Improving water quality downstream of blueberry farms: Trial of a novel surface-flow bioreactor design

Coffs Harbour City Council Environmental Levy Program

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1. Executive summary

Nitrogen leaching from agricultural land use is known to impact Coffs Harbour stream water quality. On-farm denitrifying woodchip bioreactors can potentially mitigate nitrogen, particularly nitrate (NO_3^-) pollution by maximising denitrification capacity in between farms and creeks. However, denitrification may release the powerful greenhouse gas nitrous oxide (N_2O), swapping from aquatic (NO_3^-) to atmospheric (N_2O) pollution.

Here, we assess nitrate nitrogen (NO_3^--N) removal and N_2O emissions from a new edge-of-field surface-flow bioreactor design during ten rain events on intensive farming land.

Our nitrate removal rates (NRR) varied between 5.4 and 76.2 g NO_3^--N m^{-3} wetted woodchip d^{-1} with a mean of 30.3±7.3 g NO_3^--N m^{-3} d^{-1}. The nitrate removal efficiency (NRE) ranged from ~73% in ideal conditions to ~18% in non-ideal conditions. Overall, 9.9 kg NO_3^--N ha^{-1} yr^{-1} were removed via the bioreactor, representing an overall 30% efficiency when incorporating all flow and overflow events. However, inflows and treated outflows from the bioreactor are ~254 and ~138 fold higher than ANZECC guideline values, respectively, indicating that there is still a significant risk to local waterways from treated effluent.

The bioreactor did not contribute higher N_2O emissions than what naturally occurs if the bioreactor was absent, implying minor swapping from aquatic to atmospheric pollution. NO_3^--N that was removed in the bioreactor and converted to N_2O (rN_2O) was ~3.3 fold lower than the expected 0.75% IPCC emission factor.

Our modelled NO_3^--N removal from the bioreactor would cost AUS$17.8 per kg NO_3^--N removed. Whilst off-farm NO_3^- losses are expected, even under best management practice, the removal cost using this bioreactor is ~5 fold greater than the estimated cost of nitrogen fertiliser application. Reducing on-farm NO_3^- use to lower environmental losses may be more cost-effective than treating effluents; however, the combination of both management techniques is likely necessary to protect environmental assets.

With minor design modifications, the bioreactor's efficiency will likely increase. Overall, edge-of-field surface-flow bioreactors can be a useful tool to reduce NO_3^--N runoff in eastern Australian intensive horticulture catchments and play an integral role in the suite of NO_3^--N management solutions. This bioreactor represents a proof-of-concept and a new tool to protect vital aquatic habitats such as the Solitary Islands Marine Park.

2. Introduction

As part of the Environmental Levy Grants program, Southern Cross University has performed nutrient removal trials in collaboration with local farmers, North Coast Local Land Services, Coffs Harbour City Council (CHCC) and Coffs Harbour Regional Landcare, using a novel edge-of-field surface-flow woodchip bioreactor. This project aimed to determine if bioreactors could be used in conjunction with other nutrient loss management solutions to reduce fertiliser loss from farms and protect downstream habitats from negative impacts.

This project follows our previous research collaborations with CHCC in the region, motivated by community concerns over the impacts of intensive horticulture on regional water quality and the Solitary Islands Marine Park (SIMP) (Conrad et al., 2018, 2019; Wadnerkar et al., 2020a; White & Santos, 2018; White, 2016). The nitrogen (N) loads 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 a combination of upstream fertiliser use and/or recycled greywater (White et al., 2020).

Fertiliser loss from agricultural lands via groundwater leaching and/or surface flow drives nitrogen pollution in waterways (Frei et al., 2020; Seitzinger et al., 2005). Denitrifying woodchip bioreactors are an emerging solution to reduce losses of nitrogen from agricultural lands (Addy et al., 2016). Bioreactors are designed to intercept nitrogen-rich waters and rely on the natural denitrification process to reduce nitrate (NO_3^-) (Schipper et al., 2010). In-reactor NO_3^- removal is a complex process mainly dependant on denitrifier communities, temperature, hydraulic residence time (HRT) and carbon availability (Schipper et al., 2010). The bacterial mediated denitrification process converts aqueous NO_3^- to nitrogen gases, primarily inert dinitrogen (N_2). Many bioreactors are below-ground structures filled with locally available woodchips that create an anaerobic environment for bacteria to carry out rapid denitrification of leachate. The woodchips offer the carbon source required for bacterial growth.

Initially used to treat groundwater flows, denitrifying bioreactor designs and applications have now expanded to many agricultural crops and are often categorised as denitrification walls and denitrification beds (Addy et al., 2016; Schipper et al., 2010). Denitrification walls intercept shallow groundwater at a depth of ~1-2 m, by excavating and filling a long narrow

trench perpendicular to groundwater flows with woodchips facilitating denitrification across the trench (Fahrner, 2002; Schipper et al., 2010). Denitrification beds are usually 1-2 m deep and are long shallow structures constructed below ground, lined with an impermeable membrane that can house woodchips. The flow enters and exits the structure longitudinally via pipes, and flow rates can be controlled (Christianson et al., 2012b; Ghane et al., 2015).

