Nutrient transport and sources in headwater streams surrounded by intensive horticulture

Coffs Harbour City Council Environmental Levy Program

Shane A. White; Stephen R. Conrad; Rebecca L. Woodrow; James P. Tucker; Wei Wen Wong; Perran M. Cook; Christian J. Sanders, Praktan D. Wadnerkar; Kay L. Davis; Ceylena J. Holloway; Isaac R. Santos

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Southern Cross University

School of Environment, Science and Engineering

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Contact:

Shane White

Phone: 0404 211 357

Email: shane.white@scu.edu.au

Address: National Marine Science Centre

2 Bay Drive

Charlesworth Bay

Coffs Harbour, NSW

Australia, 2450

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Executive Summary

We report water quality observations along a transect of Double Crossing Creek, a tributary of Hearnes Lake which drains to the Solitary Islands Marine Park. We quantify nitrogen (N) loads and the capacity of the creek to attenuate N runoff naturally. We also use stable isotopes to assess the contribution of N derived from recycled greywater versus fertilisers.

We found significant nitrate (NO_3^-) loads in the creek consistent with the leaching of N from fertilised soils and recycled greywater usage. Creek NO_3^- fluxes were 136% of the estimated N input to the catchment at the most upstream site and 12% at the most downstream site. Fluxes exceeding 100% imply that the real N input in the catchment is higher than estimated here and/or our 91 days of observations during an unusually dry period overestimate annual N loss.

There was significant NO_3^- attenuation between the furthest upstream site (mean concentrations were ~5000 times the ANZECC water quality guidelines) and the furthest downstream site (~17 times the ANZECC guidelines). NO_3^- attenuation was 52 – 84 % per km of the creek depending on hydrological conditions. NO_3^- loads at the most downstream site were 0.2 – 9.7 % of loads at the most upstream site. These results imply that the creek has a large capacity to attenuate NO_3^- during dry and first-flush events, providing a valuable ecosystem service. However, during subsequent periods of high water flow and saturated soils, high loads of NO_3^- are exported downstream, essentially turning the creek from a natural bioreactor to a flow-through pipe.

Farms in the catchment receive recycled greywater from the local sewage treatment plants, delivering ~2176 kg NO_3^- yr^{-1}. Stable isotope analysis ($\delta^{15}N$-NO_3^-) indicates a mixed fertiliser and greywater source of N to the creek, although fertiliser was the dominant source of NO_3^- in the upper creek (~50 to ~75 %).

While the creek naturally reduces N loads reaching the Solitary Islands Marine Park, significant concentrations and loads, well above ANZECC guidelines and what is expected for natural systems are still found along the creek. As both fertiliser and greywater contribute to N loads, our results further highlight the need for decreasing fertiliser use, capturing N on farms and/or reducing greywater N concentrations before excess N is lost to local creeks and the Solitary Islands Marine Park.

1. Introduction

As part of the Environmental Levy Grants program, Southern Cross University has performed nitrogen investigations along Double Crossing Creek, upstream of Hearnes Lake, NSW, Australia. This project follows our previous research in the lower Hearnes Lake catchment, motivated by community concerns over the impacts of intensive horticulture on water quality in Hearnes Lake and the Solitary Islands Marine Park (SIMP) (Conrad et al., 2018; White et al., 2018a). Historic banana farming in the catchment has shifted to blueberry farms and hothouse horticulture, consistent with the regional trends across the Coffs Harbour Local Government Area (CHLGA) (Bevan, 2006; Rural Lands Council, 2016).

The Coffs Harbour City Council Biodiversity Action Strategy 2012–2030 outlines Coffs Harbour City Councils (CHCC) responsibility to be aware of land-use change detrimentally affecting local waterways (Coffs Harbour City Council, 2012). The nitrogen (N) loads (kg N ha yr^{-1}) previously found in Double Crossing Creek were amongst the highest ever recorded in a natural waterway on the east coast of Australia (White et al., 2018a). The source of this N is most likely upstream fertiliser use and/or recycled greywater.

The CHCC Ecohealth reports undertaken at Hearnes Lake have provided a vital information base for environmental management (Ryder et al., 2011; Ryder et al., 2016). However, these surveys are not concentrated on rainfall events, missing large fluxes of dissolved N in flushing events (White et al., 2018a). The increasing density of blueberries and hothouse horticulture in the region, the use of recycled greywater in the catchment, as well as the change in land use from banana farming, are likely contributing to the high N loads seen in Double Crossing Creek after rainfall (White & Santos, 2018; White et al., 2018a). Therefore, scientific knowledge on the sources, transport and attenuation of nitrogen from the farms to the downstream catchment is essential to manage any impact on the valuable ecosystems along the Coffs Coast.

Currently, the recommended N fertiliser regime for blueberries is 121 kg N ha yr^{-1} using commercially available fertilisers (Barker & Pilbeam, 2015; Doughty et al., 1988; Ireland & Wilk, 2006). The validity of this data in an Australian context is questionable because this figure is based on a study done in the 1980s in the USA on a variety that is no longer grown commercially in Australia (Doughty et al., 1988; Ireland & Wilk, 2006). The varieties that are now grown in CHLGA are more varied, giving farmers the financial benefit of multi-seasonal picking. This varietal change may alter the N requirements of blueberries over the growing season. Due to the natural cycling of N and the role soil bacteria plays in transformations, it is not possible to achieve 100% plant uptake of applied fertiliser. Between 20 and 80% of fertilisers are either lost to local waterways or stored in soils, where N can leach out for decades (Bindraban et al., 2015; Sebilo et al., 2013).

The diminishing availability of water for irrigation during drought periods creates a demand for other sources of irrigation water. The consistent outflow of greywater from treated sewage effluent has become an attractive source of irrigation water in many areas, such as the North China Plain (Guo et al., 2017), Sahara Desert (Gurjar et al., 2017), Nigeria (Abegunrin et al., 2016), India (Alghobar & Suresha, 2017), Turkey (Avci & Deveci, 2013), Dubai (Qureshi et al., 2016), USA (Pereira et al., 2011) and France (Tarchouna et al., 2010). In Australia, recycled greywater from sewage treatment plants accounts for 1.5 % of the water used for irrigation annually (Australian Bureau of Statistics, 2017). As greywater typically contains high amounts of N, reuse of greywater on crops may also have the added benefit of supplying nutrient loads and allowing reductions in fertiliser use (Khajanchi et al., 2015). Though the benefit of extra water can be attractive, adding greywater to standard fertiliser application practices may introduce excess N into the soils, unbalancing the crop demand whilst not increasing production (Gu et al., 2016; Ju et al., 2009). The form of N (particularly nitrate (NO_3^-), ammonium (NH_4^+) or particulate nitrogen) and the relative concentrations in the greywater also need to be considered in relation to the crop demand. Applying a high NO_3^- concentration greywater to a crop that preferentially uptakes NH_4^+, such as blueberries, can create excess NO_3^- in soils that is not utilised by the target crop (Merhaut & Darnell, 1995).

N stored in horticultural soils can be flushed into ground or surface waters during rain events via overland runoff and groundwater seepage (Creed & Band, 1998; Follett & Hatfield, 2001). Many studies show a link between groundwater pollution and horticulture, where groundwater contaminated with N is released downstream over periods of days to decades (Eckhardt & Stackelberg, 1995; Helena et al., 2000; Zhang et al., 1996). When N fertiliser contaminates waterways, there is a high possibility of algal blooms and hypoxia occurring within the receiving waters (Backer et al., 2015; Hoagland et al., 2002; Jeppesen et al., 1998).

Possible sources of N in creek water can be estimated using stable isotopes, linking in-stream biogeochemistry and land use (Fadhullah et al., 2020; Wong et al., 2018). The dual isotopic compositions of NO_3^- ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-, expressed as ‰) are widely used to investigate sources of N in receiving waters (Zhang et al., 2019). Understanding the sources of N in a creek system can provide managers with vital information for land use planning and the restoration of impacted creeks (Kaushal et al., 2011). Each source of N in a catchment (i.e., sewage greywater, fertiliser, soil N, animal manure or atmospheric deposition) has a distinctive isotopic signature. As denitrification processes preferentially utilise the lighter isotopes ^{14}N and ^{16}O (rather than the heavier isotopes ^{15}N and ^{18}O), a predictable kinetic fractionation can be used to identify N sources in receiving waters.

In this report, we describe 91 days of observations at a time series site and 14 sampling campaigns of 6 spatial sites along a transect of Double Crossing Creek, Sandy Beach, NSW, Australia. Observations were performed during a dry period and over subsequent rain events to understand the drivers and loads of N within the creek. Specifically, we quantify the N sources (i.e., recycled greywater versus fertilisers used in intensive horticulture) and natural attenuation in the creek (the removal of N) away from its sources during both dry and wet periods. Our analysis includes:

1) A comparison of the results to Australia and New Zealand Environment and Conservation Council [ANZECC] pollution trigger values for lowland streams in NSW.
2) A comparison of nutrient loads along a creek transect.
3) Nitrogen source estimates using stable isotopes
4) Estimates of potential fertiliser loss from horticultural industries.
5) Examination of nitrogen attenuation within the creek.

2. Methods

2.1. Study area

Our investigations were performed in Double Crossing Creek in the catchment draining to Hearnes Lake, Sandy Beach, NSW, Australia. Hearnes Lake (-30.1362, 153.1975) is located ~ 25 km north of Coffs Harbour. It is a culturally important natural asset on Gumbaynggirr Aboriginal Country, forming part of the NSW north coast bioregion, SIMP, and the Coffs Coast Regional Park (Office of Environment and Heritage, 2017; Roper et al., 2011). Commercial activities are restricted in Hearnes Lake as it is designated as a habitat protection zone of the SIMP (Haines, 2009).

Mean annual rainfall in the area is 1685 mm per year, though ~ 60% of rain events occur between January and May (Department of Land and Water Conservation, 2001). The upstream catchment is 6.8 km^2, draining to Hearnes Lake primarily via Double Crossing Creek. Our study focuses on Double Crossing Creek from the upper catchment (41 m AHD) to the lower catchment (4 m AHD). Land use in the catchment above the most downstream site (Site 5) is 30.7% currently fertilised land

and 46.9% current and historically fertilised soil (Figure 1; Table 1). Since N can be stored in soils and leached over time, a consideration of total historically fertilised soils is essential. Soils in the catchment were determined using the Australian Soil Classification (Isbell, 2016). The major soil classification across the catchment is Kandosol (Figure 2), with areas closer to the creek classified as Hydrosol and Kurosol (NSW Office of Environment and Heritage, 1999).

2.2. Time-series Site

A time-series station was set up at spatial Site 3, approximately in the middle of the transect of 5 sites (1451 m downstream of Site 1 and 1605 m upstream of Site 5, Table 2). Water was continuously pumped from the creek into a small purpose-built sheltered sampling station and then back to the creek 10 m downstream, providing the instruments with a constant supply of creek water. A calibrated Hydrolab MS5 measured dissolved oxygen (DO), pH, electrical conductivity (EC) and temperature. Discrete creek water sampling occurred over 91 days at this site with a total of 222 discrete samples of N taken between 7th January and 8th April 2019. Discrete sampling occurred daily at ~09:00 am during dry periods. Sampling frequency increased to hourly during rainfall periods >20mm in a day, progressively reducing to 3 hourly, 6 hourly and 12 hourly after rainfall. Discrete sampling is described further in section 2.5.

2.3. Spatial surveys

Six sites were sampled along the creek transect, chosen based on where creek access was available. A “Control” site located on a branching tributary adjacent to Site 2 was determined to assess potential external influences on downstream samples and the ability of samples taken from Sites 1, 2, 3, 4, and 5 to be deemed a transect. The creek branches into two distinct sub-catchments upstream of Site 2. The control Site allows for a direct comparison to Site 2 because it has a similar catchment land use (36.1% and 37.4% currently fertilised land at Site 2 and Control, respectively) and the same creek order (Strahler order 2).

Sites along the transect (Sites 1 to 5) were spaced 562–1043 m apart, with slopes between 0.7% and 2.0% (Figure 3; Table 2). Sampling was undertaken at each site approximately weekly during dry times and approximately twice daily during first flush and secondary flush events. A total of 14 sampling campaigns were undertaken with a total of 81 samples collected. A calibrated handheld Hach HQ40D multimeter measured DO, pH and temperature, whilst EC and salinity were measured using a calibrated YSI salinity probe. Discrete sampling is described further in section 2.5.

2.4. Land use classifications

Classification of catchments upstream of each of the sites was achieved using the upper limits of 1 m interval contour data, creating a polygon of the catchment in Environmental Systems Research Institute [ESRI] ArcGIS™ mapping software (Australia, 2015). Catchment land uses were classified using aerial imagery and field scouting, enabling % land use calculation of each sub-catchment based on December 2018 imagery (Google Earth Pro, 2018; Land and Property Information NSW, 2017). Land uses (% catchment) are reported in Table 1.

Table 1: Coordinates of sampling points, areas and land use classifications (% of catchment) of the catchments upstream of the sampling sites along Double Crossing Creek, NSW as of 4th January 2019. The Control Site represents a tributary draining to the main creek segment and is directly comparable to Site 2.

Site	1	2	3	4	5	Control
Catchment area (ha)	13.9	94.7	175.9	188.9	223.3	49.2
Blueberry horticulture	23.5%	32.4%	30.6%	28.6%	25.6%	24.5%
Hothouse horticulture	2.6%	1.2%	1.7%	1.5%	1.3%	2.7%
Banana horticulture	0.0%	0.1%	3.4%	3.2%	2.7%	10.2%
Avocado horticulture	0.0%	2.4%	1.3%	1.2%	1.0%	0.0%
Total currently fertilised land	26.1%	36.1%	37.0%	34.5%	30.7%	37.4%
Abandoned horticulture	10.3%	20.8%	20.5%	19.1%	16.2%	33.2%
Total fertilised soils	36.4%	57.0%	57.6%	53.7%	46.9%	70.7%
Remnant vegetation	43.9%	25.9%	24.4%	25.5%	29.6%	5.8%
Cleared Land	19.7%	17.1%	18.1%	20.8%	23.5%	23.5%

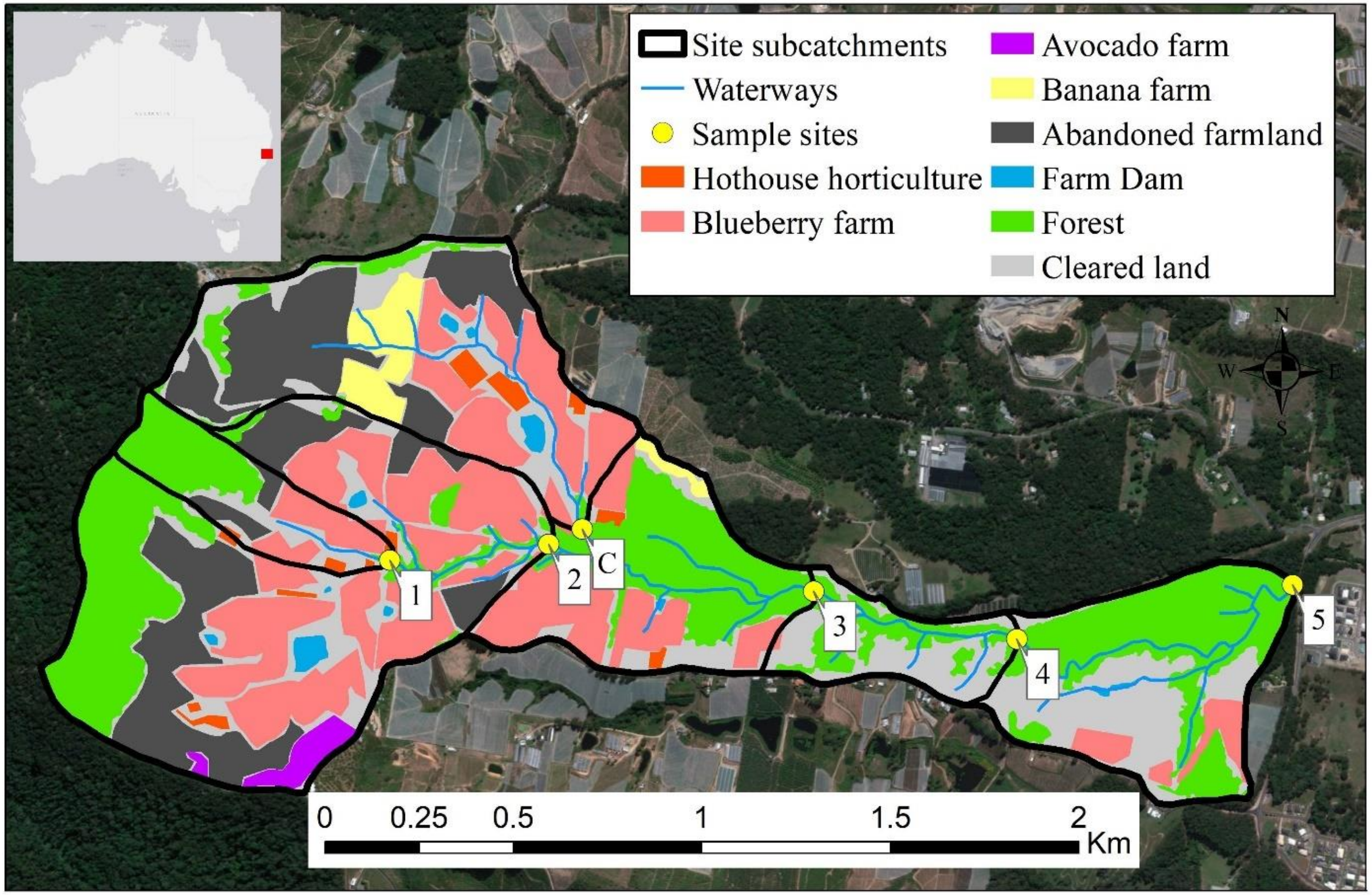

Figure 1: Land use classification upstream of the sampling points along Double Crossing Creek. Sampling sites are identified as 1-5 and Control (C). 'Forest' incorporates wet and dry sclerophylls, rainforests and introduced species. 'Cleared land' includes roads, pasture and houses. 'Abandoned farmland' land use data is taken from Conrad et al. (2019).

