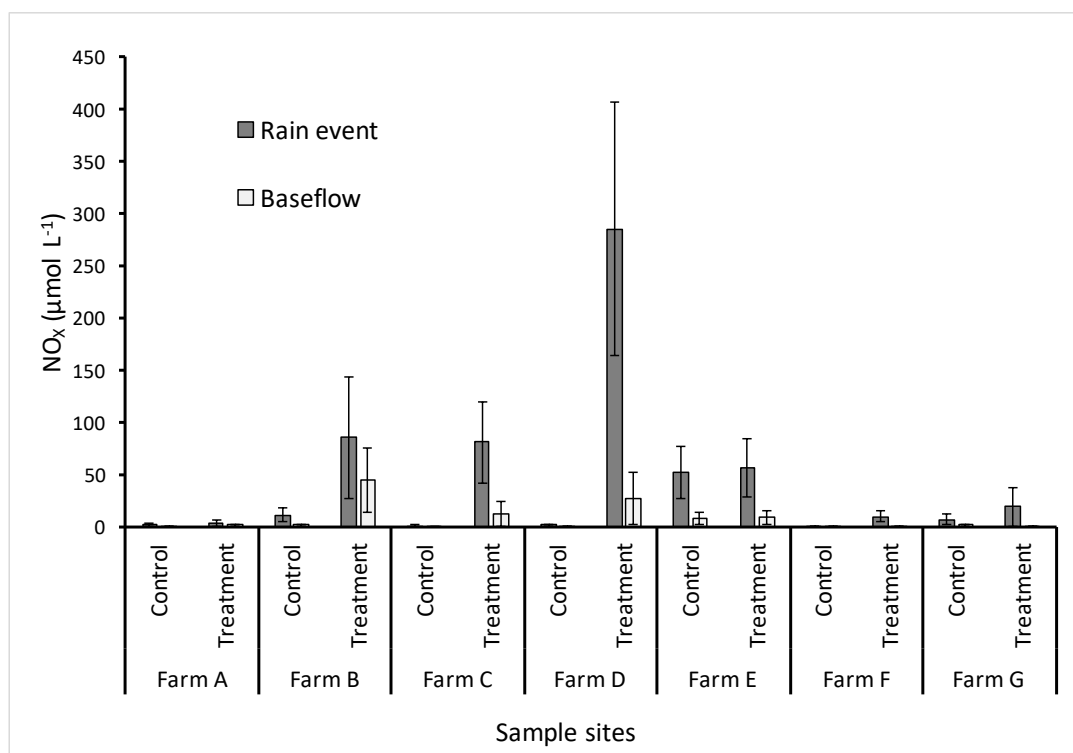


Figure 10: Bar graph of mean NO_x concentrations at control and treatment sites in rain event (>25mm rain in 48 hrs prior to sample) and baseflow (<25mm rain in 48 hrs prior to sample), showing that farms B, C and D are the have the highest NO_x concentrations during rain events.

3.7. Nutrient loads

Nutrient load is a measurement of a constituent based on the flow of a stream and the area of upstream catchment. Our results indicate that the average load of NO_x, NH₄, DON, TDN, PO₄ and TDP at treatment sites was greater than control sites (Table 6). The only nutrient load that was lower at treatment sites was DOP. NO_x was the highest contributory load in our calculations and was on average >13 fold higher at treatment sites (21.8 kg N-NO_x ha yr⁻¹) than control sites (1.6 kg N-NO_x ha yr⁻¹).

Nitrogen loads are highly variable throughout the world and are dependent on geology, population, atmospheric deposition and land use (Seitzinger, et al., 2002). Average loads on the Australian east coast have been estimated to be <1 kg N ha yr⁻¹, though can be >5 fold higher in India, China and Europe (>5 Kg N ha yr⁻¹) (Seitzinger, et al., 2002). Comparatively, Sadat Noori, et al. (2016) studied an estuary at Hat Head, NSW and found that loads were 0.3 kg N-NO₃ ha yr⁻¹ and 15 kg N-TDN ha yr⁻¹. Santos et al. (2013) reported TDN loads of 8.5 kg N-TDN ha yr⁻¹ in the Tuckean Swamp, NSW. We found that the control site average was 1.6 fold higher than the Australian east coast average and the treatment site average was >20 fold higher than the Australian east coast average. These differences may be related not only to the presence of blueberries, but also the scale of the different investigations. While our study focuses on small catchments in headwater streams, Santos et al. (2013) and Sadat-Noori et al. (2016) focused on a much larger area with a lower proportion of intensive land uses such as horticulture.

Table 6: Mean nutrient loads from control and treatment sites over the 90 day sampling period.

Site	NO _x load (Kg N-NO _x ha yr ⁻¹)	NH ₄ load (Kg N-NH ₄ ha yr ⁻¹)	DON load (Kg N-DON ha yr ⁻¹)	TDN load (Kg N-TDN ha yr ⁻¹)	PO ₄ load (Kg P-PO ₄ ha yr ⁻¹)	DOP load (Kg P-DOP ha yr ⁻¹)	TDP load (Kg P-TDP ha yr ⁻¹)
A _C	0.1	0.5	4.8	5.4	0.08	0.06	0.14
A _T	0.3	0.5	4.5	5.3	0.08	0.02	0.10
B _{C1}	0.7	0.1	2.9	3.8	0.08	0.03	0.11
B _{C2}	0.8	0.4	3.9	5.1	0.09	0.02	0.11
B _T	34.9	0.3	7.7	42.9	0.12	0.08	0.20
C _C	0.1	0.4	5.0	5.5	0.09	0.12	0.21
C _T	21.0	1.2	7.6	29.8	0.06	0.04	0.11
D _C	0.2	0.8	10.2	11.2	0.12	0.23	0.35
D _{T1}	61.8	1.2	15.8	78.9	0.09	0.01	0.10
D _{T2}	42.5	0.9	12.1	55.4	0.37	0.21	0.58
E _C	10.2	0.1	1.7	12.0	0.08	0.06	0.14
E _T	10.6	0.1	2.3	12.9	0.09	0.04	0.13
F _C	0.1	0.2	4.7	5.0	0.08	0.05	0.13
F _T	2.1	0.5	6.4	9.0	0.08	0.04	0.12
G _C	0.5	0.2	3.1	3.9	0.06	0.03	0.10
G _T	1.3	0.3	1.7	3.2	0.06	0.00	0.06
Control Mean	1.6	0.3	4.5	6.5	0.08	0.08	0.16
Treatment Mean	21.8	0.6	7.3	29.7	0.12	0.06	0.17