While nitrate-removal efficiency (NRE; % NO_3^--N removed) has been quantified in multiple bioreactors (Addy et al., 2016), less attention has been paid to the pollution swapping effects of removing NO_3^- whilst producing the potent greenhouse gas nitrous oxide (N_2O) (Davis et al., 2019; Rivas et al., 2020). N_2O emissions from anthropogenic activities, primarily agriculture, have contributed to increased global N_2O atmospheric concentrations and detrimental effects to the global climate (Hensen et al., 2013; Oertel et al., 2016; Portmann et al., 2012). In sub-ideal conditions, incomplete denitrification can halt the denitrification process and produce N_2O as a by-product. Incomplete denitrification in bioreactors may contribute to N_2O losses to the atmosphere, potentially counteracting some of the benefits of NO_3^--N removal from agricultural runoff waters. The complete transformation to N_2O is dependent on many parameters, such as oxygen and carbon availability, microbial community population and abundance, temperature and redox potential (Hefting et al., 2003; Walker et al., 2002).

N_2O is a long-lived greenhouse gas (GHG) that contributes to ozone depletion in the atmosphere (Montzka et al., 2011; Portmann et al., 2012) with a sustained global warming potential (SGWP) 250 times the equivalent of CO_2 on 20-year timescales (Neubauer & Megonigal, 2015). Indirect emissions from agriculture (emissions from NO_3^--N rich leachate entering surrounding waterways) have large uncertainties in areas with episodic rather than seasonal rainfall patterns due to the difficulty of sampling these leachates (Mosier et al., 1998; Reay et al., 2012; Tian et al., 2019). If bioreactors are to be considered as a widespread solution to remove agricultural NO_3^- leachate, the possibility of increased N_2O emissions from bioreactors should also be examined. Schipper et al. (2010) suggest that all denitrification structures and management technologies should be investigated as potential pollution swapping sources.

We developed an edge-of-field surface-flow fed bioreactor to intercept an existing drainage ditch and capture surface runoff from a heavily fertilised blueberry farm. As our bioreactor was not subject to groundwater flows, our sampling regime encapsulates natural rainfall and runoff from fertiliser-intensive horticulture in a catchment that receives episodic rather than seasonal rainfall.

In this report, we:

1. Examine the bioreactor's nitrogen removal efficiency and nitrogen removal rate during ten surveys in varying rainfall conditions.
2. Contrast the drivers of NO_3^--N consumption and N_2O production.
3. Investigate CO_2-eq N_2O emissions from the field, drainage channel, bioreactor inlet, bioreactor outlet and downstream watercourse.
4. Model NO_3^--N consumption using weather data from the last five years and estimate NO_3^--N removal over the bioreactor lifetime.
5. Investigate the cost-benefit of edge-of-field surface-flow bioreactors as potential NO_3^--N removal devices.
6. Draw comparisons of inflow and outflow NO_3^--N concentrations to the Australia and New Zealand Environment and Conservation Council guideline for lowland rivers in eastern NSW.

3. Methods

3.1. Study site and bioreactor design

Our investigations were performed in a constructed edge of field bioreactor installed in an existing surface flow drainage ditch on a ~3 ha blueberry farm in subtropical Australia (Figure 1A). The bioreactor construction was completed on 1 June 2018, and sampling began roughly one year later (28 June 2019) in line with recommended field trial best practice (Schipper et al., 2010). The drainage ditch flows ~30 m downstream of the bioreactor to the nearby Double Crossing Creek, and on to Hearnes Lake, a habitat protection area of the Solitary Islands Marine Park. The surrounding catchment is dominated by horticulture (cucumbers, tomatoes, bananas, avocados, and blueberries). Previous investigations have shown large loads of NO_3^- are transported downstream following rain events (Wadnerkar et

al., 2021; Wadnerkar et al., 2019) and high N_2O emissions from regional waterways (Reading et al., 2020).

As a trial pollution reduction measure, we designed, installed, and monitored an edge of field surface flow bioreactor (Figure 1, Figure 2). The bioreactor dimensions were primarily defined by the available space and a comparison of this potential footprint against historical rainfall volumes, durations, and the expected percentage capture of the period of first-flush that mobilises nitrates (15-30 min) and the potential initial capture volume. The bioreactor excavation was 1 m deep at the infiltration basin, 4 m wide and 14 m long (Figure 1C). Woodchips in the bioreactor occupy 12 m of the length, and the infiltration basin is 2 m long. The bioreactor floor was sloped on a consistent gradient of 0.2%, ensuring that the drainage pipe inlet (200 mm from the bioreactor base) was at the level of the infiltration basin. The drainage pipe outflow (6 m downstream of the bioreactor) was a further 200 mm below the drainage pipe inlet, providing constant head conditions when the floor of the infiltration basin reached a height of 50 mm. The entire reactor was bounded in geotextile to protect the structure from the surrounding soil profile. Bentofix geotextile was placed on the upper surface of the reactor to reduce vertical exfiltration. The infiltration basin and reactor were capped with ~200 mm rock to protect the structure during surcharging flow conditions.