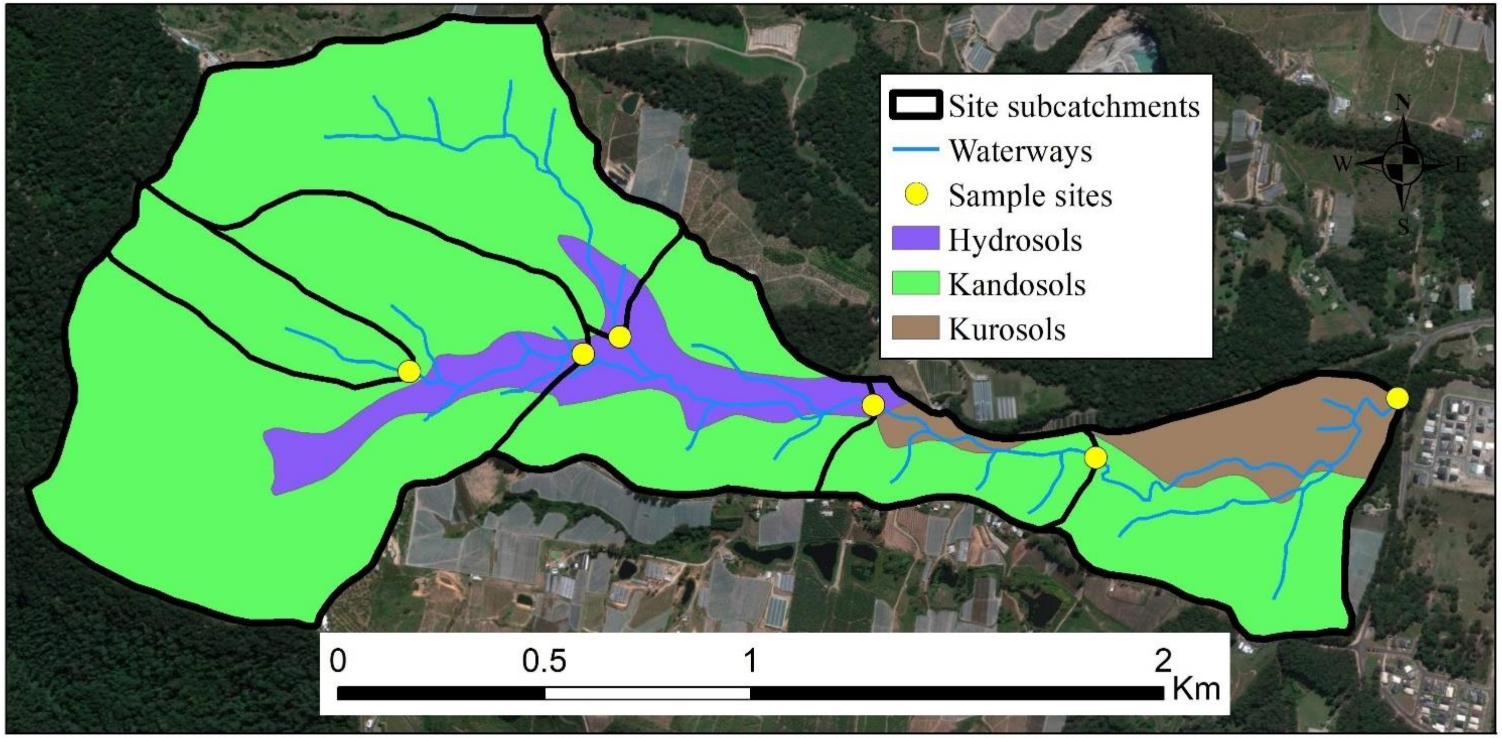

Figure 2: Soil type classification upstream of the sampling points along Double Crossing Creek (NSW Office of Environment and Heritage, 1999).

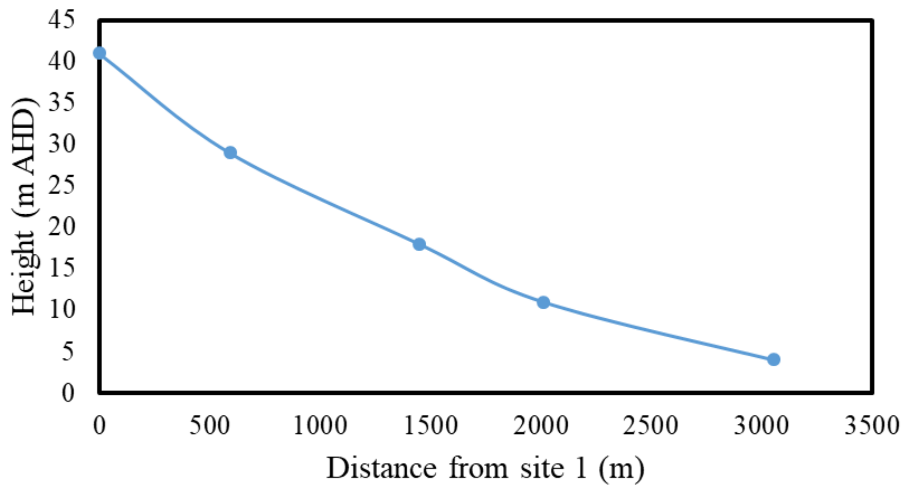

Figure 3: Vertical elevation profile of the sampling points along Double Crossing Creek (Google Earth Pro, 2018).

Table 2: Strahler stream order, distance along the transect, the height of sites and slope between sites along Double Crossing Creek.

Site	1	2	3	4	5	Control
Stream order	1	2	3	3	3	2
Distance from site 1 (m)	0	592	1451	2013	3056	-
Height (m ASL)	41	29	18	11	4	28
Slope between sites (%)	-	-0.020	-0.013	-0.012	-0.007	-

2.5. *Nutrient sampling and analysis*

Discrete water samples at the time series and spatial sites were collected using a sample rinsed 60 mL polyethylene syringe, and filtered using a Satorious™ 0.45 µm syringe filter into a 10 mL sample rinsed capped polyethylene tube. Samples were temporarily stored on ice and in darkness for <5 hours before being frozen until laboratory analysis. NO_3^- concentrations were analysed colourimetrically using a Lachat Flow Injection Analyser [FIA]. Eyre and Ferguson (2005) highlight detection limits and further analysis of this method. Since NO_3^- was determined to account for 78% of total dissolved nitrogen species in this catchment (White et al., 2018a), here we assume that NO_3^- will be the most important dissolved N species and focus our analysis on NO_3^-.

2.6. *Hydrology*

A Global Water Company flow probe was used to determine water velocity at each sampling site. Horizontal surface area of the creek was calculated using the trapezoidal method, by means of manual measurements across the creek. Creek discharge was calculated as horizontal surface area multiplied by velocity. Data from the Australian Landscape Water Balance (AWRA-L) model (Australian Bureau of Meteorology, 2018), calibrated by remote sensing data and surface flow, was used to obtain root zone soil moisture. A rain gauge was installed at Site 3, and rainfall volumes were documented for each Site 3 time series data point.

Data summaries in tables are means ± standard error unless otherwise noted. Where needed, unit conversions were applied. Fertiliser loss was calculated as our assumed recommended fertiliser (kg ha yr^{-1}) divided by the mean creek flux of NO_3^- calibrated to land use percentage in the catchments.

The load (flux per area, per time) of NO_3^- was calculated using the equation:

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

Where *F* is the flux of nutrients (kg ha day^{-1}), *C* is the concentration of NO_3^- (µM), M is the molecular weight of the element (g per mol), *Q* is discharge (m^3 day^{-1}), and *A* is catchment area (ha), unit conversions were used where appropriate.

2.7. *Isotope analysis*

46 aqueous samples were selected from the spatial survey and 32 aqueous samples from the time series to represent the hydraulic gradients of discharge variation in the creek waters. These selected samples were analysed for $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- using the chemical-azide method outlined in McIlvin and Altabet (2005). NO_3^- was quantitatively converted to NO_2 via cadmium reduction, then to N_2O using sodium azide. The efficiency of the conversion was 98±2%. Resultant N_2O was analysed on a Hydra 20-22 continuous flow isotope ratio mass spectrometer (CF-IRMS; Sercon Ltd. UK) interfaced to a cryoprep system (Sercon Ltd. UK). The isotopic ratios of N and O are expressed in per mille (‰) relative to atmospheric air (AIR) and Vienna Standard Mean Ocean Water (VSMOW), respectively. The external reproducibility of the isotopic analyses was within ±0.3‰ for $\delta^{15}N$ and ±0.5‰ for $\delta^{18}O$. The final $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values of the samples were calculated based on international reference materials which include USGS 32 ($\delta^{15}N$: 180‰; $\delta^{18}O$: 25.7‰), USGS 34 ($\delta^{15}N$: -1.8‰; $\delta^{18}O$: -27.9‰), USGS 35 ($\delta^{15}N$: 2.7‰; $\delta^{18}O$: 57.5‰) and IAEA-NO_3^- ($\delta^{15}N$: 4.7‰; $\delta^{18}O$: 25.6‰). A mix standard with $\delta^{15}N$ of 39.8‰ and $\delta^{18}O$ of 25.6‰ was also prepared using USGS32 and IAEA-NO_3^-. Lab-internal standards (KNO_3^- and $NaNO_2^-$) with pre-determined isotopic values were also processed the same way as the samples to check on the efficiency of the analytical procedure.

3. Results and Discussion

3.1. *Time-series observations*

Our observations covered a dry summer with only 244.1 mm of accumulated rainfall. During the 91 day experiment, two rain events > 30 mm in a day were able to significantly alter the flow regime and create spikes of discharge (Figures 4 & 5). The time series dataset was classified into three hydrological stages:

1) Dry period: < 30mm rain per day; from 7th January to 29th March 2019.

2) First flush: first rain event > 30mm in a day post dry period; from 30th March to 1st April 2019.

3) Secondary flush: second rain event > 30mm in a day; from 2nd April to 8th April 2019.

We observed a clear shift in NO_3^- and water flow between these three hydrological events. Mean NO_3^- concentrations at the time series site (Site 3) were 50, 74 and 137 fold higher than the ANZECC guidelines (ANZECC) during dry, first flush and secondary flush periods respectively (ANZECC, 2000). The ANZECC guideline for lowland streams in slightly disturbed catchments (eastern NSW) is 2.85 µM (ANZECC, 2000). Double Crossing Creek is a highly disturbed catchment. There are no ANZECC guidelines for catchments as disturbed as Double Crossing Creek. During the time series, the minimum recorded NO_3^- concentration was 105.9 µM and the maximum was 484.9 µM. These are 37 and 170 fold higher than ANZECC guidelines, respectively. NO_3^- in the dry period was always > 37 fold greater than ANZECC guidelines.

There was a significant relationship between root zone soil moisture and NO_3^- concentrations ($p=<0.001$; Figure 6), indicating that N may have been stored in catchment soils and flushed during rain events when soil moisture increases (Van Meter et al., 2016). NO_3^- is highly soluble in water. Therefore, when soil saturation increases, the probability of NO_3^- leaching either via overland runoff or groundwater seepage also increases (Puckett, 1994).

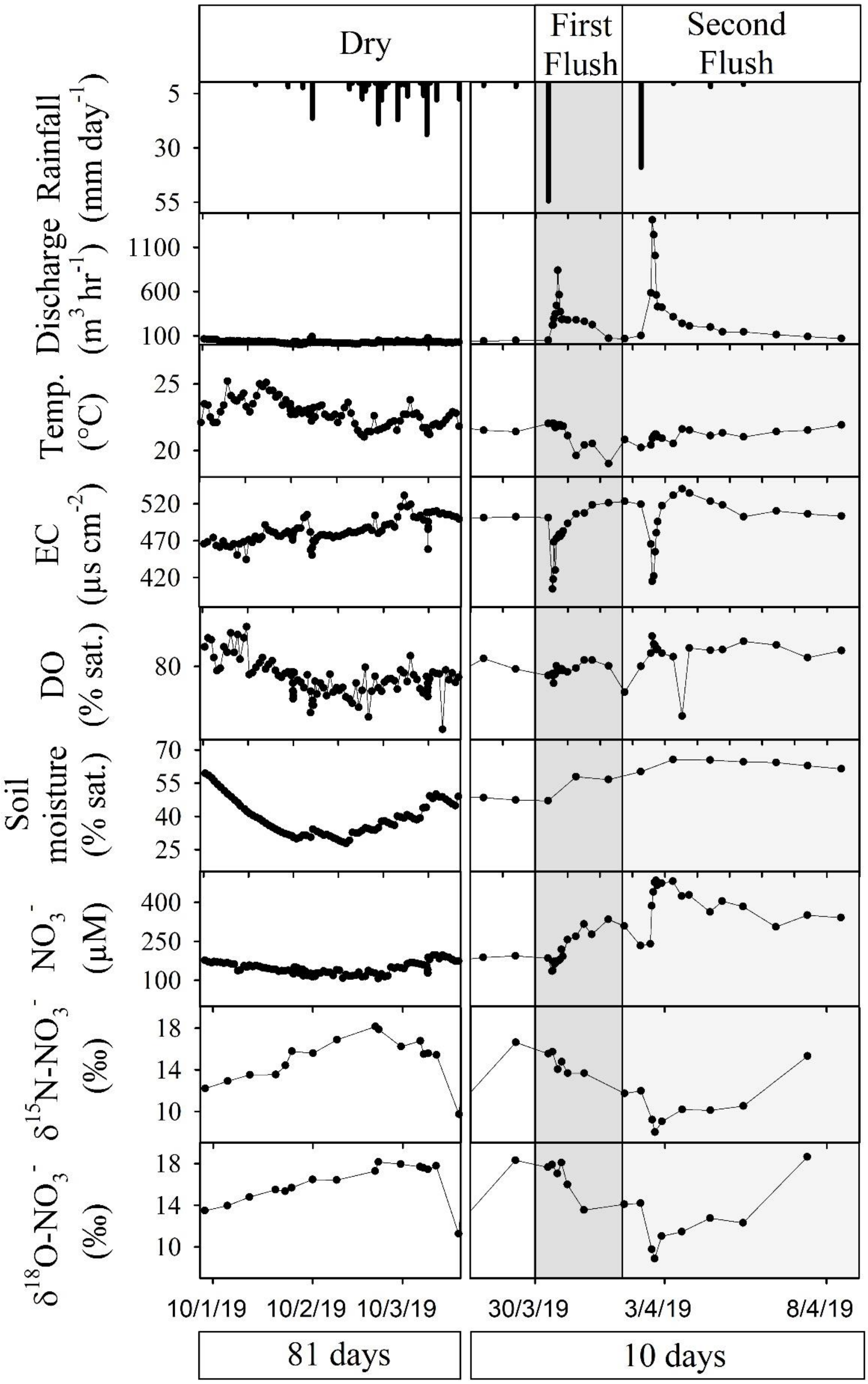

Figure 4: Time series observations over a 91 day period at Double Crossing Creek, NSW. Notice the break in the X axis scale to highlight the changes during the major rain event.