The N fertilisers used in blueberry horticulture include ammonium nitrate, ammonium sulfate and urea (Krewer & NeSmith, 1999). Concentrated superphosphate, potassium chloride and di-ammonium phosphate are the main forms of P and K applied to blueberries, but pose significantly less environmental risk than N fertilisers (Krewer & NeSmith, 1999; Vimpany & Lines-Kelly, 2004). The southern highbush and rabbiteye blueberry varieties native to the USA are well suited to the Coffs Harbour climate (Bevan, 2006). These varieties require fertilization of 121 kg N ha yr⁻¹ and 83 kg P ha yr⁻¹ plus other micronutrients (Doughty et al., 1988). The rate of N addition in blueberries is similar to pineapples (up to 150 kg N ha⁻¹, Omotoso & Akinrinde, 2013), sugarcane (128 kg N ha yr⁻¹, Schroeder et al., 2010) and bananas (100 kg N ha yr⁻¹, Newley, et al., 2008). Assuming that our 90 days of observations can be upscaled to annual exports, and that local farmers use the recommended amount of fertiliser (121 kg N ha yr⁻¹), an average between 18.0% (calculated on N-NO_x) and 24.5% (calculated on N-TDN) of this fertiliser is lost to the creeks.

3.8. Influence of blueberry area on NO_x

We plotted farm land use (% catchment) against mean NO_x concentrations to examine whether the percentage of catchment occupied by blueberries has influence on nutrient concentrations (Figure 11A). At <15% of blueberry land use, there was no detectable influence in mean NO_x concentrations. With increasing blueberry density, mean NO_x concentrations in creeks clearly increased. For every 1% of upstream catchment occupied by

a blueberry farm, it is expected that mean NO_x concentrations would increase by $1.8 \mu\text{mol L}^{-1}$ ($p < 0.001$). Based on these calculations, a catchment with 15% blueberry land use will have mean NO_x concentrations >25 fold higher than the ANZECC trigger value downstream. The minimum percentage of a catchment one land use occupies to be considered the dominant nutrient contributor has not been strictly defined in the literature. Percentages of dominant nutrient contribution in a catchment land use have been reported as low as 5% for bananas (Bainbridge et al., 2009), up to 100% for forestry (Hunter & Walton, 2008). Sugar cane has been classified as the major nutrient contributor (Rohde et al., 2008) when representing >25% of the catchment land use. We suggest that any catchment with >15% blueberry land use will create a measurable impact on downstream nutrient concentrations.

The loads of NO_x also correlated to the percentage of blueberry farms in the catchment (Figure 11B). Similar to the NO_x concentrations in Figure 11A, we suggest that catchments with >15% blueberry land use will have downstream nutrient loads dominated by this land use. Based on our load calculations, a catchment with 15% of blueberry farm land use may have downstream nutrient loads of $11.1 \text{ kg N-NO}_x \text{ ha yr}^{-1}$ ($p < 0.001$). Changes in land use have been shown to be the key factor in alteration of nutrient concentrations downstream (Harris, 2001) and runoff from surrounding lands are the primary nutrient inputs to streams (Puckett, 1994; Seitzinger et al., 2005).

Little is known about blueberry horticulture runoff, though loads, cycling and storage of nutrients is expected to be similar to other agricultural practices (Carpenter et al., 1998; Howarth et al., 1996; Jordan et al., 1997; Puckett, 1994). Hunter & Walton (2008) reported N fluxes of $0.7 \text{ kg N ha yr}^{-1}$ from unsewered areas, $0.38 \text{ kg N ha yr}^{-1}$ from sugar cane and $0.42 \text{ kg N ha yr}^{-1}$ from bananas in the Johnstone River system in north eastern Australia. Land use in tropical Australia has been estimated to have a significant impact on N exports when compared to undisturbed land, particularly in cropland (13.7 fold N export increase), horticulture (28.9 fold N export increase) and urban areas (7.3 fold N export increase) (Young et al., 1996). Our calculated N exports are significantly higher than those reported elsewhere, though similar to expected increases related to horticultural land use.

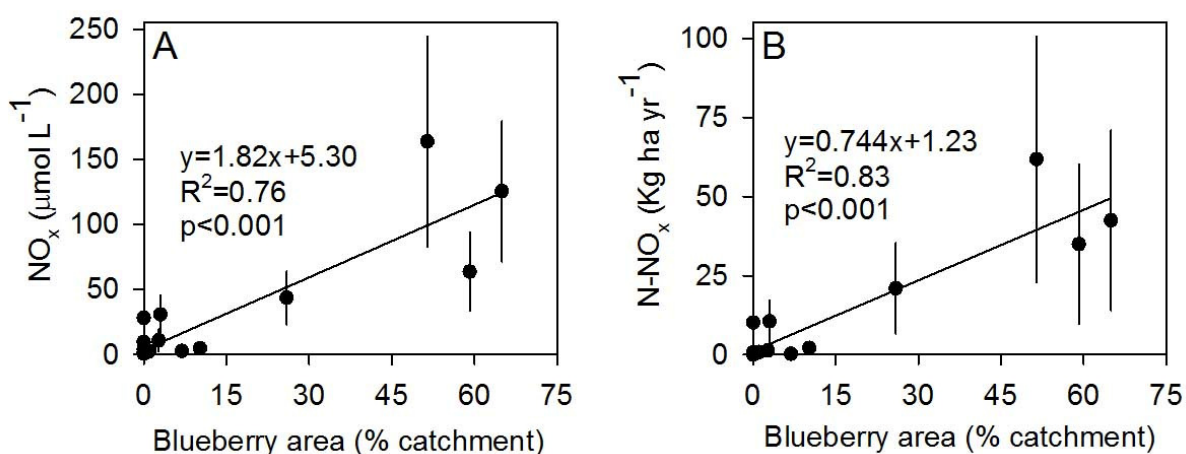


Figure 11: **A)** Plot of mean NO_x concentrations against the percentage of catchment occupied by blueberry land use, showing highly significant correlation ($p < 0.001$). Error bars are standard error. **B)** Plot of mean NO_x loads from control ($n=8$) and treatment ($n=8$) sites against the percentage of catchment occupied by blueberry land use, showing a highly significant correlation ($p < 0.001$). Error bars are standard error.