Soils on the farm have been stripped to form rows of blueberry mounds ~40 cm high, leaving a shallow A-horizon (~2-3 cm) overlying a hard clay soil (Wilk et al., 2008). Blueberry grow mounds are ~3.5 m apart, covered in a weed control mat, leaving an inter-row of grass for plant and machinery access. Previous investigations in the catchment revealed that groundwater was not a major nutrient contributor to the nearby creeks (White et al., 2018a; White et al., 2018b), indicating that the bioreactor design should target surface flow rather than groundwater. The inter-rows commonly pool water in wet periods that flows overland to the drainage ditch. Recommended blueberry fertilisation rates are 121 kg N ha yr^{-1}, delivered via two drip irrigation lines on each blueberry mound under the weed control mat with drippers every 30cm (Doughty et al., 1988; Ireland & Wilk, 2006). Blueberries are dominantly fed with ammonium (NH_4^+) based fertilisers because the plants preferentially uptake NH_4^+ over NO_3^- (Merhaut & Darnell, 1995).

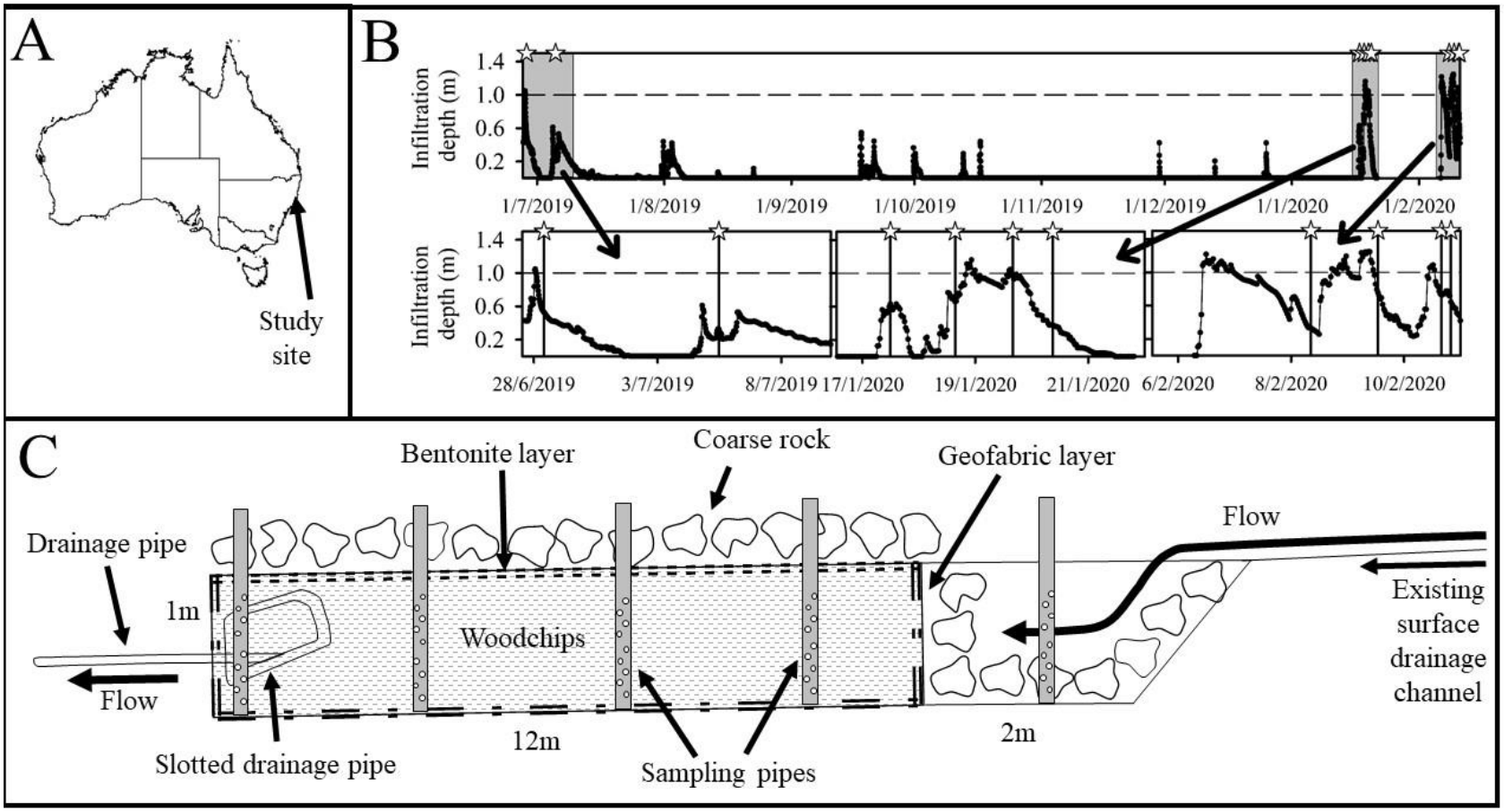

Figure 1: (A) Location of study site on the east coast of Australia (Sandy Beach, NSW). (B) Depth in the infiltration basin of the bioreactor over the 228-day sampling period. The dotted line represents 1 m depth in the infiltration basin, and values above this line indicate bioreactor overflow. Stars indicate sampling (taking ~2.5 hrs to complete) and grey areas represent highlighted periods in the plots below. (C) Theoretical longitudinal diagram of the bioreactor design.