Table 3: Mean ± standard error of observations over a 91 day time series at Double Crossing Creek, NSW.

	Temp (°C)	pH	DO (% sat.)	EC (µs cm^{-1} @ 25°C)	Stream discharge (m^3 hr^{-1})	NO_3^- (µM)	NO_3^- (µmol m^2 day^{-1})
Dry	23.0 ± 0.1	7.47 ± 0.02	74.3 ± 0.4	487.6 ± 1.8	22.4 ± 1.17	141.2 ± 1.3	44.4 ± 2.5
First Flush	21.3 ± 0.2	7.28 ± 0.03	78.1 ± 0.6	479.4 ± 8.5	294.4 ± 46.1	210.9 ± 17.1	746.7 ± 83.5
Secondary flush	21.1 ±0.1	7.26 ± 0.02	84.2 ± 1.4	496.2 ± 9.0	422.7 ± 100.4	393.3 ± 19.3	2938.5 ± 592.8

Dry First Flush Secondary flush

Figure 5: Images of Double Crossing Creek at the time series site (Site 3) during dry (6th March), first flush (30th March) and secondary flush (2nd April).

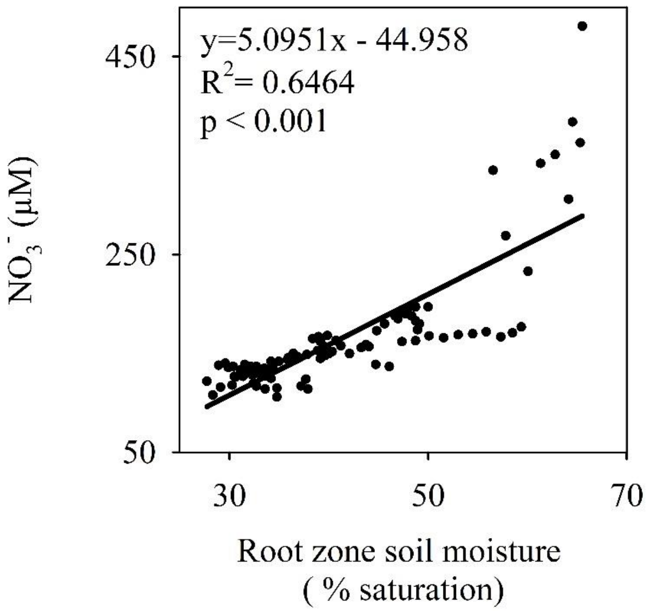

Figure 6: Relationship between NO_3^- concentrations and root zone soil moisture at the time series site (Site 3) over a 91 day period in Double Crossing Creek, NSW.

3.2. Spatial surveys

Fourteen spatial surveys were undertaken at the five transect sites and the Control Site (Table 4) to assess whether the creek can naturally attenuate N runoff. Overall, the survey observations imply significant attenuation of NO_3^- along the creek transect (Figure 7; Table 5). The furthest upstream running creek water was found at Site 1. This site was just downstream of a commercial hothouse growing tomatoes and within the direct vicinity of blueberry horticulture (23.5% blueberry horticulture and 2.6% hothouse horticulture). Although water discharge was low, mean concentrations of NO_3^- at Site 1 were 5490 fold higher than ANZECC guidelines. The highest NO_3^- concentration observed in this study was 27198 µM at Site 1, equating to 9543 fold higher than ANZECC guidelines. The lowest concentration sample at Site 1 was 38 fold higher than ANZECC guidelines. When this low-concentration sample was taken, the nearby tomato hothouse had not begun crop-growing operations. By the time of the next sampling campaign, the growing operations had started, and creek NO_3^- increased to 6140 fold higher than ANZECC guidelines.

NO_3^- concentrations decreased along the flow path to the downstream sites. Site 2 samples ranged from 94 to 245 fold higher than ANZECC guidelines, Site 3 samples ranged from 42 to 148 fold higher than ANZECC guidelines and Site 4 ranged from 24 to 135 fold higher than ANZECC guidelines. Mean NO_3^- concentrations at the most downstream site, Site 5 were much lower at 48.5 µM, though this is still 17 fold higher than ANZECC guidelines. The lowest water sample concentration in our study was at Site 5 on sampling campaign 5, where NO_3^- was 2.3 µM, which was within acceptable ANZECC concentrations. This was the only sample out of the 81 samples along the spatial transect and the 222 water samples at the time series site that was below the ANZECC guidelines. Conversely, during the secondary flush, NO_3^- concentrations at Site 5 that drains directly into Hearnes Lake were 314.6 µM, 114 fold higher than the ANZECC guidelines.

Table 4: Dates of sampling at spatial sites along a transect of Double Crossing Creek, NSW over the 72 day sampling regime.

Sampling campaign	Date of sample	Rainfall in previous 3 days (mm)	Root zone soil moisture (% sat.)	Mean dissolved oxygen (% sat.)	Classification
1	24/01/2019	1.0	43.8	46.9 ± 10.9	Dry
2	1/02/2019	0.0	32.1	68.4 ± 10.1	
3	14/02/2019	0.0	31.7	55.5 ± 6.5	
4	20/02/2019	0.0	27.7	63.3 ± 11.8	
5	1/03/2019	5.2	33.7	72.4 ± 9.2	
6	8/03/2019	17.2	40.0	71.8 ± 9.2	
7	15/03/2019	0.2	39.2	66.3 ± 13.6	
8	22/03/2019	8.0	48.7	69.0 ± 12.2	
9	29/03/2019	11.0	47.4	69.2 ± 12.3	
10	30/03/2019	48.5	47.0	71.3 ± 4.3	First flush
11	30/03/2019	63.0	47.0	78.5 ± 4.5	
12	31/03/2019	63.0	57.8	75.5 ± 3.4	Secondary flush
13	3/04/2019	39.5	65.5	78.4 ± 4.0	
14	5/04/2019	3.0	64.6	83.0 ± 3.1	

Table 5: Mean and standard errors of observations at spatial sites over the 72 day spatial sampling regime along a transect of Double Crossing Creek, NSW.

	Temp (°C)	pH	DO (% sat.)	EC (µs cm^{-1} @ 25°C)	Stream discharge (m^3 hr^{-1})	NO_3^- (µM)	NO_3^- (µmol m^2 day^{-1})	NO_3^- (kg N-NO_3^- ha yr^{-1})
Site 1	25.8 ± 0.8	7.45 ± 0.18	97.6 ± 10.2	3465.4 ± 662.9	16.4 ± 10.4	15648.3 ± 3442.5	2890.9 ± 602.9	147.7 ± 30.8
Site 2	22.8 ± 0.2	6.82 ± 0.13	44.5 ± 4.5	518.4 ± 9.6	115.9 ± 29.4	360.7 ± 33.0	1297.1 ± 459.1	66.3 ± 23.5
Site 3	22.1 ± 0.3	7.30 ± 0.07	74.7 ± 2.1	491.5 ± 6.8	109.7 ± 32.7	202.8 ± 26.3	377.1 ± 125.5	19.3 ± 6.4
Site 4	22.8 ± 0.3	7.23 ± 0.09	74.7 ± 2.4	497.5 ± 6.7	125.4 ± 29.5	154.9 ± 26.6	331.9 ± 109.9	17.0 ± 5.6
Site 5	22.6 ± 0.3	7.44 ± 0.12	61.2 ± 3.7	498.6 ± 4.3	146.5 ± 29.5	48.5 ± 26.7	118.4 ± 69.4	6.0 ± 3.5
Control	22.9 ± 0.2	6.49 ± 0.12	56.9 ± 3.5	483.6 ± 21.9	84.0 ± 25.5	350.2 ± 32.9	1793.4 ± 658.5	91.6 ± 33.6

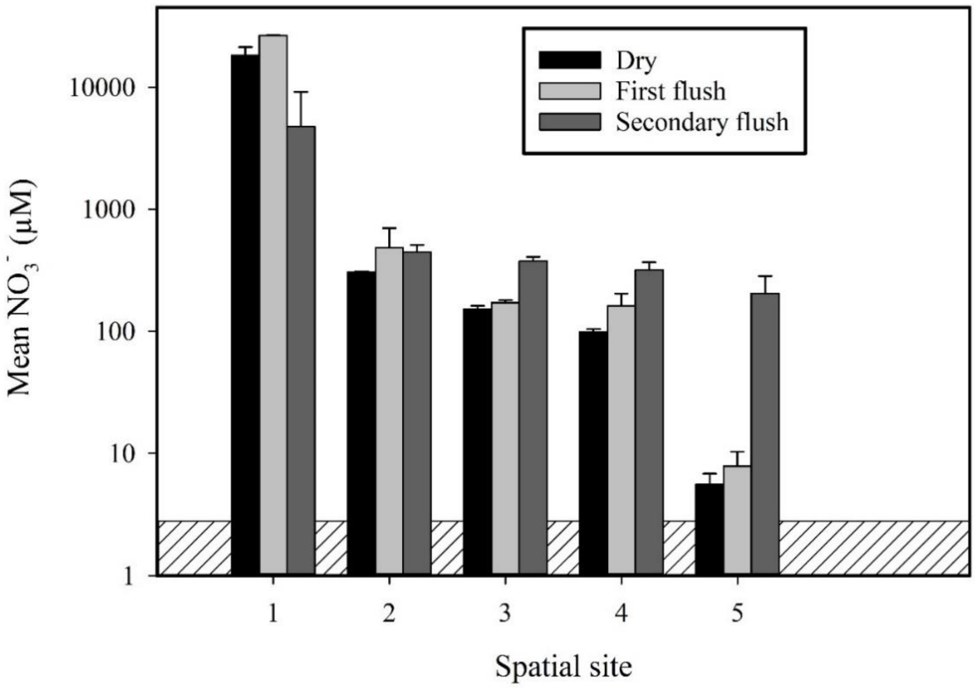

Figure 7: Mean and standard errors of NO_3^- concentrations at spatial sites during dry, first flush and secondary flush classifications over the 72-day spatial sampling regime along a transect of Double Crossing Creek, NSW. Note the Y-axis is in logarithmic scale. Lined box in the bottom of plot indicates the ANZECC guideline for lowland streams (eastern NSW) of 2.85 µM (ANZECC, 2000).

3.2.1. Comparison of Site 2 and control

Comparisons were made between Site 2 and the Control Site to determine if the Control Site influenced the NO_3^- loads flowing to the main creek segment investigated. The catchment area of Site 2 is 1.9 times larger than the Control Site, and the total current fertilised land is 36.1 % and 37.4% at Site 2 and the Control Site respectively (Figure 8). Catchment area-weighted NO_3^- loads from the Control Site were 1.04, 1.4 and 1.5 fold higher than Site 2 in dry, first flush and secondary flush, respectively (Figure 9). There was no statistical difference between NO_3^- loads at the Control Site and Site 2 in all spatial campaigns ($t_{(26)}$=0.6182, p=0.5418), or when data was classified into dry ($t_{(16)}$=0.2326, p=0.1890), first flush ($t_{(2)}$=0.4490, p=0.6974) and secondary flush ($t_{(4)}$=1.1130, p=0.3281). These two sites are determined to make a similar contribution to NO_3^- at the sites downstream, supporting our assumption of using stations 1-5 as a one-dimensional continuous segment in the attenuation analysis (section 3.5).

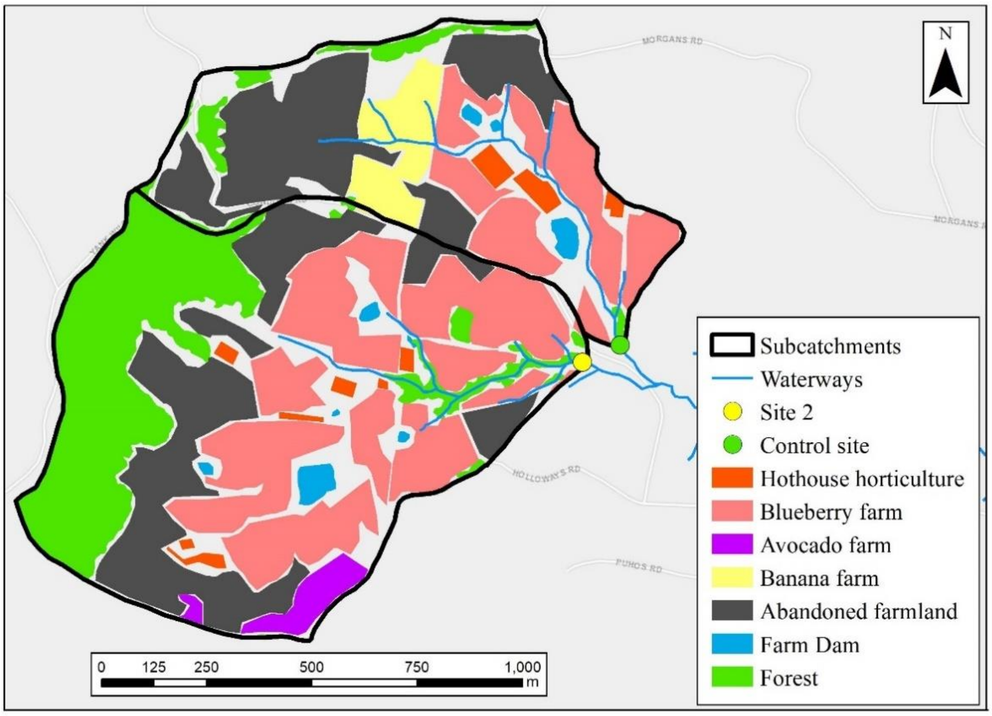

Figure 8: Comparison of land use at the Control Site and spatial Site 2 at Double Crossing Creek, NSW.

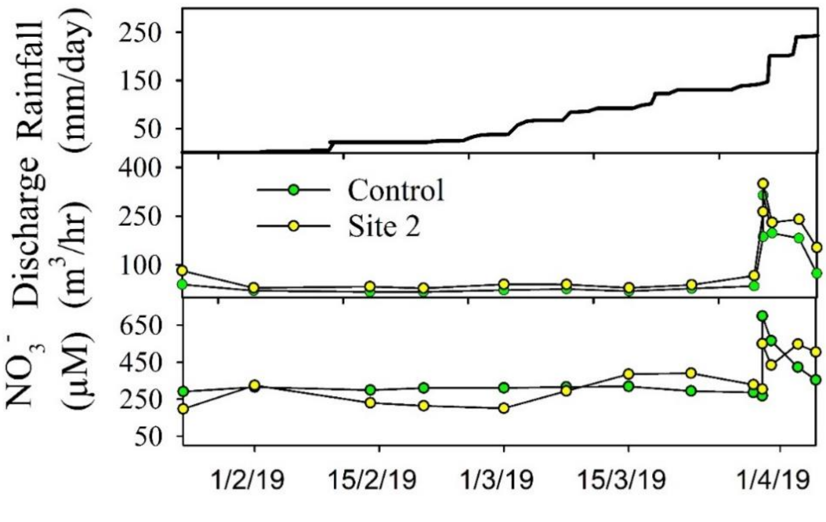

Figure 9: Comparison of observations at the Control Site and spatial Site 2, showing similar hydrology and NO_3^- concentration trends at both sites over the 72 day spatial sampling regimes at Double Crossing Creek, NSW.