4. Conclusions

- 1) The 43 pesticides sampled in baseflow conditions were below detection limits. These observations are inconclusive as to whether blueberry farms are a source of pesticides to creeks. Further sampling is required both in storm events and in sediments to examine the fate and impact of pesticides used in blueberry farms.
- 2) There was a significant difference in NO_x between sites downstream of blueberry farms and control sites. We showed that 24% of NO_x samples downstream of blueberries were between 50 and 800 fold higher than the ANZECC trigger values, primarily after rain events. Dissolved phosphorus was below the ANZECC guidelines.
- 3) The main pathway of nutrient loss from farms was surface runoff rather than groundwater discharge. The highest NO_x concentrations were measured when surface runoff increased with a storm event after a period of dry weather.
- 4) Groundwater nitrogen concentrations were generally lower than those in the creeks downstream of blueberry farms. While we cannot identify whether the source of nitrogen to groundwater is natural or anthropogenic, we speculate that fertilisers have not yet reached the aquifers underlying the farms due to the longer time often required to contaminate aquifers.
- 5) There was a significant correlation between blueberry area and creek NO_x concentrations and loads. A catchment with >15% blueberry land use created a change in downstream nutrient concentrations and loads. Catchments with >15% blueberries may produce NO_x concentrations >25 fold higher than the ANZECC trigger values. Therefore, any initial water quality management should focus on catchments with >15% blueberries.

Overall, this report represents the first attempt to assess the impact of blueberry farms on creek water quality in the Coffs Harbour region. Several lines of evidence demonstrated a strong influence of blueberry farming on creek water quality, in particular nitrate.

We strongly recommend management of nitrogen runoff and an assessment of potential impacts to downstream waterways.

5. Recommendations

5.1. *Water quality monitoring needs*

- Develop baseline monitoring of nutrients in soils and creeks before, during and after land development.
- Incorporate monitoring into any future planning capacities.
- Investigate creek self-purification capacity and impacts in downstream waterways such as estuaries, fisheries and the Solitary Islands Marine Park.
- Focus on rain events for monitoring.
- Focus monitoring and management on catchments with >15% blueberry farming.
- Pesticide monitoring is needed both in sediments and sampling following rain events.
- Create reporting mechanisms to understand what is applied on the farms and what may be lost to creeks and downstream waterways.

5.2. *Management options*

We recommend management of nitrogen runoff to prevent local and downstream impacts including algae blooms, estuarine contamination, fisheries losses and impacts to the Solitary Islands Marine Park. The management of nitrate in agricultural lands has been well researched and the options available to land and water managers are vast. The following approaches may be required to minimize nutrient runoff from blueberry farms:

- 1) Woodchip bioreactors (as denitrification beds or denitrification walls) can be installed instream or in constructed drainage ditches and have been shown to remove up to 22 g N m³ of bioreactor day⁻¹ (Schipper, 2010 and references therein; Figure 12).
- 2) The use of constructed wetlands and macrophyte plants or rice crops have been shown to reduce NO_x loads downstream by up to 2 kg N ha of wetland day⁻¹ (Bachand & Horne, 1999; Kirk Kronzucker, 2005; Lindau et al, 1990; Figure 12).
- 3) Increasing riparian buffer zones by planting trees, shrubs and macrophytes is also an important management consideration and has been shown to reduce N exports to creeks by 4% for every m of planting (Hill, 1996).
- 4) Tail-water recovery systems have been used extensively downstream of farms in the U.S.A. to recover leached NO_x and reuse waters with high NO_x concentrations to irrigate farms (Carruth et al., 2014; Rice et al., 2001). These systems have been recommended as part of a best management practice design on farms that are susceptible to NO_x leaching (Waskom, 1994). This management option could reduce the downstream concentrations of leaching NO_x, whilst also increasing irrigation and water holding capacity on the farms.

The efficiencies and costs of those approaches have not been assessed in a blueberry context in northern NSW. However, the efficiency of each approach is likely to be site specific, and a combination of approaches may be necessary. Further research is required to identify suitable management approach and to engage farmers in improving nutrient retention in their farms.