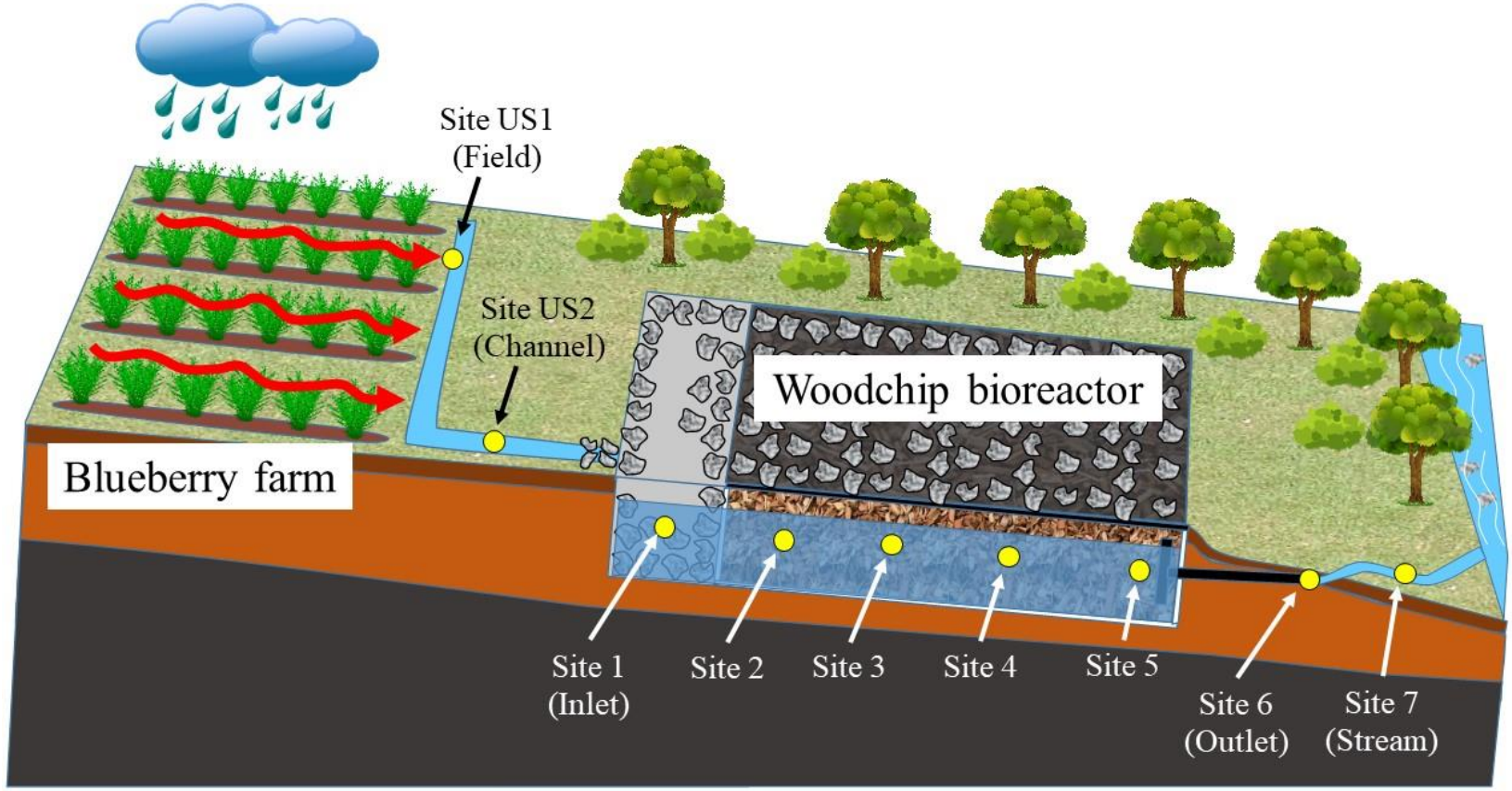

Figure 2: Conceptual diagram of sampling sites upstream, downstream and within an edge-of-field surface-flow woodchip bioreactor on an Australian east coast blueberry farm (Sandy Beach, NSW).

3.2. Sample collection

A transect of samples was taken along the bioreactor flow path (Figure 2). Sample sites were 44 m upstream of the bioreactor at the bottom of the blueberry rows (site US1), 32 m upstream of the bioreactor in an existing drainage channel (site US2), in the infiltration basin of the bioreactor (site 1), within the bioreactor at 3, 6, 9 and 12 m from the infiltration basin (sites 2, 3, 4, and 5), at the outlet of the bioreactor (site 6) and 10 m downstream of the bioreactor (site 7). During construction, 100 mm piezometer pipes were installed within the bioreactor at the designated sample points. Pumps were installed in each of the pipes to retrieve water for sampling. Our surface flow bioreactor is designed to capture surface runoff after episodic rainfall events rather than more commonly investigated continuous seepage. Therefore, samples were taken during and after rain events that created sufficient runoff over the 228 day sampling period between 28 June 2019 and 10 February 2020 (Figure 1B). Data was not collected at US1 or US2 during sample 1, sampling at these sites occurred for sample campaigns 2 to 10.