3.3. Tracing nitrogen sources using isotopes

Farms in the catchment receive recycled greywater from the local sewage treatment plants, delivering ~ 2400 m^3 d^{-1} to the catchment, or ~ 2176 kg NO_3^- yr^{-1}. Two samples of greywater collected from the greywater supply system had NO_3^- concentrations of 229.3 and 125.7 µM enriched with heavy $\delta^{15}N$-NO_3^- (21.9 and 20.9 ‰) (Table 6). These concentrations are ~10 times lower than creek concentrations at Site 1, and within the range of samples at Sites 2 and Control, indicating that greywater cannot be the dominant contributor to creek NO_3^- at Site 1, but may be more important at Sites 2 and Control. Six samples of nitrogen fertilisers were obtained from the OzGroup Cooperative (a local farmer cooperative and agricultural supplier) capturing sources of N that are recommended by agronomists to farmers (personal communication, George Mittasch). Fertilisers were light in $\delta^{15}N$-NO_3^-, ranging from -8.0 to -0.1 ‰. These fertiliser values are within the range of those reported elsewhere in the literature and negative values represent the processes in which the fertilisers are derived (Bateman & Kelly, 2007). Creek water samples from all sites during sampling campaigns 2, 5 and 7 in the dry period, 10 and 12 in the first flush, and 13, 14 and 15 in the secondary flush were analysed for $\delta^{15}N$-NO_3^- (‰) and $\delta^{18}O$-NO_3^- (‰) to estimate the source of NO_3^- in the creek water at each of the sites (Table 7).

Our results indicate a mixed source of N in the creek waters, as expected. Discussions with farmers indicate that they are filling dams with greywater, pumping that water through fertigation systems where additional fertilisers are added, then applying the mixed water to crops. Blueberries do not preferentially uptake NO_3^-, instead preferring N in the form of NH_4^+ (Merhaut & Darnell, 1995). Therefore, NO_3^- in the greywater that is being applied to blueberry crops is likely stored in the upper soils to be flushed during rainfall events, volatilised to N gases, or leached to the creek via shallow groundwater in dry periods.

Estimations of source (greywater or fertiliser) contributions to creek waters were made using the US EPA one isotope two sources model (Phillips & Gregg, 2001). The y-intercept and standard error of the y-intercept on a Keeling plot were used as this is predicted to be more accurate than mean mixture populations (Phillips & Gregg, 2001). Source estimations from each site were done using the assumption that the two primary sources of N in the catchment were fertiliser (approximately 11031 kg N yr^{-1}, if recommended doses are used) and greywater (approximately 2812 kg N yr^{-1}, if loads estimated by flow are accurate. These estimates do not take into account N sources from atmospheric deposition into the creek during rainfall (estimated at 1115 kg N yr^{-1}; (Angus & Grace, 2017), animal manure (though this catchment is not operated commercially for livestock) or other N sources. Data imply that fertiliser was the dominant source (~75%) of NO_3^- in the creek at Site 1, whereas Sites 2 and control were ~50% greywater and ~50% fertiliser (Figure 10). Due to the fractionation of ^{15}N along the creek via denitrification and instream processes (Wong et al., 2018; Zhang et al., 2019), estimations of N source at Sites 3, 4 and 5 are not reported, as the reliability of estimations can decrease with distance from the source.

Denitrification is the most likely driver of the attenuation of N along the creek transect during the dry period (Figure 11). Denitrification is the process of converting NO_3^- to (non-bioavailable) N_2 gas. This occurs in anaerobic or anoxic conditions in soils, riparian zones and saturated sediments by soil bacteria (Bange, 2006; Statham, 2012). Denitrification rates are influenced by many parameters, such as residence time, microbial communities, dissolved oxygen, temperature, pH, and carbon (Hefting et al., 2003; Walker et al., 2002). $\delta^{15}N$-NO_3^- increased with distance from Site 1 in the dry period, suggesting that denitrification processes are preferentially utilising the lighter isotope ^{14}N instead of the heavier isotope ^{15}N. This process appears to partially diminish during the first flush and further diminish during the secondary flush. During periods of high flow and saturated soils, high loads of NO_3^- are exported into the creek and travel instream where denitrification rates are inhibited, flushing NO_3^- far downstream and turning the creek from a natural bioreactor to a flow-through pipe.

Denitrification along the creek is not only the likely cause of diminishing concentrations, but also alteration of isotopic signatures at the downstream sites. Sequential clusters of samples plot primarily along the denitrification lines in the $\delta^{15}N$-NO_3^- vs. $\delta^{18}O$-NO_3^- plot (Figure 12). These observations imply that nitrogen transformations (i.e., denitrification), rather than additional greywater inputs, additional fertiliser inputs or other sources of N downstream of Sites 1, 2 and Control are driving nitrogen distributions and loads.

Table 6: Analytical results of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$, recommended fertilisers and recycled greywater applied to Double Crossing Creek catchment farms.

Dry sources		
Source	N content	$\delta^{15}N\text{-}NO_3^-$ (‰)
Calcium nitrate	13%	-3.8
Urea	44%	-0.1
Di-ammonium phosphate	18%	-1.9
Mono-ammonium sulfate	12%	-1.1
Ammonium sulfate	21%	-4.1

Liquid Sources			
Source	NO_3^- (mg L^{-1})	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)
Greywater sample 1	3.21	21.9	12.3
Greywater sample 2	1.76	20.9	13.6
Easy N fertiliser	104000	-8.0	12.1

Table 7: Mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in creek water samples at sites along Double Crossing Creek during dry, first flush and second flush events.

	Dry				First Flush				Second Flush			
Site	NO_3^- (µM)	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)	Flow (m^3 hr^{-1})	NO_3^- (µM)	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)	Flow (m^3 hr^{-1})	NO_3^- (µM)	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)	Flow (m^3 hr^{-1})
1	21810.2 ± 1840.7	3.0 ± 0.7	29.7 ± 0.6	0.6 ± 0.2	23090.0 ± 1572.5	2.9 ± 0.1	32.2 ± 0.1	1.1 ± 0.3	287.2 ± 33.6	13.5 ± 2.6	12.1 ± 1.6	68.9 ± 18.3
2	284.4 ± 8.1	13.7 ± 0.7	19.1 ± 0.5	33.0 ± 3.6	356.0 ± 86.7	12.6 ± 2.6	12.2 ± 6.0	207.9 ± 115.4	369.5 ± 25.8	11.5 ± 1.5	9.7 ± 1.1	207.9 ± 27.4
3	131.6 ± 12.2	16.4 ± 1.1	16.8 ± 0.7	18.6 ± 3.5	156.3 ± 2.0	15.7 ± 0.9	18.2 ± 0.1	203.3 ± 131.6	306.1 ± 15.1	11.5 ± 1.1	12.4 ± 0.6	210.5 ± 35.8
4	95.5 ± 4.1	18.5 ± 1.1	16.3 ± 0.7	48.5 ± 7.4	156.9 ± 23.9	16.0 ± 3.2	20.0 ± 2.3	204.1 ± 117.7	308.5 ± 28.2	11.4 ± 1.7	13.3 ± 0.9	229.4 ± 27.0
5	3.4 ± 0.9	No data	No data	70.8 ± 5.0	17.5 ± 7.7	14.6 ± 3.0	10.6 ± 1.8	227.3 ± 129.7	181.9 ± 70.1	13.5 ± 2.8	14.0 ± 1.7	238.2 ± 15.5
Control	229.7 ± 32.8	9.4 ± 0.5	20.1 ± 0.8	20.4 ± 0.9	300.1 ± 13.4	9.3 ± 1.1	19.0 ± 4.4	174.2 ± 113.8	415.1 ± 25.2	7.0 ± 1.4	13.6 ± 0.2	151.1 ± 39.0
All sites	148.9 ± 27.2	12.2 ± 1.5	15.8 ± 1.3	38.3 ± 5.5	197.4 ± 39.4	11.8 ± 1.5	14.8 ± 1.5	203.4 ± 45.7	316.2 ± 23.9	11.3 ± 0.8	10.6 ± 1.1	207.4 ± 13.1
Time series	145.0 ± 5.7	15.1 ± 0.5	16.2 ± 0.5	34.5 ± 3.8	171.4 ± 29.3	14.2 ± 0.5	16.3 ± 0.7	280.4 ± 99.4	298.4 ± 15.4	10.5 ± 1.3	12.4 ± 1.8	445.9 ± 282.3

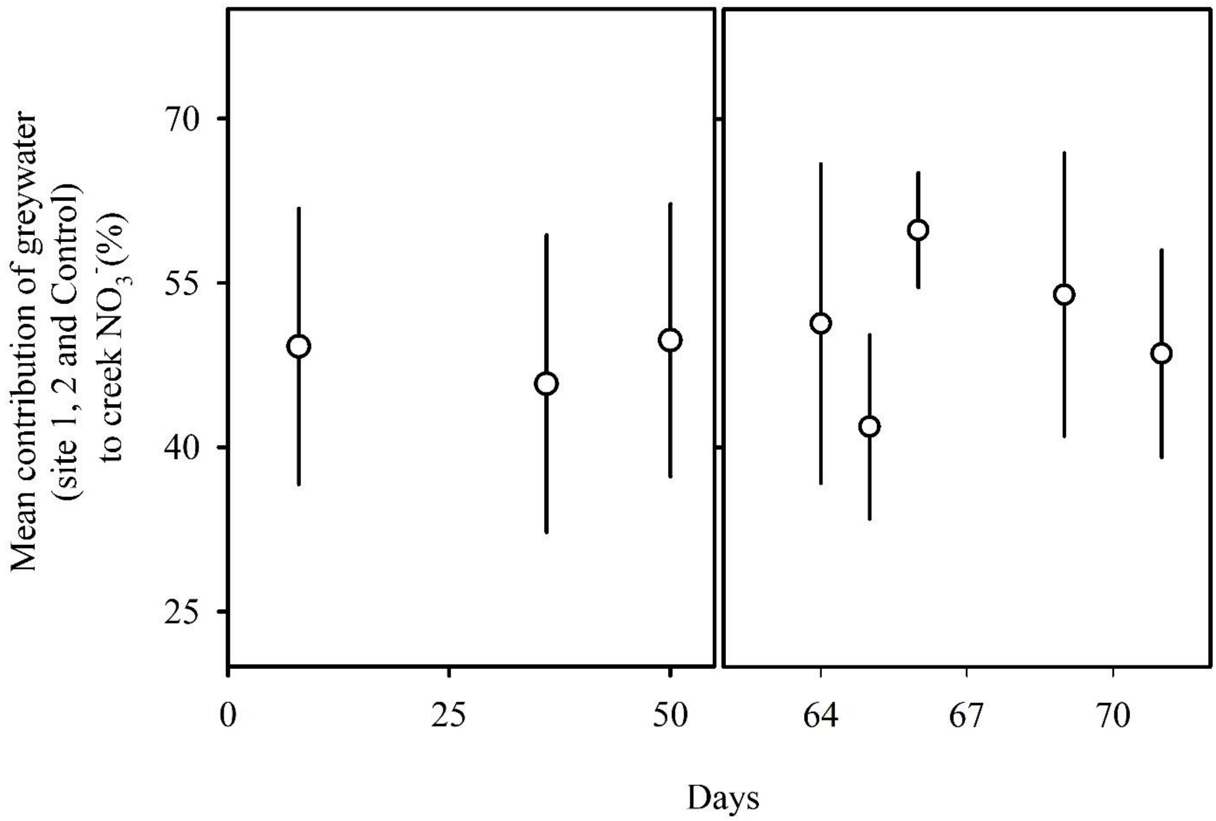

Figure 10: Estimations of mean greywater contributions (%) to creek waters at spatial Sites 1, 2 and control along Double Crossing Creek. Estimations were made using the US EPA one-isotope two-sources model (Phillips & Gregg, 2001). Bars represent standard deviation from the mean.

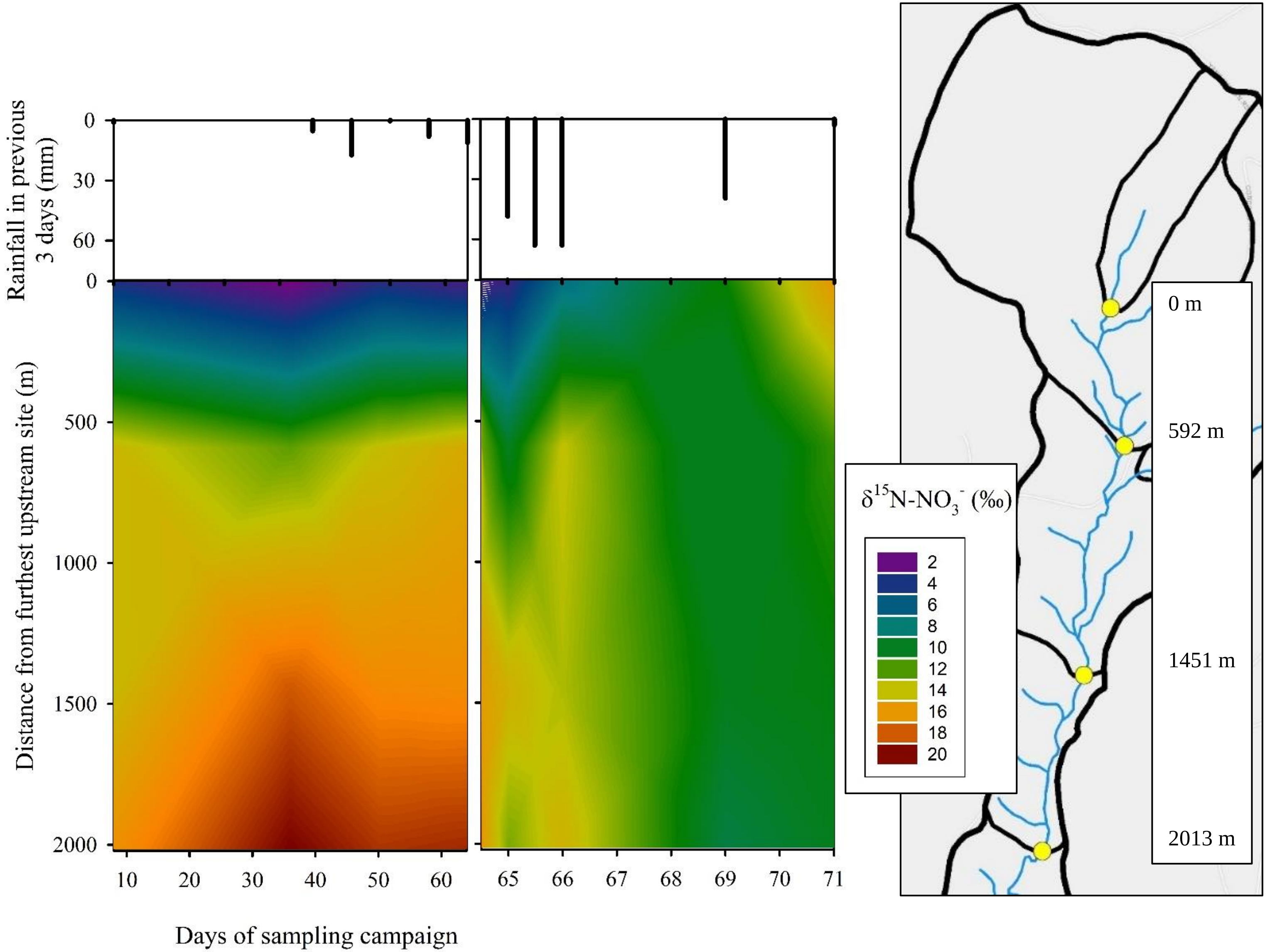

Figure 11: Contour plot of $\delta^{15}N$-NO_3^- at spatial sites over the 72-day spatial sampling regime, along a transect of Double Crossing Creek, NSW. Break indicates the transition from dry to first flush. Note that rain in the top box is cumulative rain in the three days prior to sampling. Site 5 was excluded due to lack of some data points. Colours grading to red indicate more denitrification consistent with the observed removal of NO_3^- in the stream.