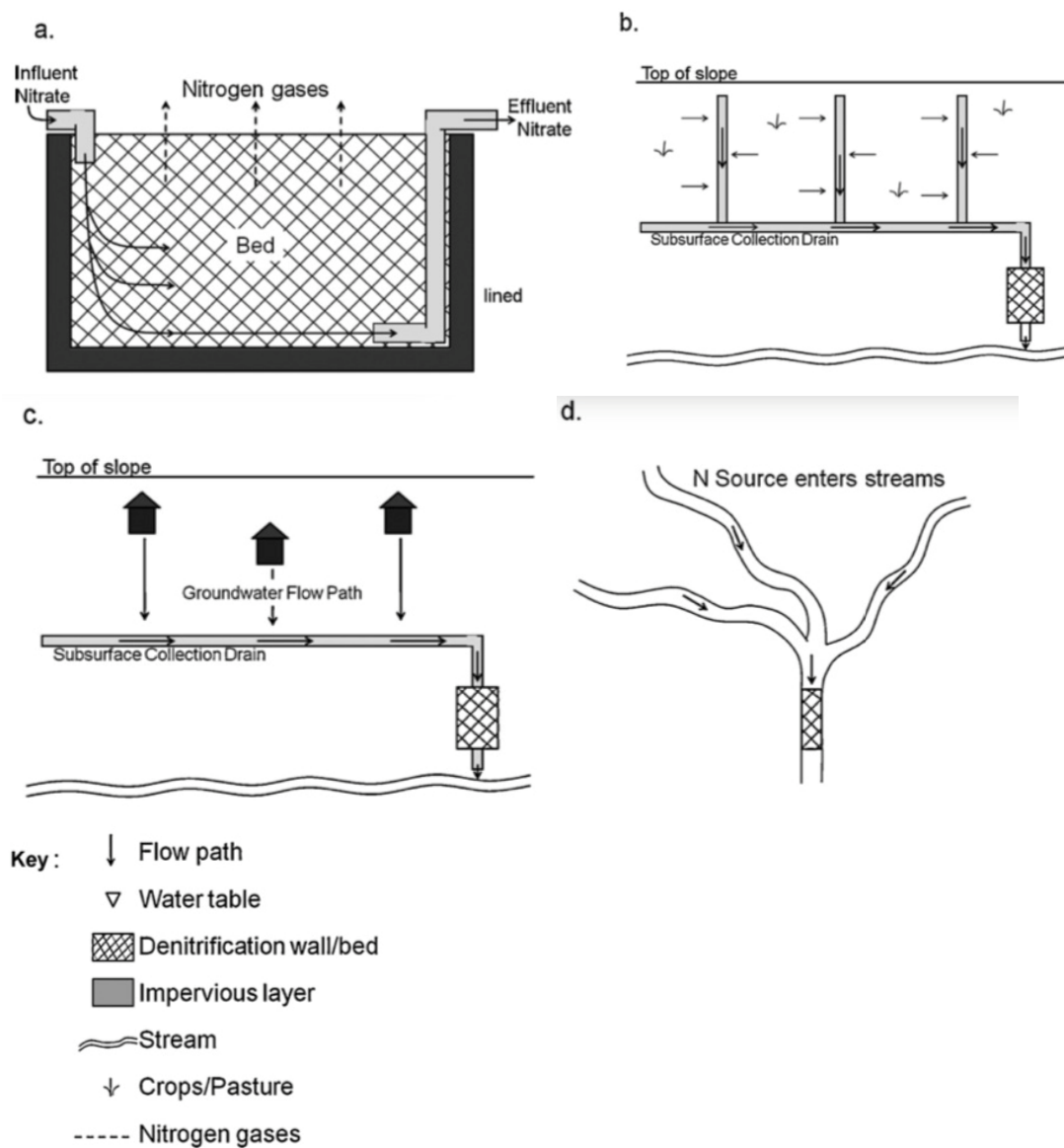


Figure 12: Conceptual diagram of the possible designs of denitrification bioreactors A) Side view of woodchip bioreactor. B) Top view of woodchip bioreactor designed to capture water from agricultural land use. C) Top view of woodchip bioreactor designed to collect surface and subsurface runoff. D) Top view of an instream woodchip bioreactor. (Source: Schipper, 2010)

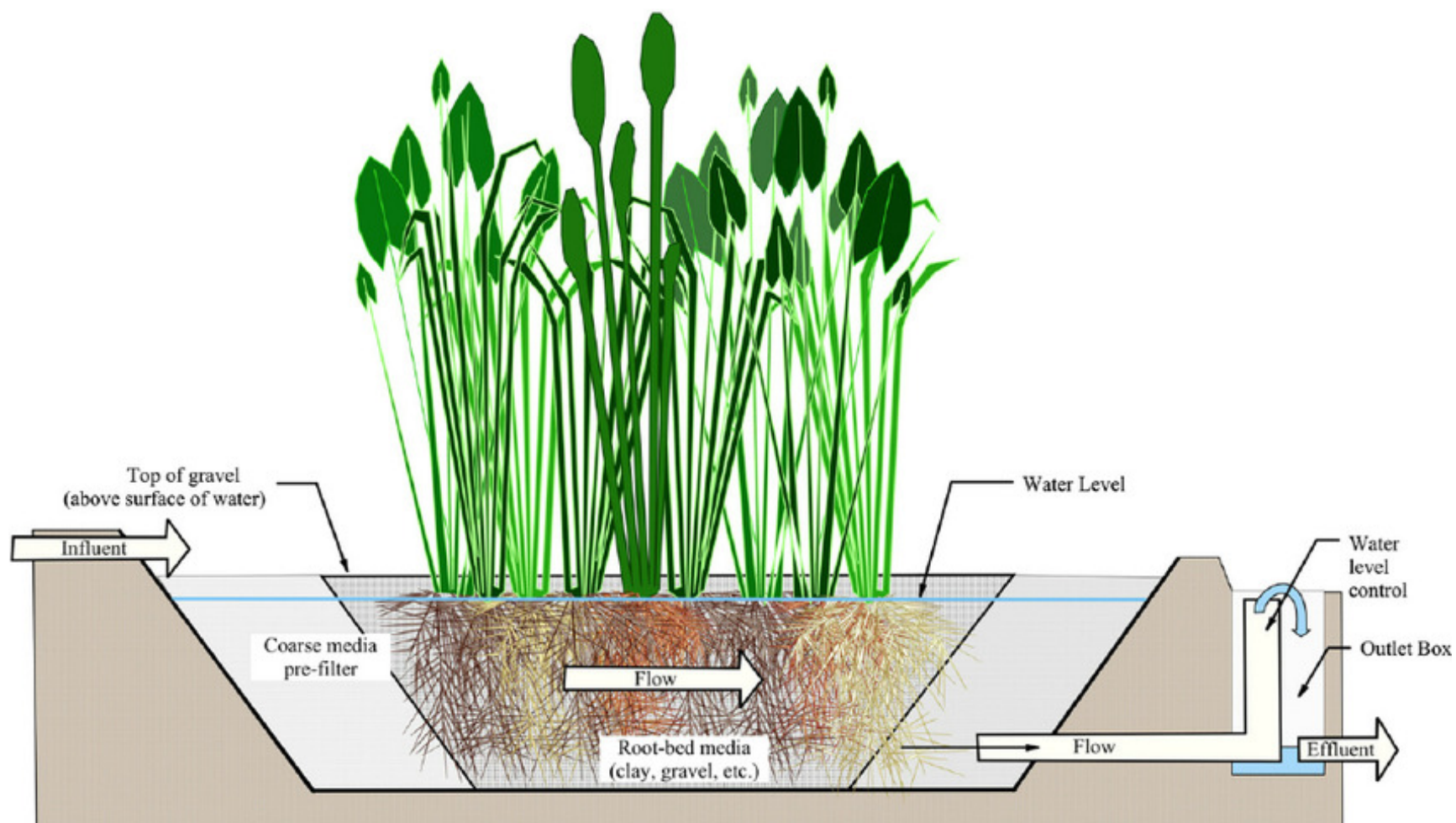


Figure 13: Conceptual model of constructed wetland designed to increase residence time, uptake N via macrophytes and allow denitrification of N to inert gases (Source: White, 2013).

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7. Appendices

Appendix 1: Table of threatened and endangered species that are known to inhabit the Bucca Bucca Creek Catchment. These species are listed as vulnerable (V) or endangered (E) under the Commonwealth *Environment Protection and Biodiversity Conservation Act 1999* [EPBC Act], *NSW Threatened Species Conservation Act 1995* [TSC Act] and/or *NSW Fisheries Management Act 1994* [FM Act] (CHCC, 2012a; CHCC, 2012b).