Samples of dissolved organic carbon (DOC), NH_4^+-N, NO_3^--N, orthophosphate (PO_4^{3-}-P) and greenhouse gases (N_2O, methane (CH_4) and carbon dioxide (CO_2)) were taken at each site in the transect during each sampling campaign. A multimeter (HQ40d Hach, USA) was used to measure temperature, pH and dissolved oxygen (DO), and a Global Water Co. flow probe measured water velocity exiting the bioreactor during each sampling campaign. A miniDOT oxygen sensor (Precision Measurement Engineering Inc.), with a copper mesh to avoid biofouling, was installed at the bioreactor outlet to monitor DO every 10 min. We report mean DO concentrations (mg L^{-1}) per sample campaign. Water discharge (m^3 hr^{-1}) was calculated by multiplying pipe cross-sectional wetted area by velocity. A Solinst Level logger was installed in the infiltration basin of the bioreactor to monitor water depth (cm). Bioreactor water depth was highly variable due to runoff and throughflow. Therefore, to obtain NO_3^--N removal and N_2O production rates as a function of wetted woodchip, water depth in the bioreactor was multiplied by bioreactor width and length to give wetted volume during sampling as a comparable measure of NO_3^--N removal rates (NRR).

Samples for DOC analysis were collected in polyethylene syringes and filtered into 40 mL borosilicate vials (USP Type I) using precombusted 0.7 µm GF/F filters (Whatman). Samples were stored <5°C and treated with 30 µL of H_3PO_4 before being analysed using an Aurora 1030W TOC Analyser (Thermo Fisher Scientific, ConFLo IV). NH_4^+-N, NO_3^--N and PO_4^{3-}-P

samples were filtered through 0.7 µm glass fibre syringe filters into 10 mL polyethylene vials, stored at <5°C for <5 hours before being frozen for colourimetric analysis on a Lachat Flow Injection Analyser (Wadnerkar et al., 2020b). N_2O, CH_4 and CO_2 in water were determined by collecting 50 ml of sample water in each of four 150 mL polyethylene syringes and adding 100 mL of known gas to each syringe. This creates a gas transfer headspace for water-air gradient gas transfer. Syringes were shaken for 2 min, allowing gas equilibration between the water and air in the syringes. Headspace in the syringes was transferred to 1 L Tedlar gas (Supelco company) bags. N_2O, CH_4 and CO_2 values in the air were analysed in a cavity ring-down spectrometer (Picarro G2308) (Erler et al., 2015). N_2O, CH_4 and CO_2 saturation and concentrations in water were calculated as a function of salinity and temperature from solubility constants using the difference between the known gas and the equilibrated sample (Pierrot et al., 2009; Weiss & Price, 1980; Yamamoto et al., 1976). CO_2-eq emissions are calculated using solubility equations (Yamamoto et al., 1976), as well as 20 yr and 100 yr SGWP estimations (Neubauer & Megonigal, 2015). To compare our measured results to the IPCC indirect emissions model, we use the updated default EF_5 emission factor (0.0075 kg N_2O-N kg^{-1} N, uncertainty range 0.025 to 0.0005 kg N_2O-N kg^{-1} N) (De Klein et al., 2006). Hydraulic residence time (HRT) was calculated by dividing wetted volume by discharge assuming a steady-state during sampling (~2.5 hrs).

3.3. Nitrogen removal calculations

NO_3^--N removal efficiency (NRE; % NO_3^--N removed) was calculated following Christianson et al. (2017):

$$NRE = \frac{N_{in} - N_{out}}{N_{in}} \times 100 \qquad (1)$$

where N_{in} and N_{out} are the NO_3^--N concentrations (mg NO_3^--N L^{-1}) at the inlet and outlet respectively.

NO_3^--N removal rates (NRR; g NO_3^--N m^{-3} d^{-1}) were calculated following Tsukuda et al. (2015) and Warneke et al. (2011a):

$$NRR = \frac{(N_{in} - N_{out})Q}{V_{ww}} \qquad (2)$$

where V_{ww} is the volume of wetted woodchips calculated as the average depth in the bioreactor at sampling multiplied by the length, multiplied by the width. Similar calculations

were made to estimate PO_4^{3-}-P reduction as well as DOC and N_2O production. NO_3^--N removed that was converted to N_2O, was calculated by dividing N_2O produced (g N_2O hr^{-1}) by NO_3^--N removed (g NO_3^--N hr^{-1}).