3.4. *Aquatic nitrogen losses versus catchment inputs*

The dominant fertiliser-intensive land uses in the catchments upstream of our spatial sites are blueberries, bananas, and hothouse horticulture (mostly cucumbers and tomatoes). During the dry period, surrounding creeks were not flowing where greywater was not used in the catchment, and horticulture was not present. Double Crossing Creek was always flowing during the dry period, likely due to wastewater from irrigation and greywater use. We estimated NO_3^- loss rates to the creek by comparing total estimates of nitrogen sources to the catchment and our calculated aquatic NO_3^- loads observed along the creek. Data on the timing of fertiliser application across all industries (blueberries, tomatoes, cucumbers and bananas) and the specific amount of applied fertiliser by local farmers are not available; therefore, we use estimates.

We estimate external sources to the catchment. Our estimations show that the catchment receives 15877 kg N yr^{-1} delivered as fertiliser, based on the assumption that farmers are applying 100 kg N ha yr^{-1} to bananas (Newley et al., 2008) and 121 kg N ha yr^{-1} to blueberries (Doughty et al., 1988; Ireland & Wilk, 2006). Communications with farmers in the catchment revealed that each hothouse usually produces between two and four crops per year and crops are rotated depending on market prices. Therefore, we assume that farmers are growing three crops of tomatoes or cucumbers per year, that cucumbers in hothouses require 2859 kg N ha yr^{-1} assuming three crops per year (Grewal et al., 2011) and tomatoes in hothouses require 1200 kg N ha yr^{-1} assuming three crops per year (Tei et al., 2002). As the crop inside the hothouse was not known at all sites, we make the conservative assumption that all farmers using hothouses are growing the higher N crop, cucumbers. We also estimate that the greywater system delivers 2812 kg N yr^{-1} to the catchment, based on our greywater sample concentrations, an average of 2400 m^3 d^{-1} of greywater, and that greywater is distributed evenly throughout the catchment. We estimate that rainfall would deliver ~1115 kg N yr^{-1} to the catchment (Angus & Grace, 2017).

Combined, these external nitrogen sources add up to 1678 kg N yr^{-1} and 19805 kg N yr^{-1} across the catchment upstream of Site 1 and Site 5 respectively. Our observed aquatic nitrogen fluxes ranged from 2284 kg N- NO_3^- yr^{-1} at Site 1 to 1350 kg N- NO_3^- yr^{-1} at Site 5. Therefore, we estimate that 136%, 74%, 18%, 17%, 7% and 68% of the N inputs in the catchment are reaching the creek at Sites 1, 2, 3, 4, 5 and control respectively (Table 8). These values of N losses exceeding 100% N input loss are presumably impossible and values >60% are improbable, implying that one or more of our assumptions may be incorrect. Possible explanations for aquatic losses exceeding 100% of inputs include:

(1) The actual fertiliser application rate on the farms in the catchments of Sites 1, 2 and Control, may be far higher than our assumed fertilisation rates and those recommended by the relevant industry peak body (Yadav et al., 1997). We have no direct data on the amount or timing of fertilisers applied before and during our observations and had to rely on the assumption that farmers are not over fertilising their crops.

(2) Significant nitrate leaching may be occurring from overlooked land uses or sources including septic systems (Gerritse et al., 1995), or soil storages of N from historical fertiliser application are being leached at excessive rates (Sebilo et al., 2013). We have no data on septic systems, or legacy soil nitrogen in this catchment, though the land use is clearly dominated by current agricultural activities. The legacy banana industry requires less nitrogen than the recent blueberry industry. It is difficult to conceive legacy aquatic nitrogen fluxes exceeding expected annual fertilisation rates for ~20 years after banana plantations were replaced by more intensive blueberry horticulture.

(3) Our 91 days of observations of creek water quality may not be representative of long-term N loss. Indeed, the summer of 2019 was quite dry with <100 mm of rain between day 1 and day 68. The annual long term rainfall mean is 1685 mm per year, with ~60% of rain events occurring between January and May (Department of Land and Water Conservation, 2001). Our observations occurred in a particularly dry period where only 244.1 mm of rain fell between January and April which is equivalent to ~25% of the expected historical rainfall for those 91 days. It would be reasonable to expect that the lower rainfall drove lower-than-average nitrate concentrations and loads during our observations. Therefore, our observations are likely at the low end of the long term annual average loads.

Our load calculations at Site 5 (equivalent to 7% of fertiliser loss) are lower than our 2018 observations (White et al., 2018a) when we estimated 14 % $N\text{-}NO_X$ loss in the lower part of this catchment at a site ~600 m downstream, and our 2017 observations when we estimated $N\text{-}NO_X$ losses in Bucca Bucca Creek at 18 % $N\text{-}NO_X$ of fertiliser use. There may be discrepancies in load calculations between previous studies and our current study. First, there were very different rainfall events during these surveys, possibly leading to different soil flushing conditions, creek concentrations and calculation outcomes. Second, here we directly measure velocity using a Global Water Company flow probe with horizontal surface area calculated with manual measurements across the creek. Our previous reports relied on flow data from the Australian Landscape Water Balance model (Australian Bureau of Meteorology, 2018) via the AWRA-L model. Direct measurements here are assumed to be more accurate than remotely sensed data.

Table 8: Estimated applied fertiliser loss to Double Crossing Creek from fertiliser intensive land uses, incorporating the area of the catchment occupied by each land use.

	Catchment area (ha)	$N\text{-}NO_3^-$ load (µmol m^2 day^{-1})	$N\text{-}NO_3^-$ load (kg $N\text{-}NO_3^-$ ha yr^{-1})	Catchment $N\text{-}NO_3^-$ load (kg yr^{-1})	Blueberry horticulture land use (ha)	Banana horticulture land use (ha)	Hothouse horticulture land use (ha)	Fertiliser N applied to catchment (kg yr^{-1})	N delivered via rainfall (kg yr^{-1})	N delivered via sewage greywater (kg yr^{-1})	Total N inputs (kg yr^{-1})	% $N\text{-}NO_3^-$ fertiliser loss from farms
Site 1	13.9	3221.1	164.6	2284.2	3.3	0.0	0.4	1435.7	69.4	174.8	1679.8	136.0%
Site 2	94.7	1297.1	66.3	6279.9	30.7	0.1	1.1	6860.6	473.7	1193.3	8527.6	73.6%
Site 3	175.9	377.1	19.3	3389.3	53.9	6.0	2.9	15470.2	879.5	2215.4	18565.1	18.3%
Site 4	188.9	331.9	17.0	3203.6	54.0	6.0	2.9	15482.2	944.5	2379.2	18805.9	17.0%
Site 5	223.3	118.4	6.0	1350.4	57.3	6.0	2.9	15876.6	1116.3	2811.9	19804.8	6.8%
Control	49.2	1793.4	91.6	4509.6	12.1	5.0	1.3	5758.3	246.0	619.8	6624.1	68.1%

3.5. *Nitrogen loads and attenuation*

Nitrogen loads along our creek transect varied widely over both space and time. Hydrology, soil moisture and distance along the creek transect likely drove changes in NO_3^- concentrations and loads. We plotted NO_3^- concentration (Figure 13), discharge (Figure 14) and NO_3^- loads (Figure 15) against distance from Site 1 and days of sampling campaign. In the dry period, flows increased steadily along the creek and NO_3^- concentrations and loads decreased with increasing distance from the upper catchment where most of the intensive horticulture land uses are (Figure 1). A change in the system processing appears to have occurred after the first flush at day 64, when rainfall drives increasing discharge and NO_3^- concentrations.

Konohira et al. (2001) shows that rainfall reduces riparian denitrification due to increased flow. Here we also observed reduced attenuation of NO_3^- during high flow events. Increasing catchment degradation can shift estuaries from having the behaviour of a natural bioreactor, where N is removed, to a pipe where N is flushed through and delivered to the ocean (Wells & Eyre, 2018). These two hypotheses can be combined with Meyer and Likens (1979) suggestion of nutrient cycling in low flows and nutrient throughput in high flows. Headwater streams with high fertiliser land use and subsequently high soil N concentrations may phase shift between two nutrient processing modes: nutrient cycling during low flows where longer residence times through riparian sediments allow for denitrification and reduction of aquatic NO_3^-, and a high flow throughput similar to a pipe, where high velocity and low residence times circumvent N cycling instream and transport most of the NO_3^- load to downstream receiving waters.

During the dry period until the first flush, conditions remained relatively constant throughout the catchment. Loads at Site 5 are 0.2 %, 0.5 % and 9.7 % of loads at Site 1 even though water flux increased by 98.5 %, 99.6 % and 71.1 % during dry, first flush and secondary flush respectively. We use the log-linear decay rate constant to estimate the attenuation similar to Ensign et al. (2006). This method allows estimation of the NO_3^- removal from the water column by numerous biogeochemical processes such as denitrification or plant uptake (Duff et al., 2008; Peterson et al., 2001). This method assumes a log-linear decay of the constituent load at Site 1 and no external inputs, consistent with general trends seen in Figure 7.

We estimate that during the dry period this transect of Double Crossing Creek has the capacity to remove 83.9 % (R^2=0.956, p=<0.001) of the NO_3^- load at Site 1 per km of the creek. During the first flush, the creek attenuated 81.3 % per km (R^2=0.934, p=<0.001), whilst during the secondary flush, this attenuation capacity dropped further to 52.2 % per km (R^2=0.944 p=<0.001). This implies that the creek has a large capacity to attenuate NO_3^- during dry and first flush events, providing a valuable ecosystem service. The ability to attenuate is reduced when soil moisture, flow and nutrient loads increase during a secondary flush event.

We also plotted NO_3^- attenuation against possible drivers (Figure 16). We found a significant inverse correlation between root zone soil moisture and NO_3^- attenuation (R^2=0.5808, p=<0.05), indicating that soils may be storing high loads of N, then releasing it via overland runoff when soil saturation reaches a critical point. Relationships between NO_3^- attenuation and soil moisture suggest that the critical tipping point in this catchment where soils switch from storage to release is ~50% root zone water saturation, as predicted from the AWRA-L model (Australian Bureau of Meteorology, 2018).

Knowledge of longer term soil N storage has been increasing. From over 2000 sites in North America, Van Meter et al. (2016) found soil storage in agricultural landscapes to be between 25 and 70 kg N ha^{-1}. It was once believed that the denitrification that occurs in agricultural soils would remove this N. However, the storage of N in soils may be linked to long term flushing during rain events when soil moisture reaches a critical point (Worrall et al., 2015). We found no significant correlations between NO_3^- attenuation and discharge or NO_3^- attenuation and accumulated rainfall in the 3 days prior to sampling. There may be a relationship here, as both discharge and rainfall are linked to soil moisture, but the temporal resolution of discharge and rainfall data prevent a detailed analysis. A significant inverse relationship also exists between NO_3^- attenuation and dissolved oxygen (R^2=0.553, p=0.05). This correlation is likely to indicate the reduction of denitrification in high flow periods due to shorter residence time and increased gaseous exchange in the water column inhibiting anaerobic conditions in the riparian and hyporheic zones (Konohira et al., 2001).

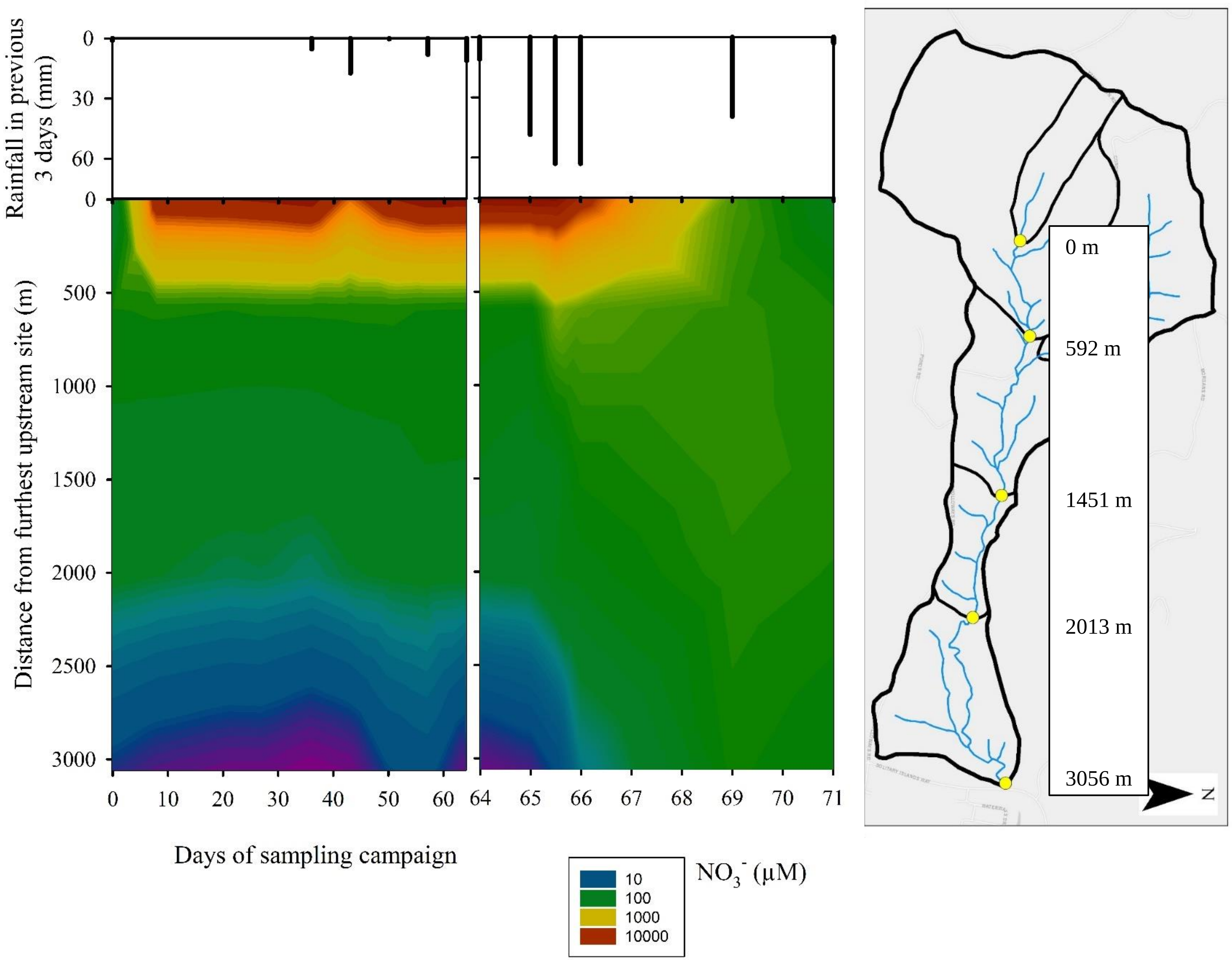

Figure 12: Contour plot of NO_3^- concentrations at spatial sites over the 72 day spatial sampling regimes along a transect of Double Crossing Creek, NSW. Colours are in log scale indicating NO_3^- concentrations. Break indicates the transition from dry to first flush. Note that rain in the top box is cumulative rain three days prior to sampling.