Type	Common name	Scientific name	EPBC Act status	TSC Act status	FM Act status
Plants	Moonee Quassia	<i>Quassia sp.</i> Moonee Ck	E	E	
	Orara Boronia	<i>Boronia umbellata</i>	V	V	
	Rusty Plum	<i>Niemeyera whitei</i>		V	
Amphibians	Giant Barred Frog	<i>Mixophyes iteratus</i>	E	E	
Reptiles	Stephens' Banded Snake	<i>Hoplocephalus stephensii</i>		V	
Birds	Swift Parrot	<i>Lathamun discolor</i>	E	E	
	Sooty Owl	<i>Tyto tenebricosa</i>		V	
	Masked Owl	<i>Tyto novaehollandiae</i>		V	
	Powerful Owl	<i>Ninox strenua</i>		V	
	Glossy Black Cockatoo	<i>Calyptorhynchus lathamii</i>		V	
Fish	Eastern Freshwater Cod	<i>Maccullochella ikei</i>	E		E
Mammals	Spotted-tailed Quoll	<i>Dasyurus maculatus</i>	E	V	
	Koala	<i>Phascolarctos cinereus</i>	V	V	
	Grey-headed Flying Fox	<i>Pteropus poliocephalus</i>	V	V	
	Yellow-bellied Glider	<i>Petaurus australis</i>		V	
	Rufous Bettong	<i>Aepyprymnus rufescens</i>		V	
	Eastern Freetail Bat	<i>Mormopterus norkolkensis</i>		V	
	Broad-nosed Bat	<i>Scoteanax ruepellii</i>		V	
	Little Bentwing Bat	<i>Miniopterus australis</i>		V	

Appendix 2: Results of ancillary water parameters and nutrient analysis at control (n=8) and treatment (n=8) sites in the Bucca Bucca Creek catchment between 7/217 and 7/5/17. Dates of each sample are given in Table 3. All nutrients (NO_x, NH₄, DON, TDN, PO₄, DOP and TDP) are given in units of $\mu\text{mol L}^{-1}$.

Site & Sample	pH	Temp. (°C)	EC ($\mu\text{s/cm}$ @25°C)	DO (%sat.)	NO _x	NH ₄	DON	TDN	PO ₄	DOP	TDP
A _C 1	6.25	22.6	535.0	55.6	0.6	43.1	64.2	107.9	0.3	0.3	0.6
A _C 2	6.52	22.3	405.8	9.7	1.3	132.3	82.6	216.2	0.5	0.6	1.1
A _C 3	6.38	19.4	246.2	37.8	0.9	72.7	59.0	132.6	0.3	0.4	0.7
A _C 4	5.22	20.2	237.2	69.1	1.2	2.4	42.9	46.5	0.2	0.2	0.4
A _C 5	6.40	21.0	207.8	18.6	1.1	31.0	60.0	92.1	0.4	0.1	0.5
A _C 6	5.48	21.7	195.2	58.1	9.2	0.8	23.3	33.3	0.2	0.1	0.3
A _C 7	5.61	22.5	217.5	32.4	0.6	2.2	24.0	26.8	0.2	0.1	0.4
A _C 8	5.74	21.6	130.4	71.2	0.9	1.4	34.9	37.1	0.2	0.2	0.4
A _C 9	6.00	18.6	240.1	33.9	0.4	2.1	23.8	26.2	0.2	0.5	0.7
A _C 10	6.09	17.3	297.8	19.7	0.4	7.4	30.1	37.9	0.2	0.2	0.5
A _C 11	6.39	15.9	344.3	10.3	0.5	9.9	20.4	30.8	0.3	0.2	0.5
A _T 1	6.28	24.1	317.1	37.1	0.6	27.1	48.0	75.6	0.4	0.2	0.6
A _T 2	6.26	22.1	291.3	21.0	0.7	24.3	73.0	97.9	0.6	0.6	1.2
A _T 3	6.00	19.8	107.2	24.8	0.5	8.0	16.8	25.3	0.3	0.2	0.4
A _T 4	5.51	19.6	108.1	79.5	2.5	1.5	22.9	26.9	0.2	0.1	0.4
A _T 5	5.54	20.7	285.6	24.0	0.4	1.0	33.4	34.8	0.2	0.4	0.6
A _T 6	5.40	22.7	198.3	70.4	16.3	1.0	34.2	51.5	0.2	0.1	0.3
A _T 7	5.50	23.6	218.6	68.3	1.9	1.8	24.3	27.9	0.2	0.1	0.3
A _T 8	6.20	23.5	111.6	86.7	1.2	3.8	30.3	35.3	0.2	0.0	0.2
A _T 9	6.27	20.1	181.2	50.4	0.8	4.4	36.6	41.8	0.2	0.0	0.3
A _T 10	5.95	17.7	285.0	23.2	7.7	6.5	24.1	38.3	0.2	0.0	0.2
A _T 11	6.13	16.4	309.6	14.8	0.5	4.5	19.3	24.3	0.2	0.1	0.3
B _{Cl} 1	6.57	24.7	287.7	33.9	0.5	130.9	12.2	143.6	0.5	0.0	0.5
B _{Cl} 2	6.56	25.0	182.4	59.9	0.6	7.8	51.5	59.8	0.3	0.3	0.6
B _{Cl} 3	6.51	21.6	67.7	66.7	0.3	1.9	38.8	41.0	0.2	0.1	0.4
B _{Cl} 4	6.05	20.5	173.5	42.9	47.9	7.5	10.4	65.7	0.2	0.0	0.2
B _{Cl} 5	6.43	21.4	167.3	28.2	0.6	1.1	42.3	44.0	0.4	0.2	0.6
B _{Cl} 6	5.85	20.5	156.4	69.8	49.1	1.6	34.5	85.2	0.3	0.0	0.3
B _{Cl} 7	6.46	21.1	148.4	84.8	3.4	0.6	13.3	17.3	0.2	0.1	0.3
B _{Cl} 8	6.76	20.7	85.6	91.4	2.7	0.6	23.2	26.6	0.2	0.1	0.3
B _{Cl} 9	6.69	18.9	145.9	67.2	2.6	0.6	8.5	11.6	0.2	0.1	0.3
B _{Cl} 10	6.27	18.4	181.7	34.3	1.0	1.1	8.5	10.6	0.2	0.0	0.2
B _{Cl} 11	6.45	17.3	208.2	31.4	0.4	0.8	5.4	6.6	0.2	0.0	0.2