4. Results

4.1. Bioreactor hydrology

Bioreactor overflow occurred on seven occasions in the 228 day sampling period as revealed from the depth time series (Figure 1B). Overflow events occurred both during the day and night. Sampling was avoided during overflow because mixing between treated and untreated water would have biased results. The bioreactor was flowing when depth in the infiltration basin was >5 cm. Flow periods represented 15% (830 hrs) of the sampling period (5492 hrs) and overflow periods represented 4% (34 hrs) of flow periods or 0.62% of the sampling period. Water depth in the bioreactor was significantly correlated to outflow discharge ($r = 0.64$, $p < 0.05$), indicating head pressure drove outflow volumes. NO_3^--N concentrations into the bioreactor decreased as runoff increased. ($y = -0.241x + 15.38$, $r^2 = 0.818$, $p < 0.01$, $n = 10$). Hydraulic residence time (HRT) was generally low, ranging from ~2 to ~6 hours (mean 3.6±0.4 hours) (Table 1).

4.2. Nutrient removal

NO_3^--N accounted for 93 to 100% of dissolved inorganic nitrogen (DIN) when NO_3^--N was >0.94 mg L^{-1}. Therefore, we focus our interpretation on NO_3^--N. NH_4^+-N was relatively low in all sites varying between 0.01 and 0.26 mg NH_4^+-N L^{-1}. Upstream samples close to the blueberry rows were always the highest along the transect and varied between 2.9 and 23.8 mg NO_3^--N L^{-1}. Inflows into the bioreactor were slightly lower varying from 2.2 to 17.9 mg NO_3^--N L^{-1} implying some initial natural attenuation, dilution or atmospheric loss, whilst outflows from the bioreactor had concentrations between 0.5 and 17.0 mg NO_3^--N L^{-1}. The edge of field surface flow bioreactor had variable nitrogen removal efficiency (NRE) and nitrogen removal rates (NRR) in different flow conditions, antecedent conditions and HRTs (Figure 3). NRE varied from 5.1% (sample 1) to 85.2% (sample 3). NRE >50% was achieved in six of the ten sampling campaign conditions. Our NRR varied between 5.4 (sample 1) and 76.2 g NO_3^--N m^{-3} d^{-1} (sample 5), with a mean of 30.3±7.3 g NO_3^--N m^{-3} d^{-1} (n=10). Overall,

inflows and outflows from the bioreactor were 254.3±45.5 and 137.6±42.4 fold higher than the ANZECC guidelines (0.04 mg L^{-1}) for lowland rivers in eastern NSW (Australian and New Zealand Environment and Conservation Council, 2000), hereafter called ANZECC guidelines.

Though our surface flow bioreactor was primarily designed to remove N, a secondary outcome of the design was the removal of PO_4^{3-}-P. Between 19.1 (sample 3) and 70.0% (sample 4) of PO_4^{3-}-P was removed (Table 1), representing 0.48±0.19 g PO_4^{3-}-P hr^{-1} removed. Mean DOC production was 31.6±13.4 g DOC hr^{-1} ranging from 0.1 (sample 1) to 125.3 g DOC hr^{-1} (sample 5).