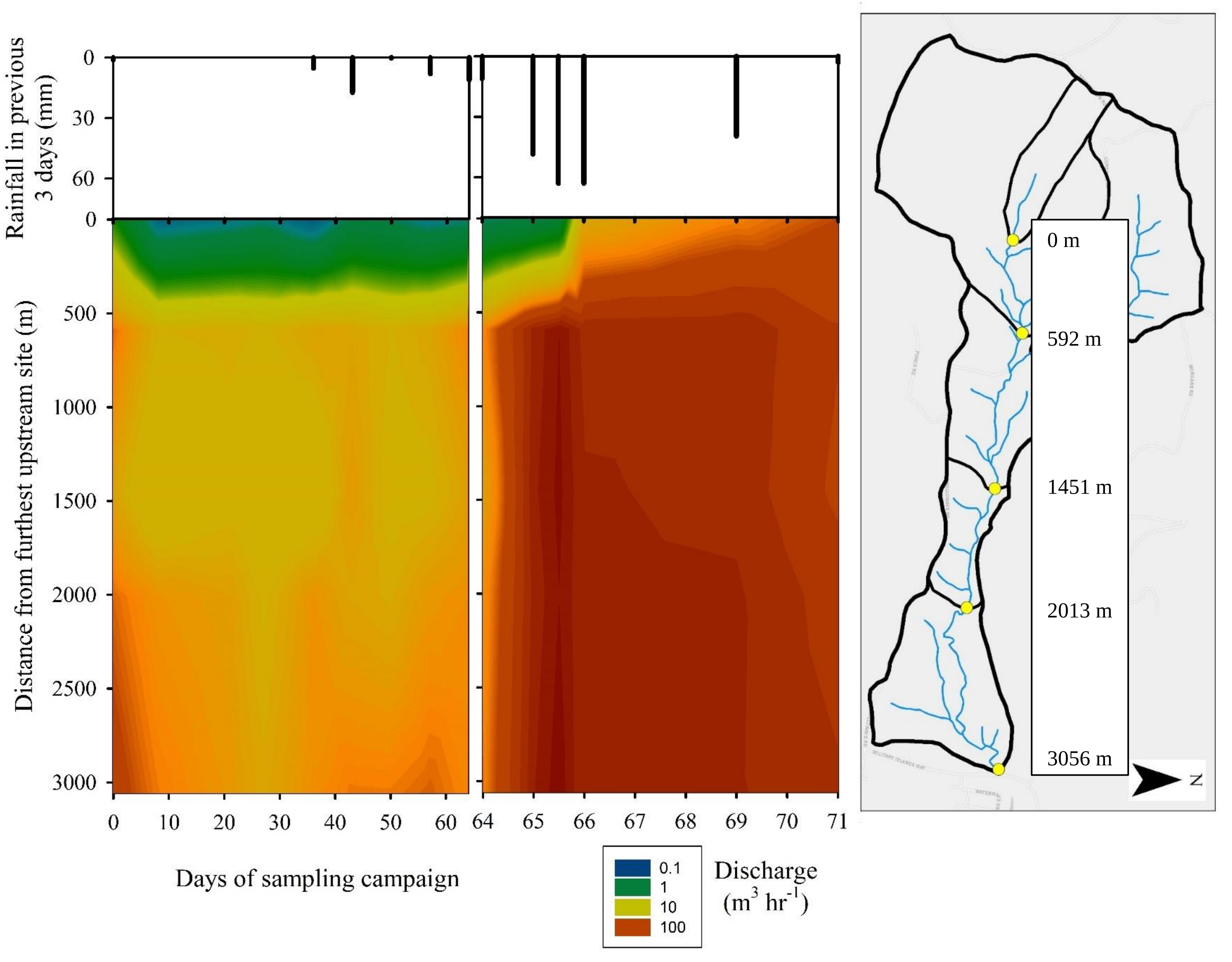

Figure 13: Contour plot of creek discharge at spatial sites over the 72 day spatial sampling regimes along a transect of Double Crossing Creek, NSW. Colours are in log scale indicating discharge. Break indicates the transition from dry to first flush. Note that rain in the top box is cumulative rain three days prior to sampling.

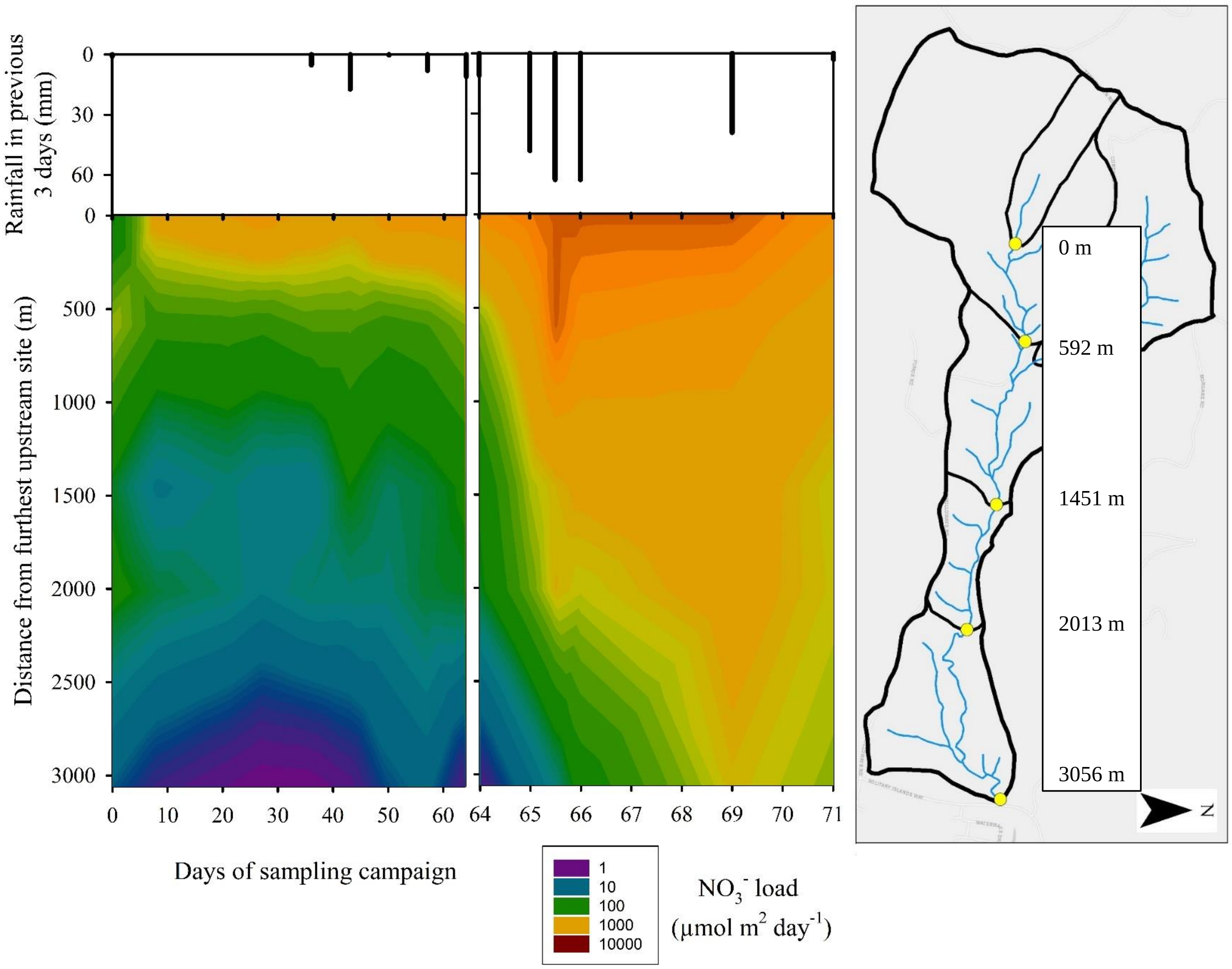

Figure 14: Contour plot of NO_3^- loads at spatial sites over the 72 day spatial sampling regimes along a transect of Double Crossing Creek, NSW. Colours are in log scale indicating NO_3^- load in µmol per m^2 of catchment per day. Break indicates the transition from dry to first flush. Note that rain in the top box is cumulative rain three days prior to sampling.

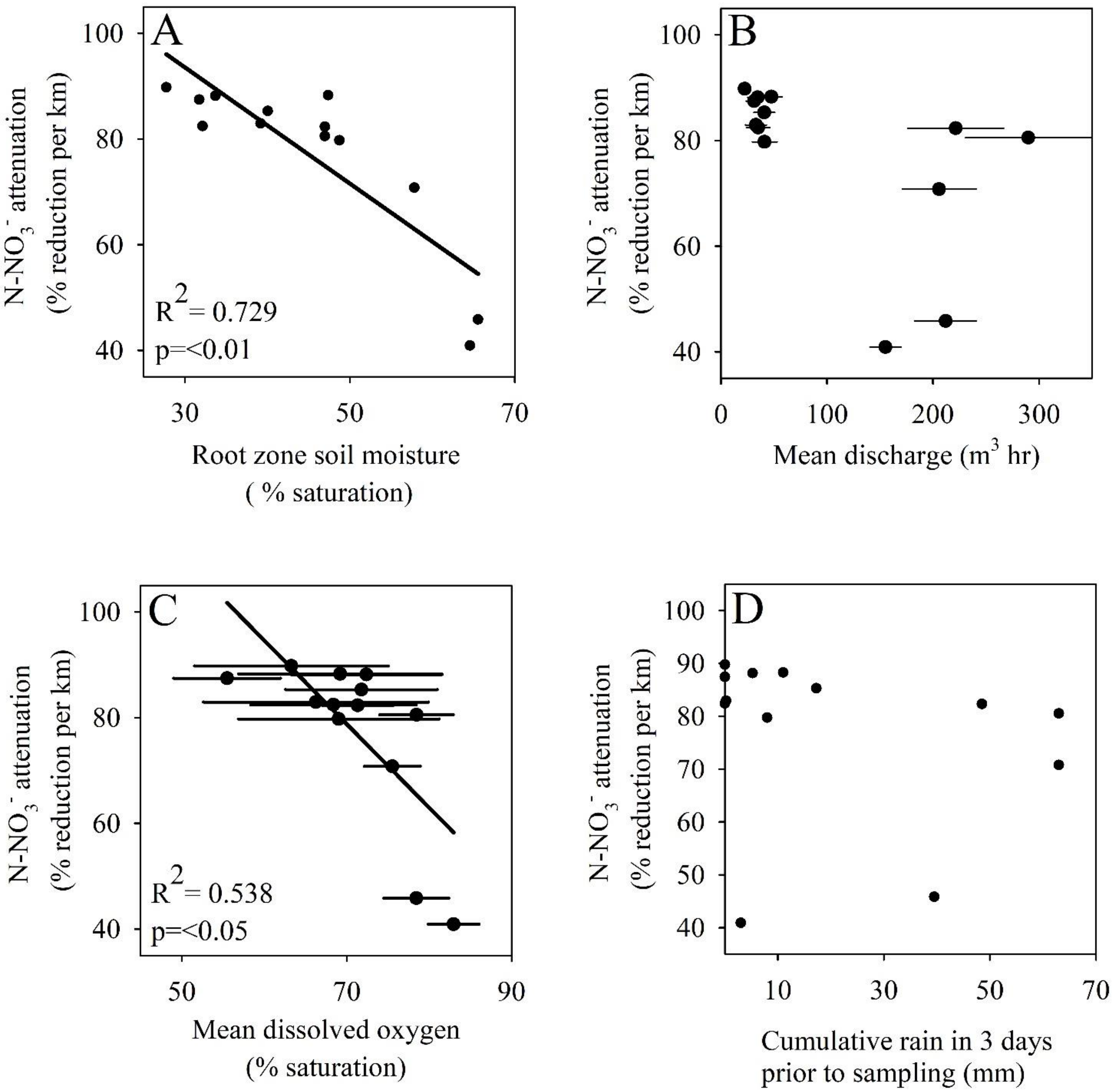

Figure 15: Correlations between N- NO_3^- attenuation per km of upstream creek reach and (A) root zone soil moisture showing a significant inverse correlation, (B) mean discharge of all spatial sampling sites showing no significant correlation, (C) mean dissolved oxygen saturation at all sample sites showing a significant correlation, and (D) cumulative rainfall in the 3 days prior to each sampling campaign showing no significant correlation.

3.6. Implications for management

Globally, the use of fertilisers has altered the cycling of N. With that change, there has been widely reported impacts to ecosystems downstream due to the increased export of nutrients in many catchments worldwide (Boynton et al., 1995; Van Meter et al., 2016; Vitousek et al., 1997). Changes in landscapes, predominantly through agriculture and deforestation, have altered biogeochemical processes and modified natural cycles, dramatically increasing NO_3^- concentrations relative to natural systems (Martin et al., 2004; Schilling & Libra, 2000; Van Herpe & Troch, 2000). N applied via fertilisers has been shown to accumulate in soils between 25 and 70 kg N ha^{-1} (Van Meter et al., 2016). Therefore, stream N concentrations in watersheds with fertilised soils are often driven by rainfall or groundwater seepage, whereby N is deposited and accumulates during the low rainfall periods, escapes during or after rainfall and modifies waterways from N deficient to N enriched (Vink et al., 2007). The limiting nutrient for algal growth in freshwater is generally phosphorous, whereas in estuaries and coastal marine systems often the limiting nutrient is N (Fabricius, 2005; Redfield, 1934; Smith et al., 2003). Therefore, when large fluxes of N enter saline waters from freshwater catchments, rapid eutrophication and algal blooms can occur in receiving waters (Howarth, 1988; Howarth et al., 1996; Nixon et al., 1996).

The legacy of agricultural NO_3^- storage in soils, flushing and leaching, particularly in relation to time-frames of export in different soil types is beginning to be better understood. Soils can store significant amounts of N and leach this to waterways over time. Conrad et al. (2019) found highly enriched phosphorous concentrations in Hearnes Lake sediments; here we find highly enriched N exports from Double Crossing Creek into Hearnes Lake. These preceding circumstances and the high probability of continued leaching of N from soils, may indicate a predisposition for downstream impacts to ecosystems, providing ideal conditions for algae blooms and the flow-on effects of eutrophication, hypoxia and fish kills. Semi-enclosed systems like Hearnes Lake may be particularly vulnerable due to reduced flushing and high residence times. As Hearnes Lake is an important part of the Solitary Islands Marine Park, this possible impact and the legacy effects of long-term N and P releases from agricultural landscapes are a major concern that are only now being understood within a regional context. Downstream receiving waters may have impacts for years to decades after termination of agricultural land uses upstream due to soil nutrient storage (Grimvall et al., 2000; McCrackin et al., 2017), that could lead to long-term ecosystem problems. The predicted recovery time of receiving waters such as Hearnes Lake from the stresses of anthropogenically caused algae blooms and eutrophication are variable, ranging from <1 year to >100 years after termination of horticulture in the catchment (McCrackin et al., 2017). The median recovery rate in a fertilised catchment such as Hearnes Lake is likely to be >15 years after termination of agricultural nutrient inputs (McCrackin et al., 2017).

4. Conclusions

A clear shift in NO_3^- and flow was seen between the three hydrological events with greater loads and concentrations during wet conditions. NO_3^- was greater than ANZECC guidelines at the time series and spatial survey sites in 302 out of 303 samples. There was a significant relationship between root zone soil moisture and NO_3^- concentrations ($p < 0.001$), indicating that N had been stored in soils and was flushed during rain events when soil moisture increases.

Nitrogen loads along our creek transect varied widely. In the dry period, flows increased steadily along the creek and NO_3^- concentrations and loads decreased with increasing distance from the upper catchment where most of the intensive horticulture land uses are. During the dry period, there was significant nitrate attenuation between the furthest upstream site where average concentrations were ~5000 times higher than the ANZECC guidelines and the furthest downstream site, where average concentrations were ~17 times the ANZECC guidelines. Though the creek provides a valuable ecosystem service by naturally reducing NO_3^-, there are still significant loads of NO_3^- seen entering Hearnes Lake and the probability of ecosystem impacts are high.

Nitrogen isotopes were used to identify sources of N in creek waters. Farms in the catchment receive recycled greywater from the local sewage treatment plants, delivering ~2176 kg NO_3^- yr^{-1}. Our results indicate a mixed source of N in the creek waters, as expected. The NO_3^- in the creek water appears to originate from a mixture of fertilisers (average 49.8 % based on stable isotopes at Sites 1, 2 and Control) and greywater (average 50.2 % based on stable isotopes at Sites 1, 2 and Control). Denitrification modifies the nitrogen isotopic composition, preventing a quantitative source assignment for stations away from the main source.

After the first flush, system function changed from high attenuation to high export of NO_3^-. We estimate that during the dry period, this transect of Double Crossing Creek has the capacity to remove 83.9 % of the NO_3^- load at Site 1 per km of the creek downstream. During the first flush, the creek attenuated 81.3 % per km, whilst during the secondary flush, this attenuation capacity dropped further to 52.2 % per km. This implies that the creek has a large capacity to attenuate NO_3^- during dry and first flush events, providing a valuable ecosystem service. The ability to attenuate is reduced when soil moisture, flow and nutrient loads increase. During periods of high flow and saturated soils, high loads of NO_3^- are exported downstream, essentially turning the creek from a natural bioreactor to a flow-through pipe. This suggests that nitrogen management during high flow events should be a priority.