Site & Sample	pH	Temp. (°C)	EC (µs/cm @25°C)	DO (%sat.)	NO _x	NH ₄	DON	TDN	PO ₄	DOP	TDP
B _{C2} 1	6.00	25.3	170.2	54.3	0.1	1.8	8.6	10.4	0.2	0.0	0.2
B _{C2} 2	6.42	23.3	186.2	15.5	0.3	3.1	10.1	13.4	0.4	0.1	0.4
B _{C2} 3	6.37	21.3	143.7	34.4	0.2	0.9	12.9	14.1	0.2	0.1	0.3
B _{C2} 4	6.28	20.3	120.0	42.1	0.4	0.1	37.9	38.3	0.2	0.2	0.4
B _{C2} 5	6.33	21.3	134.4	32.3	0.5	0.3	23.3	24.1	0.3	0.1	0.4
B _{C2} 6	6.33	20.2	159.5	69.2	2.8	0.6	5.6	9.1	0.2	0.0	0.2
B _{C2} 7	6.36	21.9	115.4	97.0	4.3	1.9	21.1	27.3	0.2	0.1	0.3
B _{C2} 8	6.95	22.2	77.6	98.6	6.8	3.1	28.5	38.4	0.3	0.0	0.3
B _{C2} 9	6.56	20.9	98.6	82.6	2.8	3.4	21.2	27.3	0.2	0.1	0.3
B _{C2} 10	6.22	19.7	113.3	72.9	3.8	2.2	14.6	20.6	0.2	0.0	0.2
B _{C2} 11	6.31	17.8	130.3	63.3	9.9	3.3	3.4	16.6	0.3	0.0	0.3
B _T 1	6.44	25.2	167.7	24.2	0.4	3.4	0.0	3.7	0.3	0.0	0.3
B _T 2	6.70	23.7	94.0	3.5	0.3	6.6	2.6	9.4	0.3	0.1	0.4
B _T 3	6.36	21.4	157.6	24.4	0.1	3.3	1.1	4.5	0.2	0.1	0.4
B _T 4	6.50	20.5	140.9	51.7	0.3	3.3	2.9	6.4	0.3	0.0	0.3
B _T 5	6.52	21.6	152.7	35.7	0.3	1.7	8.0	10.0	0.3	0.1	0.4
B _T 6	6.13	20.6	140.1	81.3	1.0	0.9	50.6	52.5	0.3	0.3	0.6
B _T 7	6.35	22.6	100.3	94.1	293.3	1.3	53.5	348.2	0.3	0.2	0.5
B _T 8	6.55	20.9	78.3	68.2	136.3	2.1	43.2	181.5	0.4	0.3	0.7
B _T 9	6.54	21.0	97.9	79.6	184.5	1.0	31.8	217.3	0.2	0.3	0.5
B _T 10	6.55	18.7	92.6	75.7	82.5	0.9	31.8	115.3	0.2	0.2	0.4
B _T 11	6.81	16.6	101.9	64.7	3.1	4.5	46.1	53.7	0.5	0.6	1.1
C _C 1	5.93	24.3	280.7	31.6	0.2	0.6	1.5	2.4	0.2	0.0	0.2
C _C 2	5.84	22.8	290.9	14.1	0.1	2.4	4.9	7.4	0.2	0.2	0.3
C _C 3	6.34	22.0	139.5	54.0	1.2	10.5	48.1	59.8	0.2	0.7	1.0
C _C 4	6.14	19.8	72.6	90.3	4.2	3.6	65.5	73.4	0.5	0.6	1.1
C _C 5	5.95	22.8	477.4	38.1	0.4	0.4	38.1	38.9	0.2	0.5	0.7
C _C 6	5.91	20.5	296.8	67.3	1.0	4.1	59.8	65.0	0.4	0.5	0.9
C _C 7	5.96	23.2	210.6	48.3	0.4	2.2	29.5	32.1	0.3	0.4	0.7
C _C 8	6.03	23.5	106.1	67.9	0.4	2.6	29.9	32.9	0.3	0.2	0.5
C _C 9	6.01	19.3	309.5	51.0	0.1	0.5	24.3	24.9	0.2	0.3	0.5
C _C 10	5.90	17.9	470.9	45.9	0.2	2.1	4.3	6.6	0.2	0.1	0.3
C _C 11	5.65	16.0	534.0	43.1	0.3	2.4	0.6	3.4	0.1	0.2	0.3