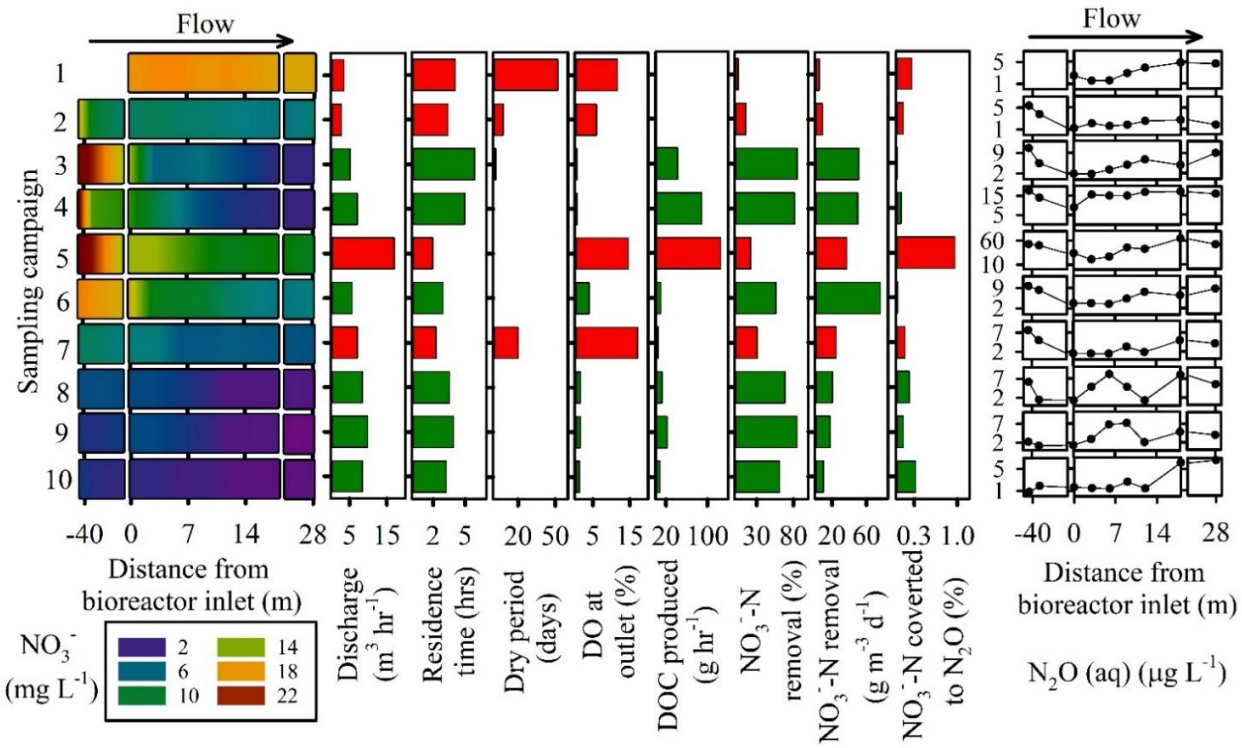

Figure 3: Results from 10 sampling campaigns along a transect in a surface-flow bioreactor, from near blueberry crops (-44 m) to the bioreactor inlet (0 m), through the bioreactor to 10 m downstream (28 m). Left: NO_3^--N concentrations along the transect. Colours are indicative of NO_3^--N concentrations. Centre: Bar plots of discharge at the bioreactor outlet; estimated hydraulic residence time (HRT) in the bioreactor; days the bioreactor had been dry for before sampling; dissolved oxygen (DO) at the outlet of the bioreactor; dissolved organic carbon (DOC) produced in the bioreactor (outlet minus inlet); NO_3^--N removal rate; and percentage of NO_3^--N removed that was estimated to be produced as N_2O. Red bars indicate sampling campaigns with <50% NO_3^--N removal efficiency and green bars indicate sampling campaigns with >50% NO_3^--N removal efficiency. Right: N_2O concentrations in water along the transect. Note the different scales for each sampling campaign.

Table 1: Results from 10 sampling campaigns along a transect in an edge-of-field surface-flow bioreactor from near blueberry crops (-44 m) to the inlet of the bioreactor (0 m) through the bioreactor to 10 m downstream (28 m). Data is from within the bioreactor constraints, not accounting for upstream or downstream samples.

Classification	Dry	Dry	$High_{inf}$	$High_{inf}$	$Peak_{inf}$	$High_{inf}$	Dry	Low_{inf}	Low_{inf}	Low_{inf}	Dry	$High_{inf}$	Low_{inf}	Total
Sample campaign	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**				
Water depth in bioreactor (cm)	29.5	20.0	62.5	70.0	96.5	34.5	32.3	62.5	79.0	57.0	27.3 ± 3.7	55.7 ± 10.8	66.2 ± 6.6	54.4 ± 7.8
Discharge (m^{-3} hr^{-1})	3.5	2.8	5.1	7.1	22.6	5.7	7.1	8.5	9.9	8.5	4.5 ± 1.3	5.9 ± 0.6	9.0 ± 0.5	8.1 ± 1.8
Residence time (hrs)	4.1	3.4	5.9	5.0	2.0	2.9	2.3	3.5	3.9	3.2	3.3 ± 0.5	4.6 ± 0.9	3.6 ± 0.2	3.6 ± 0.4
Wetted woodchip (m^3)	14.2	9.6	30.0	33.6	46.3	16.6	15.5	30.0	37.9	27.4	13.1 ± 1.8	26.7 ± 5.2	31.8 ± 3.2	26.1 ± 3.7
Temperature (°C)	18.7	17.7	27.4	27.3	28.8	27.1	24.4	25.6	25.1	22.2	20.3 ± 2.1	27.3 ± 0.1	24.3 ± 1.1	24.4 ± 1.2
Dissolved O_2 at outlet (% sat.)	11.7	5.9	0.6	0.8	14.6	3.9	17.1	1.6	1.6	1.3	11.6 ± 3.2	1.8 ± 1.1	1.5 ± 0.1	5.9 ± 2.0
DOC produced (g hr^{-1})	0.1	0.4	42.1	88.7	125.3	10.6	5.1	12.3	22.4	8.8	1.9 ± 1.6	47.1 ± 22.7	14.5 ± 4.1	31.6 ± 13.4
Influent concentration (mg NO_3^--N L^{-1})	17.9	8.3	14.7	12.1	14.6	16.5	7.4	4.4	3.4	2.2	11.2 ± 3.4	14.4 ± 1.3	3.3 ± 0.6	10.2 ± 1.8
Δ NO_3^--N bioreactor inlet to outlet (mg L^{-1})	0.9	1.3	12.5	9.9	3.2	9.3	2.3	3.0	2.9	1.4	1.5 ± 0.4	10.6 ± 1.0	2.4 ± 0.5	4.7 ± 1.3
NO_3^--N removed (g hr^{-1})	3.2	3.6	63.9	70.1	72.1	52.6	16.1	25.6	28.4	11.7	7.6 ± 4.2	62.2 ± 5.1	21.9 ± 5.2	34.7 ± 8.7
NO_3^--N reduction in bioreactor (%)	5.1	15.2	85.2	81.7	21.8	56.3	30.6	68.6	84.9	61.2	17.0 ± 7.4	74.4 ± 9.1	71.6 ± 7.0	51.1 ± 9.6
NO_3^--N removal (g m^{-3} wetted woodchip d^{-1})	5.4	8.9	51.1	50.1	37.4	76.2	25.0	20.5	18.0	10.2	13.1 ± 6.0	59.1 ± 8.5	16.2 ± 3.1	30.3 ± 7.3
N_2O produced in bioreactor (mg hr^{-1})	8.2	4.2	14.8	58.2	695.0	15.2	23.6	55.5	34.3	37.5	12.0 ± 5.9	29.4 ± 14.4	42.4 ± 6.6	94.6 ± 67.0
N_2O production (mg m^{-3} wetted woodchip d^{-1})	13.8	10.5	11.9	41.6	360.1	22.1	36.6	44.4	21.7	1.4	20.3 ± 8.2	25.2 ± 8.7	22.5 ± 12.4	56.4 ± 34.0
NO_3^--N removed produced as N_2O (*r* N_2O %)	0.26	0.12	0.02	0.08	0.96	0.03	0.15	0.22	0.12	0.32	0.17 ± 0.04	0.05 ± 0.02	0.22 ± 0.06	0.23 ± 0.09
PO_4^{3-}-P removed (mg hr^{-1})	187.5	186.6	183.8	1555.0	1628.6	84.8	381.7	101.8	197.9	288.4	251.9 ± 64.9	607.8 ± 474.4	196.0 ± 53.9	479.6 ± 187.4
PO_4^{3-}-P load reduction (%)	57.4	67.3	19.1	70.1	51.1	21.1	69.2	22.2	27.8	47.9	64.7 ± 3.7	36.8 ± 16.7	32.6 ± 7.8	45.3 ± 6.6