We estimate that 136%, 74%, 18%, 17%, 7% and 68% of the N inputs to each sub-catchment reach the creek at Sites 1, 2, 3, 4, 5 and Control respectively. Values of aquatic N losses exceeding 100% are presumably impossible, and values >60% are improbable, implying that either the real fertiliser application rate on the farms is far higher than our assumed fertilisation rates, and/or our assumptions of other N inputs are incorrect, and/or our 91 days of observations of creek water quality during an unusually dry period are not representative of annual N loss.

Our results further highlight the need for decreasing fertiliser use and/or capturing N on farms before excess N is lost to creeks and the ocean. While the creek naturally reduces nitrogen fluxes reaching the Solitary Islands Marine Park, significant loads well above natural levels and ANZECC guidelines are still found along Double Crossing Creek.

5. Recommendations

The lack of data on fertiliser application rates and the timing of application creates a challenge for interpreting our data and managing water quality. With data on fertiliser use, managers and researchers would be able to better trace nutrients in soils and creeks pre and post land-use change, incorporating monitoring into any future land use developments. Our recommendations for managing fertilisers and reducing off-farm export, echo the comments made in White and Santos (2018). We highlight on-ground works of riparian zone upgrades and bioreactor installation, as well as fertiliser management.

Catchments with >15% fertilised lands should be continuously monitored for nutrient runoff impacts, particularly in rain events (White & Santos, 2018; White et al., 2018b). We strongly suggest reporting mechanisms be put in place for all nutrient and pesticide use on farmlands to better allow managers and researchers to assess possible impacts and identify hotspots for remediation works.

We strongly recommend better management of nitrogen runoff to reduce impacts to nearby waterways and avert downstream ecosystem effects including algae blooms, fisheries losses, loss of amenity, and impacts to the Solitary Islands Marine Park. Nitrogen management in horticultural lands is well researched, and there are many options available to land and water managers. Woodchip bioreactors are currently being tested in the CHCC area on both blueberry and cucumber farms.

The dominant downstream export of N occurs during rainfall; therefore, we propose tailwater recovery systems and storage of runoff waters be implemented onsite, allowing the slow release of this water to the creek during dry periods when the creek may have increased natural denitrification capacity.

In this catchment there are areas of < 2 m riparian zone. Narrow riparian zones allow direct transport of runoff waters, presumably carrying high loads of nutrients and sediment to the creek. We suggest increasing the width of riparian zones in the upper catchment by planting trees, shrubs and macrophytes. Riparian zones have been shown to reduce N exports to creeks by 4% for every metre of planting (Hill, 1996).

As ~50% of the N in Double Crossing Creek at sites 1, 2 and control was attributed to greywater, the use and suitability of this greywater in a small horticultural catchment upstream of a protected marine park should be reexamined. The greywater samples we obtained had NO_3^- concentrations between 40 and 80 times greater than the ANZECC guidelines for the creek. Blueberries prefer N in the form of NH_4^- rather than NO_3^-. The greywater samples were high in NO_3^-, with very low NH_4^- concentrations. Therefore, the N in the greywater may not be effectively utilised by the blueberry crop, and may remain available to be leached downstream.

The efficiencies and costs of these methodologies are not assessed here; however, each management approach is likely to be site specific and combinations of approaches may be necessary, including mitigation options not mentioned here. We strongly suggest further research of methods to identify applicable management approaches, as well as direct engagement of farmers and farm suppliers to improve nutrient management and retention on farms.

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7. Appendix

Appendix 1: Raw data from the time series station at Double Crossing Creek, NSW

Date / time	Time series sample #	Rain (mm)	Daily root zone soil moisture (% sat.)	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (μs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (μM)
7/01/2019 12:25	1	0	59.4	22.1	6.98	86.6	465	64.3	176.8
8/01/2019 13:20	2	0	58.5	23.5	6.96	89.7	468	57.6	170.8
9/01/2019 14:07	3	0	57.3	23.4	7.06	89.0	418	59.7	166.8
10/01/2019 8:15	4	0	55.9	22.5	6.95	83.0	474	59.7	171.8
11/01/2019 7:35	5	0	54.5	22.1	7.27	78.5	463	57.6	169.8
12/01/2019 8:41	6	0	53.0	22.1	7.23	79.3	461	36.7	168.8
13/01/2019 11:19	7	0	51.6	22.9	7.19	86.6	469	35.4	165.8
14/01/2019 11:16	8	0	50.1	23.4	7.25	84.8	462	39.9	167.8
15/01/2019 15:07	9	0	48.7	25.2	7.21	91.4	461	43.7	162.8
16/01/2019 16:20	10	0	47.4	24.1	7.21	84.7	465	39.4	161.8
17/01/2019 17:31	11	0	46.1	23.8	7.17	90.8	450	39.9	136.8
18/01/2019 11:05	12	0	44.7	23.7	7.2	82.4	465	39.9	138.8
19/01/2019 17:39	13	0	43.3	24	7.25	89.7	468	36.3	155.8
20/01/2019 13:15	14	0	42.1	24.3	7.31	93.5	444	33.6	149.8
21/01/2019 7:56	15	0	41.2	23.3	7.2	77.2	471	40.3	157.8
22/01/2019 9:29	16	0	40.3	22.9	7.24	77.8	468	36.3	151.8
23/01/2019 9:31	17	1	39.6	23.5	7.27	79.6	476	37.4	156.8
24/01/2019 12:09	18	0	38.9	24.1	7.43	81.1	472	39.9	152.8
25/01/2019 9:57	19	0	37.8	25	7.46	83.0	475	35.0	148.8
26/01/2019 9:39	20	0	36.8	24.8	7.38	79.0	491	30.1	146.8
27/01/2019 10:26	21	0	35.8	25.1	7.34	80.7	484	32.9	143.8
28/01/2019 11:11	22	0	35.0	24.5	7.25	81.9	482	34.3	141.8
29/01/2019 10:46	23	0	34.2	24.5	7.27	78.6	481	31.5	141.8
30/01/2019 9:12	24	0	33.5	24	7.32	76.9	476	24.8	134.8
31/01/2019 9:18	25	0	32.7	24.2	7.37	76.2	476	18.6	136.8
1/02/2019 9:38	26	0	32.1	23.4	7.25	77.5	480	14.3	136.8
2/02/2019 9:26	27	2	31.6	23.8	7.33	78.1	482	13.6	137.8
3/02/2019 10:10	28	0	31.2	23.4	7.18	76.9	477	8.6	133.8
3/02/2019 20:01	29	0		23.5	7.22	78.1	480	7.0	130.8
3/02/2019 21:02	30	0		23.2	7.25	74.3	476	6.8	126.8
3/02/2019 22:03	31	0		23	7.25	71.6	471	7.0	130.8
3/02/2019 23:01	32	0		22.7	7.08	68.9	476	9.5	130.8
4/02/2019 0:04	33	0	30.5	22.9	7.27	71.2	477	11.2	126.8
4/02/2019 1:00	34	0		22.7	7.32	74.3	481	11.3	125.8
4/02/2019 2:00	35	0		22.7	7.28	69.8	481	11.6	124.8

Date / time	Time series sample #	Rain (mm)	Daily root zone soil moisture (% sat.)	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (µs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (µM)
4/02/2019 3:00	36	0		22.7	7.28	70.6	482	10.5	124.8
4/02/2019 4:00	37	0		22.6	7.31	70.9	482	9.8	128.8
4/02/2019 5:00	38	0		22.3	7.3	68.6	482	13.5	128.8
4/02/2019 6:00	39	0		22.3	7.28	70.1	483	15.4	126.8
4/02/2019 7:00	40	0		21.8	7.36	75.1	483	33.3	148.8
4/02/2019 8:00	41	0		22.4	7.45	75.7	482	11.9	149.8
4/02/2019 9:00	42	0		23	7.5	77.8	483	14.9	144.8
4/02/2019 10:00	43	0		23.6	7.61	77.2	485	16.4	147.8
4/02/2019 11:00	44	0		24	7.56	75.8	485	14.9	149.8
4/02/2019 12:00	45	0		24.2	7.61	80.1	485	12.7	147.8
4/02/2019 13:00	46	0		24.3	7.56	78.6	486	8.7	147.8
4/02/2019 14:00	47	0		24.7	7.62	79.0	487	7.6	150.8
4/02/2019 15:00	48	0		24.9	7.7	80.4	484	7.8	138.8
4/02/2019 16:00	49	0		24.4	7.61	77.3	488	7.2	141.8
4/02/2019 17:00	50	0		24.5	7.63	77.8	482	6.6	139.8
4/02/2019 18:00	51	0		24	7.57	79.2	485	8.7	139.8
4/02/2019 19:00	52	0		23.9	7.51	73.9	483	6.8	137.8
4/02/2019 20:00	53	0		23.6	7.4	70.4	483	8.0	139.8
4/02/2019 21:00	54	0		23.5	7.38	68.1	483	6.2	141.8
4/02/2019 22:00	55	0		23.3	7.37	67.9	483	6.8	136.8
4/02/2019 23:00	56	0		23.2	7.36	68.3	482	7.6	136.8
5/02/2019 0:00	57	0	29.9	23	7.42	69.2	483	16.2	135.8
5/02/2019 1:00	58	0		22.8	7.37	68.8	484	19.9	146.8
5/02/2019 2:00	59	0		22.8	7.41	71.1	484	9.5	148.8
5/02/2019 3:00	60	0		22.7	7.39	69.5	484	19.9	139.8
5/02/2019 4:00	61	0		22.6	7.41	69.4	484	20.3	142.8
5/02/2019 5:00	62	0		22.5	7.42	70.7	485	21.6	142.8
5/02/2019 6:00	63	0		22.4	7.44	71.1	486	14.3	143.8
5/02/2019 7:00	64	0		22.2	7.41	72.9	484	33.7	142.8
5/02/2019 8:00	65	0		22.4	7.48	73.0	485	16.5	140.8
5/02/2019 9:00	66	0		22.7	7.51	75.3	487	16.5	143.8
5/02/2019 10:00	67	0		23.2	7.57	77.6	488	16.5	142.8
5/02/2019 11:00	68	0		23.3	7.59	80.3	488	15.6	133.8
5/02/2019 12:00	69	0		23.5	7.61	79.3	489	12.5	138.8
5/02/2019 13:00	70	0		23.9	7.56	78.6	487	9.7	137.8
5/02/2019 14:00	71	0		23.9	7.55	74.4	486	8.6	136.8
5/02/2019 15:00	72	0		24.1	7.58	78.5	483	6.7	135.8
5/02/2019 16:00	73	0		24	7.5	74.3	485	5.7	131.8
5/02/2019 17:00	74	0		23.8	7.51	74.6	483	6.2	129.8

Date / time	Time series sample #	Rain (mm)	Daily root zone soil moisture (% sat.)	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (µs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (µM)
5/02/2019 18:00	75	0		23.8	7.5	72.9	485	4.8	131.8
5/02/2019 19:00	76	0		23.6	7.47	68.5	487	2.1	127.8
5/02/2019 20:00	77	0		23.5	7.51	70.1	486	2.2	137.8
5/02/2019 21:00	78	0		23.5	7.49	64.0	486	2.2	142.8
5/02/2019 22:00	79	0		23.5	7.5	63.7	486	4.2	139.8
5/02/2019 23:00	80	0		23.3	7.51	61.6	487	7.0	139.8
6/02/2019 0:00	81	0	30.4	23.1	7.52	65.2	486	5.4	136.8
6/02/2019 1:00	82	0		23	7.5	66.3	487	10.7	142.8
6/02/2019 2:00	83	0		22.9	7.53	67.4	487	10.7	140.8
6/02/2019 3:00	84	0		22.7	7.51	68.9	485	12.1	140.8
6/02/2019 4:00	85	0		22.7	7.57	70.2	486	10.7	141.8
6/02/2019 5:00	86	0		22.7	7.57	69.8	486	10.7	141.8
6/02/2019 6:00	87	0		22.7	7.59	70.0	485	12.1	140.8
6/02/2019 7:00	88	0		22.6	7.56	70.2	485	12.1	133.8
6/02/2019 8:00	89	0		22.8	7.64	77.2	487	13.4	140.8
6/02/2019 9:00	90	0		23.1	7.75	74.6	487	12.1	141.8
6/02/2019 10:00	91	0		23.3	7.71	77.4	488	12.1	142.8
6/02/2019 11:00	92	0		23.5	7.81	78.4	488	10.7	139.8
6/02/2019 12:00	93	0		23.8	7.8	79.1	488	10.7	139.8
6/02/2019 13:00	94	0		24.2	7.14	76.8	487	4.0	135.8
6/02/2019 14:00	95	0		24.2	7.75	76.7	488	3.7	136.8
6/02/2019 15:00	96	0		24	7.77	78.7	469	4.0	128.8
6/02/2019 16:00	97	0		24.1	7.74	77.8	490	3.5	132.8
6/02/2019 17:00	98	0		23.9	7.73	77.7	492	3.5	130.8
6/02/2019 18:00	99	0		23.9	7.72	67.7	493	3.7	134.8
6/02/2019 19:00	100	0		23.7	7.69	71.6	491	8.7	130.8
6/02/2019 20:00	101	0		23.5	7.71	71.4	523	9.1	128.8
6/02/2019 21:00	102	0		23.4	7.69	69.8	495	9.5	132.8
6/02/2019 22:00	103	0		23.3	7.71	69.3	522	15.1	141.8
6/02/2019 23:00	104	0		23.2	7.68	68.3	496	16.1	140.8
7/02/2019 0:00	105	0	31.5	23.1	7.74	69.3	497	16.1	138.8
7/02/2019 1:00	106	0		23	7.72	67.9	499	16.1	131.8
7/02/2019 2:00	107	0		22.9	7.73	68.3	499	16.1	116.8
7/02/2019 3:00	108	0		22.9	7.74	68.3	499	17.1	132.8
7/02/2019 4:00	109	0		22.8	7.74	68.4	499	17.1	135.8
7/02/2019 5:00	110	0		22.7	7.74	67.4	500	17.1	137.8
7/02/2019 6:00	111	0		22.6	7.77	69.2	499	18.1	134.8
7/02/2019 7:00	112	0		22.6	7.81	74.5	501	18.1	132.8
7/02/2019 8:00	113	0		22.8	7.78	73.5	501	18.1	135.8
7/02/2019 9:00	114	1		22.8	7.84	72.7	501	24.1	133.8
7/02/2019 10:00	115	1		22.9	7.79	70.1	527	24.1	124.8

Date / time	Time series sample #	Rain (mm)	Daily root zone soil moisture (% sat.)	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (µs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (µM)
7/02/2019 11:00	116	0.25		23	7.8	70.8	501	24.1	131.8
7/02/2019 12:00	117	0		23.2	7.83	74.4	528	24.1	131.8
7/02/2019 13:00	118	0.1		23.6	7.82	76.9	528	15.6	127.8
7/02/2019 14:00	119	0		23.6	7.82	78.2	534	15.1	119.8
7/02/2019 15:00	120	0		23.7	7.82	76.9	530	15.1	130.8
7/02/2019 16:00	121	0		23.8	7.86	73.4	504	15.1	132.8
7/02/2019 17:00	122	0		23.8	7.83	74.8	527	9.7	130.8
7/02/2019 18:00	123	0		23.7	7.78	75.4	506	9.0	129.8
7/02/2019 19:00	124	0		23.5	7.69	70.8	523	15.1	129.8
7/02/2019 20:00	125	0		23.3	7.71	70.4	502	16.1	131.8
7/02/2019 21:00	126	0		23.2	7.75	68.7	503	16.5	133.8
7/02/2019 22:00	127	0		23.1	7.79	69.3	501	16.7	132.8
7/02/2019 23:00	128	0		22.9	7.82	70.1	503	22.0	130.8
8/02/2019 0:00	129	0	31.4	22.8	7.82	67.5	500	23.3	126.8
8/02/2019 9:51	130	0		23	7.92	77.1	505	23.8	117.8
9/02/2019 9:09	131	0	30.6	23.1	7.49	64.2	481	23.6	125.8
9/02/2019 22:18	132	16.5		22.9	7.7	66.9	450	91.6	113.8
9/02/2019 11:26	133	0		22.7	7.81	71.5	457	69.4	115.8
10/02/2019 0:26	134	0	34.2	22.7	7.87	68.4	461	50.2	124.8
10/02/2019 7:08	135	0		22.2	7.83	66.7	470	26.8	118.8
10/02/2019 19:28	136	0		23.2	7.93	74.9	469	24.1	114.8
11/02/2019 8:41	137	0	33.2	22.5	7.86	70.5	474	25.4	127.8
12/02/2019 10:39	138	0	32.3	23.3	7.9	74.3	477	26.8	128.0
13/02/2019 10:22	139	0	31.5	23.4	7.73	72.6	478	23.6	135.0
14/02/2019 8:58	140	0	31.7	22.7	7.8	70.0	477	24.4	130.0
15/02/2019 10:16	141	0	31.1	22.5	7.91	77.3	477	24.1	129.0
16/02/2019 10:35	142	0	30.3	22.5	7.72	71.2	474	16.3	118.0
17/02/2019 11:19	143	0	29.6	22.7	7.72	72.7	476	16.1	140.0
18/02/2019 8:35	144	0	28.9	22.1	7.7	71.8	476	18.1	138.0
19/02/2019 9:28	145	0	28.3	22.6	8.09	72.8	478	17.5	107.9
20/02/2019 9:09	146	0	27.7	23.2	7.85	69.5	480	18.1	121.9
21/02/2019 10:03	147	3	29.1	23.6	7.8	68.9	483	18.1	115.9
22/02/2019 8:35	148	0.25	32.7	22.8	7.89	67.4	481	12.1	116.9
23/02/2019 12:49	149	0	32.4	22		74.3	481	7.6	119.9
24/02/2019 9:01	150	0.25	32.6	21.5		66.0	483	9.2	130.9
25/02/2019 9:18	151	7.5	33.6	21.2		71.8	484	24.1	113.9
26/02/2019 9:05	152	4	34.8	21		79.7	487	24.1	114.9
27/02/2019 9:45	153	1	34.4	21.4		62.7	488	22.8	136.9
28/02/2019 9:27	154	0	33.9	21.4		71.5	484	17.5	129.9