Site & Sample		pH	Temp. (°C)	EC (µs/cm @25°C)	DO (%sat.)	NO _x	NH ₄	DON	TDN	PO ₄	DOP	TDP
C _T	1	5.78	25.0	292.3	41.0	0.3	2.6	0.0	2.9	0.2	0.0	0.2
C _T	2	5.92	23.6	273.1	43.9	0.4	0.1	5.1	5.6	0.2	0.0	0.2
C _T	3	6.16	23.6	270.6	71.8	0.1	0.4	6.7	7.3	0.2	0.0	0.2
C _T	4	5.06	20.1	242.5	53.4	103.2	2.2	33.1	138.5	0.3	0.2	0.5
C _T	5	5.37	20.5	225.1	22.5	0.4	0.6	45.0	46.0	0.2	0.3	0.5
C _T	6	5.29	20.5	116.2	66.1	12.1	1.8	37.3	51.3	0.2	0.1	0.3
C _T	7	5.55	23.6	202.2	63.1	75.6	3.9	69.0	148.5	0.2	0.2	0.4
C _T	8	6.11	23.9	104.5	85.9	215.1	11.9	21.6	248.6	0.1	0.0	0.1
C _T	9	6.16	20.0	140.0	63.6	73.2	10.3	22.9	106.4	0.2	0.0	0.2
C _T	10	5.54	17.4	107.6	47.1	0.3	1.9	4.9	7.1	0.1	0.0	0.1
C _T	11	5.61	14.9	82.7	55.5	0.1	1.9	76.8	78.8	0.1	0.2	0.3
D _C	1	6.57	28.9	617.0	61.7	0.8	297.7	253.4	551.8	0.6	1.8	2.4
D _C	2	6.77	22.7	867.0	50.1	1.5	322.7	159.1	483.3	0.3	0.9	1.2
D _C	3	6.64	21.4	623.0	47.4	4.5	229.4	209.1	443.0	0.4	1.1	1.4
D _C	4	5.24	21.8	671.0	63.8	0.3	3.5	38.0	41.8	0.2	0.6	0.8
D _C	5	5.80	24.1	808.0	23.1	0.6	12.7	37.8	51.0	0.2	0.3	0.5
D _C	6	5.78	24.0	193.4	84.6	4.2	0.5	51.2	55.9	0.3	0.3	0.6
D _C	7	5.97	22.6	202.5	74.7	0.5	2.3	67.0	69.7	0.4	0.9	1.3
D _C	8	6.26	23.3	133.5	85.8	1.6	1.8	56.8	60.2	0.3	0.3	0.5
D _C	9	6.51	19.9	235.4	67.0	0.4	0.6	40.5	41.4	0.2	0.5	0.7
D _C	10	6.17	16.0	362.4	53.4	0.4	3.4	29.6	33.3	0.3	0.1	0.4
D _C	11	6.28	14.6	424.9	53.3	0.5	7.4	17.7	25.6	0.0	0.1	0.1
D _{T1}	1	6.41	24.9	177.6	16.5	0.7	21.3	43.8	65.9	0.5	0.2	0.6
D _{T1}	2	6.66	22.9	178.2	48.4	0.6	31.6	22.1	54.2	0.6	0.4	1.1
D _{T1}	3	6.31	20.6	137.8	52.0	5.1	23.5	24.0	52.6	0.4	0.6	1.0
D _{T1}	4	6.38	21.4	88.7	80.3	5.8	2.5	60.9	69.2	0.3	0.5	0.8
D _{T1}	5	6.48	22.7	120.3	82.4	2.1	7.8	55.3	65.2	0.3	0.5	0.8
D _{T1}	6	5.87	23.4	215.7	87.4	811.1	1.8	0.0	812.9	0.2	0.2	0.4
D _{T1}	7	5.99	22.5	173.3	75.9	351.6	9.4	117.2	478.2	0.2	0.0	0.2
D _{T1}	8	6.19	22.6	233.5	85.9	450.7	5.1	85.9	541.8	0.3	0.0	0.3
D _{T1}	9	6.50	19.3	157.8	78.1	159.0	6.1	22.2	187.3	0.2	0.1	0.3
D _{T1}	10	6.45	17.5	219.0	72.3	0.8	13.4	6.9	21.1	0.3	0.2	0.4
D _{T1}	11	6.64	17.9	189.7	82.5	14.1	11.1	14.3	39.4	0.3	0.0	0.3

Site & Sample		pH	Temp. (°C)	EC (µs/cm @25°C)	DO (%sat.)	NO _x	NH ₄	DON	TDN	PO ₄	DOP	TDP
D _{T2}	1	8.13	25.9	343.4	198.6	0.7	17.8	67.8	86.3	0.6	0.1	0.7
D _{T2}	2	6.67	22.1	345.6	17.0	0.5	10.6	56.8	68.0	0.4	0.5	0.8
D _{T2}	3	6.19	21.0	309.2	49.3	2.1	21.4	35.9	59.4	0.2	0.4	0.6
D _{T2}	4	5.63	20.9	315.4	53.1	166.3	1.3	60.3	227.9	0.3	1.1	1.3
D _{T2}	5	5.97	23.0	289.7	55.6	0.6	4.3	42.7	47.6	0.2	0.4	0.6
D _{T2}	6	6.05	25.8	161.6	70.8	549.8	7.0	298.8	855.7	0.2	0.9	1.1
D _{T2}	7	6.09	23.4	144.4	51.4	325.2	3.1	102.1	430.5	0.7	0.6	1.4
D _{T2}	8	6.90	24.0	142.2	80.8	189.7	8.0	34.0	231.7	0.4	0.2	0.5
D _{T2}	9	6.71	20.6	121.7	48.3	145.3	3.0	36.3	184.6	10.8	2.6	13.5
D _{T2}	10	6.39	16.2	224.3	13.8	0.4	3.6	25.2	29.2	0.3	0.3	0.6
D _{T2}	11	6.72	16.0	299.3	13.3	0.1	4.2	18.6	22.9	0.4	0.3	0.6
E _C	1	5.81	21.3	397.6	13.4	0.2	0.5	8.2	8.9	0.1	0.1	0.2
E _C	2	5.89	21.4	253.9	18.3	0.5	0.0	4.0	4.5	0.2	0.1	0.4
E _C	3	5.94	20.1	246.1	17.7	0.2	3.6	0.0	3.8	0.2	0.0	0.3
E _C	4	6.05	20.0	242.2	34.8	0.1	1.0	4.6	5.7	0.2	0.0	0.2
E _C	5	5.97	21.6	259.9	24.8	3.6	0.5	5.1	9.2	0.2	0.1	0.3
E _C	6	6.14	21.2	163.2	82.1	131.9	0.1	23.0	154.9	0.2	0.2	0.4
E _C	7	6.38	21.4	138.1	74.8	58.3	0.1	8.0	66.3	0.2	0.1	0.3
E _C	8	6.69	21.2	116.4	87.9	73.0	0.6	14.5	88.1	0.3	0.3	0.5
E _C	9	6.53	19.4	156.0	70.1	37.2	0.3	8.9	46.4	0.3	0.1	0.4
E _C	10	6.16	18.1	184.5	53.1	5.4	0.5	7.6	13.5	0.2	0.1	0.3
E _C	11	6.37	17.8	227.7	50.6	1.1	0.0	2.6	3.7	0.2	0.0	0.2
E _T	1	5.86	24.5	246.7	23.1	0.4	0.4	3.5	4.3	0.1	0.0	0.1
E _T	2	5.89	23.3	250.7	20.1	0.1	0.6	19.0	19.7	0.2	0.2	0.4
E _T	3	6.01	23.2	244.2	39.9	0.2	0.7	5.4	6.4	0.2	0.1	0.3
E _T	4	6.43	21.6	252.2	73.4	0.3	1.9	13.1	15.3	0.5	0.2	0.7
E _T	5	6.48	26.8	256.3	89.3	0.7	0.3	9.8	10.8	0.2	0.0	0.2
E _T	6	6.23	22.9	175.6	91.2	149.0	0.4	25.8	175.1	0.3	0.2	0.4
E _T	7	6.44	21.8	145.7	88.3	60.3	0.6	7.6	68.5	0.2	0.0	0.3
E _T	8	7.00	22.3	121.5	91.8	75.1	0.4	22.9	98.4	0.3	0.2	0.5
E _T	9	6.80	19.3	164.7	89.1	40.1	0.5	5.1	45.7	0.3	0.0	0.3
E _T	10	6.34	18.4	192.1	74.7	8.0	0.4	6.9	15.3	0.2	0.0	0.2
E _T	11	6.51	18.0	218.6	77.0	6.7	0.4	8.1	15.2	0.3	0.0	0.3

Site & Sample	pH	Temp. (°C)	EC (µs/cm @25°C)	DO (%sat.)	NO _x	NH ₄	DON	TDN	PO ₄	DOP	TDP
F _C 1	6.19	22.7	158.5	18.0	1.2	119.9	76.2	197.3	0.5	0.4	1.0
F _C 2	6.13	22.6	118.6	16.2	1.3	115.9	88.8	206.0	0.8	0.4	1.1
F _C 3	5.95	20.8	126.1	25.3	1.3	54.3	60.7	116.2	0.4	0.4	0.8
F _C 4	5.63	20.6	39.9	73.9	1.5	2.4	29.1	33.0	0.3	0.0	0.3
F _C 5	5.82	20.9	69.5	56.4	1.6	4.9	65.0	71.5	0.4	0.2	0.6
F _C 6	5.59	20.7	222.3	72.7	1.1	1.6	42.3	45.0	0.2	0.2	0.4
F _C 7	5.54	22.0	153.5	42.9	0.4	0.5	20.2	21.1	0.2	0.1	0.3
F _C 8	5.89	21.6	83.2	72.8	0.4	0.9	36.8	38.0	0.2	0.3	0.5
F _C 9	6.01	18.4	159.1	27.1	0.4	0.3	29.1	29.7	0.2	0.1	0.3
F _C 10	5.68	17.7	220.5	14.8	0.4	7.7	28.4	36.5	0.2	0.2	0.4
F _C 11	5.85	15.8	226.4	9.7	0.6	9.9	20.1	30.6	0.2	0.1	0.3
F _T 1	6.64	24.9	630.0	35.0	0.4	4.9	14.4	19.7	0.5	0.0	0.5
F _T 2	6.63	23.9	587.0	31.8	0.1	0.1	12.7	12.9	0.4	0.0	0.5
F _T 3	6.64	22.5	577.0	59.3	0.3	0.4	10.1	10.8	0.4	0.0	0.4
F _T 4	6.46	21.0	518.0	66.5	0.4	1.2	10.4	12.0	0.3	0.0	0.3
F _T 5	6.54	22.3	565.0	71.8	0.3	0.4	17.6	18.3	0.3	0.0	0.3
F _T 6	5.90	20.9	254.9	81.7	24.6	2.2	43.4	70.2	0.4	0.2	0.5
F _T 7	5.97	22.7	184.2	89.3	20.5	4.0	35.9	60.4	0.2	0.1	0.3
F _T 8	5.97	23.1	93.6	71.7	5.1	2.4	45.8	53.3	0.2	0.1	0.3
F _T 9	6.37	21.0	178.5	64.4	1.8	3.7	30.3	35.8	0.2	0.1	0.3
F _T 10	6.21	19.0	374.1	43.6	0.4	1.8	15.3	17.5	0.2	0.0	0.2
F _T 11	6.43	16.9	439.8	66.5	0.6	2.9	7.3	10.8	0.2	0.0	0.2
G _C 2	6.53	23.3	165.9	24.2	0.6	12.1	33.4	46.1	0.4	0.7	1.1
G _C 3	5.65	22.0	121.3	23.8	1.6	5.5	38.5	45.7	0.4	0.5	0.9
G _C 4	5.47	21.6	135.7	41.5	22.6	9.7	29.3	61.5	0.3	0.0	0.3
G _C 5	5.79	21.8	136.8	32.2	0.4	2.5	21.3	24.2	0.3	0.2	0.5
G _C 6	6.21	20.7	112.4	94.6	1.0	1.1	36.6	38.7	0.3	0.3	0.5
G _C 7	5.97	22.6	100.1	36.3	3.4	1.7	25.4	30.6	0.2	0.1	0.4
G _C 9	6.76	22.0	99.5	89.8	7.0	1.7	21.8	30.6	0.2	0.0	0.2
G _C 10	6.43	21.2	112.8	76.8	0.7	2.0	19.2	21.9	0.2	0.1	0.3
G _C 11	6.55	20.4	112.1	55.4	0.5	11.5	9.8	21.8	0.3	0.0	0.3

Site & Sample	pH	Temp. (°C)	EC (µs/cm @25°C)	DO (%sat.)	NO _x	NH ₄	DON	TDN	PO ₄	DOP	TDP
G _T 2	6.48	23.2	231.5	42.5	0.5	29.2	0.0	29.7	0.4	0.0	0.4
G _T 3	6.35	22.4	175.5	50.2	7.1	21.1	0.0	28.2	0.2	0.0	0.2
G _T 4	6.39	20.6	152.1	61.9	0.9	3.9	19.3	24.1	0.3	0.0	0.4
G _T 5	6.76	22.7	191.6	68.3	0.4	5.8	5.1	11.2	0.2	0.1	0.3
G _T 6	6.16	20.8	168.6	68.5	78.5	6.1	28.9	113.4	0.4	0.5	0.9
G _T 7	6.19	22.0	107.3	87.3	10.4	1.5	13.7	25.6	0.2	0.0	0.2
G _T 9	6.61	20.2	111.6	84.1	0.7	2.5	9.4	12.6	0.2	0.0	0.2
G _T 10	6.47	19.0	147.5	37.9	0.3	4.8	7.1	12.1	0.2	0.1	0.2
G _T 11	6.63	18.3	142.1	63.0	0.3	4.0	0.0	4.3	0.3	0.1	0.3
Min.	5.1	14.6	39.9	3.5	0.1	0.0	0.0	2.4	0.0	0.0	0.1
Max.	8.1	28.9	867.0	198.6	811.1	322.7	298.8	855.7	10.8	2.6	13.5
Mean	6.2	21.2	222.0	55.1	31.6	13.1	32.7	77.4	0.3	0.2	0.6
Std. Dev.	0.4	2.4	141.6	26.7	97.3	41.7	38.6	128.2	0.8	0.3	1.0