Date / time	Time series sample #	Rain (mm)	Daily root zone soil moisture (% sat.)	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (µs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (µM)
1/03/2019 9:50	155	0.25	33.7	22.6	6.99	76.6	504	16.1	126.9
2/03/2019 10:29	156	19	34.8	21.5	6.9	72.6	480	48.2	105.9
3/03/2019 10:22	157	8	37.7	21.6	6.63	71.5	483	36.8	123.9
4/03/2019 9:15	158	2	37.9	21.7	6.64	74.6	491	35.2	113.9
5/03/2019 9:10	159	0.25	37.2	21.8	6.95	75.6	492	35.2	116.9
6/03/2019 9:14	160	0	36.4	22.1	6.95	75.8	493	34.1	149.9
7/03/2019 11:20	161	0	35.9	22.2	6.94	75.1	488	26.0	145.9
8/03/2019 9:02	162	17	40.0	21.5	7.04	72.2	502	48.2	149.9
9/03/2019 9:05	163	1	39.7	22.2	6.8	78.7	516	36.8	147.9
10/03/2019 10:20	164	1	39.2	22.7	6.71	77.7	531	35.2	144.9
11/03/2019 9:07	165	6.25	40.7	22.7	6.74	74.8	516	46.2	162.9
12/03/2019 10:10	166	0	39.8	23.8	7.07	83.6	519	34.1	167.9
13/03/2019 9:43	167	0	39.0	22.7	6.87	77.1	502	33.8	166.9
14/03/2019 10:22	168	0	38.4	22.8	6.97	75.5	501	26.0	164.9
15/03/2019 9:26	169	0.25	39.2	22.5	7.06	72.3	504	25.4	161.9
16/03/2019 9:37	170	6	43.8	21.7	6.84	70.8	498	30.8	158.9
17/03/2019 9:22	171	3	44.0	21.7	7.01	76.5	508	23.3	156.9
17/03/2019 18:38	172	15		21.3	7.07	74.2	485	77.7	135.9
17/03/2019 19:10	173	5		21.4	6.9	71.5	458	66.6	129.9
17/03/2019 19:42	174	1		21.4	7	69.7	488	57.2	139.9
17/03/2019 20:22	175	0		21.4	7.05	72.6	487	76.6	126.9
17/03/2019 21:20	176	0		21.4	7.06	74.3	496	48.2	186.9
18/03/2019 9:18	177	0.25	49.1	21.2	7.11	75.7	508	36.8	179.9
19/03/2019 9:13	178	0	48.1	21.9	7.07	78.0	509	33.5	195.9
20/03/2019 9:45	179	8	50.0	22	7.16	77.6	510	31.8	196.9
21/03/2019 9:21	180	0	48.7	21.8	7.12	77.4	506	36.8	182.9
22/03/2019 9:24	181	0	48.7	22	7.18	58.5	507	26.8	196.9
23/03/2019 9:16	182	0	47.8	22.3	6.9	78.7	505	21.1	189.9
24/03/2019 9:27	183	0	46.7	22.6	7.09	75.4	505	26.8	187.9
25/03/2019 9:05	184	0	45.6	22.9	7.12	77.7	503	21.1	179.9
26/03/2019 9:36	185	0	44.8	22.8	6.99	74.5	502	28.5	172.9
27/03/2019 9:19	186	7.5	48.9	21.8	6.95	76.3	499	29.5	173.9
28/03/2019 9:37	187	1.5	48.3	21.5	7.08	82.6	501	36.8	187.9
29/03/2019 9:26	188	2	47.4	21.4	7.12	79.0	502	42.2	193.9
30/03/2019 9:30	189	5	47.0	22	7.8	76.8	501	44.2	184.9
30/03/2019 12:35	190	22		22	7.18	77.4	404	215.5	134.9
30/03/2019 13:05	191	10		22	7.31	76.7	417	215.8	136.9
30/03/2019 13:37	192	8		22	7.21	74.2	468	287.3	171.9
30/03/2019 14:37	193	11		21.7	7.23	77.2	430	342.1	162.9
30/03/2019 15:35	194	3		21.8	7.21	80.1	473	435.5	172.9

Date / time	Time series sample #	Rain (mm)	Daily root zone soil moisture (% sat.)	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (μs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (μM)
30/03/2019 16:30	195	0.5		21.8	7.33	78.5	474	834.0	173.9
30/03/2019 17:30	196	0		21.9	7.27	78.5	478	557.9	175.9
30/03/2019 18:30	197	0		21.9	7.35	78.8	476	364.5	179.9
30/03/2019 19:30	198	0		21.8	7.33	79.1	479	279.0	217.9
30/03/2019 20:30	199	0		21.8	7.22	78.5	483	281.2	191.9
30/03/2019 23:55	200	0		21.1	7.25	78.0	493	272.2	255.9
31/03/2019 6:09	201	0	57.8	19.6	7.32	79.3	506	273.3	268.9
31/03/2019 12:11	202	0		20.4	7.3	82.1	507	256.5	316.9
31/03/2019 18:02	203	0		20.5	7.2	82.0	518	217.7	275.9
1/04/2019 6:14	204	0	56.5	19	7.25	80.1	521	65.6	334.9
1/04/2019 18:04	205	0		20.8	7.13	71.1	523	61.9	308.9
2/04/2019 6:05	206	3	60.1	20.2	7.22	79.9	519	98.4	232.9
2/04/2019 13:25	207	27		20.4	7.25	84.4	465	579.2	239.9
2/04/2019 14:30	208	9		20.9	7.64	90.2	415	1402.7	386.9
2/04/2019 15:35	209	0		21.1	7.17	87.6	422	1233.8	439.9
2/04/2019 16:32	210	0		21.2	7.21	87.1	455	997.9	476.9
2/04/2019 17:31	211	0		21.2	7.18	85.6	480	556.0	484.9
2/04/2019 18:32	212	0		21	7.23	85.8	496	421.7	465.9
2/04/2019 21:42	213	0		20.9	7.31	84.4	517	415.0	473.9
3/04/2019 6:01	214	0.5	65.5	20.5	7.27	83.2	531	310.7	480.9
3/04/2019 12:38	215	0		21.6	7.25	63.0	540	234.9	423.9
3/04/2019 18:02	216	0		21.5	7.22	86.2	534	205.5	428.9
4/04/2019 9:41	217	1	65.3	21.1	7.28	85.4	523	192.2	362.9
4/04/2019 18:40	218	1		21.3	7.22	85.6	518	139.9	404.9
5/04/2019 10:12	219	1	64.6	21	7.29	88.5	502	140.1	383.9
6/04/2019 10:31	220	0	64.2	21.4	7.3	87.2	510	106.9	305.9
7/04/2019 9:41	221	0	62.8	21.5	7.26	82.9	506	86.4	350.9
8/04/2019 10:43	222	0	61.3	21.9	7.21	85.3	503	64.8	341.9

Appendix 2: Raw data from spatial campaigns along a transect of Double Crossing Creek, NSW.

Date / time	Site	Sample	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (µs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (µM)
24/01/2019 9:00	1	1	25.2	7.24	5.4	708	4.3	110.9
1/02/2019 11:20	1	2	28.2	8.14	107.6	2170	0.4	17518.4
20/02/2019 10:10	1	4	28.7	8.35	112.1	4930	0.7	21598.4
1/03/2019 11:40	1	5	28.1	6.53	109.2	5400	0.4	26198.4
8/03/2019 10:15	1	6	23	8.01	109.6	2463	1.0	7289.2
15/03/2019 13:30	1	7	27.8	8.03	124.2	4587	0.9	18718.4
22/03/2019 10:45	1	8	28.9	7.53	124.8	5940	0.6	27198.4
29/03/2019 10:40	1	10	23.6	6.94	118.8	5800	0.7	26198.4
30/03/2019 17:45	1	12	22.6	7.18	96.6	5010	1.4	26598.4
3/04/2019 13:20	1	14	24.2	7.08	82.2	630	71.1	521.9
5/04/2019 11:35	1	15	24	6.95	82.9	481	99.4	179.9
24/01/2019 9:25	2	1	23.5	6.81	32	480	81.7	290.9
1/02/2019 12:05	2	2	22.9	6.98	34.2	479	29.4	314.9
14/02/2019 14:20	2	3	23	7.4	33.2	478	32.8	298.9
20/02/2019 10:30	2	4	23.3	8.07	26	512	28.1	309.9
1/03/2019 12:05	2	5	23.2	6.69	43.2	517	40.2	310.9
8/03/2019 11:05	2	6	22.4	6.14	43.3	502	39.5	315.9
15/03/2019 10:45	2	7	22.5	6.28	23.3	520	29.4	318.9
22/03/2019 11:00	2	8	23.1	6.42	35.8	551	38.3	293.9
29/03/2019 11:10	2	10	22.5	6.63	28.1	544	66.5	285.9
30/03/2019 14:07	2	11	22	6.91	54.9	464	263.2	267.9
30/03/2019 18:00	2	12	22.2	6.76	63.8	540	349.3	698.9
31/03/2019 12:55	2	13	21.6	6.76	64.1	578	230.3	565.9
3/04/2019 13:25	2	14	23.2	6.76	72	573	240.0	422.9
5/04/2019 11:56	2	15	23.2	6.83	68.7	520	153.4	353.9
24/01/2019 12:09	3	1	24.1	7.43	81.1	472	39.9	152.8
1/02/2019 9:38	3	2	23.4	7.25	77.5	480	14.3	136.8
14/02/2019 8:58	3	3	22.7	7.8	70	477	24.4	130.0
20/02/2019 9:09	3	4	23.2	7.85	69.5	480	18.1	121.9
1/03/2019 9:50	3	5	22.6	6.99	76.6	504	16.1	126.9
8/03/2019 9:02	3	6	21.5	7.04	72.2	502	48.2	149.9
15/03/2019 9:26	3	7	22.5	7.06	72.3	504	25.4	161.9
22/03/2019 9:24	3	8	22	7.18	58.5	507	26.8	196.9
29/03/2019 9:26	3	10	21.4	7.12	79	502	42.2	193.9
30/03/2019 14:37	3	11	21.7	7.23	77.2	430	285.1	162.9
30/03/2019 18:30	3	12	21.9	7.35	78.8	476	364.5	179.9
31/03/2019 12:11	3	13	20.4	7.3	82.1	507	256.5	316.9
3/04/2019 12:38	3	14	21.6	7.25	63	540	234.9	423.9
5/04/2019 10:12	3	15	21	7.29	88.5	502	140.1	383.9
24/01/2019 10:38	4	1	25.1	6.62	68.1	472	84.6	120.6

Date / time	Site	Sample	Temp. (°C)	pH	Dissolved oxygen (% sat.)	EC (µs cm^{-1} @ 25°C)	Discharge (m^3 hr^{-1})	NO_X (µM)
1/02/2019 12:49	4	2	23.6	7.53	69.7	471	55.9	101.6
14/02/2019 14:50	4	3	23.6	7.4	66.6	475	45.9	82.6
20/02/2019 11:15	4	4	23.6	7.92	63.7	477	27.9	87.5
1/03/2019 13:00	4	5	24.1	7.46	76.9	549	55.7	70.5
8/03/2019 11:40	4	6	21.9	7.05	78.1	492	38.9	95.3
15/03/2019 11:40	4	7	22.7	6.96	63.5	504	33.7	106.6
22/03/2019 11:50	4	8	22.7	6.72	68.4	512	51.8	115.6
29/03/2019 12:10	4	10	22.6	6.84	68.3	498	59.9	109.6
30/03/2019 14:20	4	11	22	7.37	78.9	462	264.6	119.6
30/03/2019 18:15	4	12	22	7.47	81.3	496	348.3	203.6
31/03/2019 13:10	4	13	20.5	7.38	82.7	509	254.4	223.6
3/04/2019 13:45	4	14	22.4	7.23	89.9	535	258.2	386.6
5/04/2019 12:27	4	15	22.7	7.29	90	512	175.4	344.6
24/01/2019 11:05	5	1	24.3	7.45	48.1	493	120.3	7.0
1/02/2019 13:14	5	2	23.8	7.4	52.9	501	75.6	4.6
14/02/2019 15:20	5	3	23.5	8.01	52.2	485	53.0	3.4
20/02/2019 11:40	5	4	23.6	8.18	45.1	495	37.2	3.4
1/03/2019 13:30	5	5	22.8	7.14	56	511	60.9	2.3
8/03/2019 12:10	5	6	21.6	7.16	55.7	490	77.0	3.0
15/03/2019 12:00	5	7	22.9	7.01	48	511	76.0	9.4
22/03/2019 12:10	5	8	22.5	6.97	57.6	506	88.0	13.4
29/03/2019 12:25	5	10	21.8	6.92	51.8	505	68.5	3.6
30/03/2019 14:30	5	11	22.1	7.35	74.3	473	293.4	5.4
30/03/2019 18:25	5	12	22	7.47	71.8	472	386.1	10.3
31/03/2019 13:20	5	13	20.2	7.31	73.2	491	251.4	51.4
3/04/2019 14:00	5	14	21.8	7.33	85.1	524	255.7	314.6
5/04/2019 12:27	5	15	22.8	8.47	84.7	524	207.4	246.6
24/01/2019 10:13	C	1	22.1	6.42	35.7	468	39.6	196.9
1/02/2019 11:35	C	2	23.3	6.47	55.7	496	20.4	324.9
14/02/2019 13:50	C	3	23.6	7.3	61.1	475	16.9	229.9
20/02/2019 10:50	C	4	23.3	7.48	46.6	483	16.7	213.9
1/03/2019 12:20	C	5	23.4	6.1	55.1	537	22.0	200.9
8/03/2019 11:20	C	6	23	6.65	37.5	510	25.5	293.9
15/03/2019 11:05	C	7	23.1	5.99	47.9	507	18.9	385.0
22/03/2019 11:30	C	8	23.3	6.02	54	530	27.0	389.9
29/03/2019 11:40	C	10	22.9	5.97	51.9	533	34.8	327.9
30/03/2019 14:15	C	11	22	6.84	81.6	220	186.6	304.5
30/03/2019 18:05	C	12	22.4	6.42	60.7	494	313.6	549.6
31/03/2019 13:00	C	13	21.8	6.39	67.9	534	197.6	433.6
3/04/2019 13:30	C	14	22.7	6.43	72.1	545	182.0	547.6
5/04/2019 12:01	C	15	23.5	6.43	68.3	439	73.7	504.6