The contrasting conditions during our surveys allow us to group the sampling periods into Dry (bioreactor had been dry for 8 - 52 days; samples 1, 2 and 7), $Peak_{inf}$, (bioreactor flows were >20 m^{-3} hr^{-1}; sample 5; <1% of a year), $High_{inf}$ (bioreactor had been dry for <4 days and inflows were >12 mg NO_3^--N L^{-1}; samples 3, 4 and 6) and Low_{inf} (bioreactor had been dry for <4 days and inflows were <4.5 mg NO_3^--N L^{-1}; samples 8, 9 and 10).

Dry samples were characterised by low DOC production (1.9±1.6 g hr^{-1}) and high dissolved oxygen (DO) at the bioreactor outlet (11.6±3.2% sat.) (Figure 4). Consequently, NRE in the Dry samples was only 17.0±7.4% and NRR was the lowest observed (13.1±6.0 g NO_3^--N m^{-3}). During sample 1, 2 and 7, the bioreactor had been dry for 52, 8 and 20 days, respectively. Mean inflows and outflows in the bioreactor were 281.1±83.9 and 243.9±91.8 fold over the ANZECC guidelines, respectively.

Rainfall prior to $Peak_{inf}$ (sample 5) was 136 mm within 3 hrs. After this event, the bioreactor was overflowing the evening before sampling. In the morning of sampling, the sample was taken once the bioreactor had stopped overflowing, where the depth was 3.5 cm below the bioreactor capacity creating significant head pressure and driving extreme flow rates an order of magnitude higher than the other nine samples. $Peak_{inf}$ sample had very high DOC production (125.3 g DOC hr^{-1}), though DO at the outlet was 14.6%, indicating sub-ideal conditions for complete denitrification. Inflows and outflows in the bioreactor during $Peak_{inf}$ were 365.3 and 285.7 fold over the ANZECC guidelines, respectively.

$High_{inf}$ samples showed higher NO_3^--N inflows (14.4±1.3 mg NO_3^--N L^{-1}), NRE (74.4±9.1%) and NRR (59.1±8.5 g NO_3^--N m^{-3} hr^{-1}) than Low_{inf} and Dry samples. These high rates of NRE and NRR are attributable to optimum denitrification conditions, where DOC production was high (47.1±22.7 g hr^{-1}), DO was low (1.8±1.1%), and HRTs were highest (4.6±0.9 hours). The Low_{inf} samples (samples 8, 9 and 10) were taken after large rain events where the bioreactor had been overflowing periodically in the days prior and the catchment had likely been flushed of much of the labile NO_3^--N. Inflows of NO_3^--N were 3.3±0.6 mg NO_3^--N L^{-1} and were ~3 fold lower than the mean inflows of all samples. NRE was high (71.6±7.0%) during these samples. Due to lower NO_3^--N inflows, the NRR was 16.2±3.1 g NO_3^--N m^{-3} hr^{-1}, though the high NRE indicated that these are ideal conditions for this bioreactor to be operating. During the $High_{inf}$ samples, mean inflows and outflows in the bioreactor were 361.2±31.7 and 96.8±41.9 fold over the ANZECC guidelines, and the mean Low_{inf} samples were 83.5±15.6 and 23.0±6.3 fold over the ANZECC guidelines, respectively.

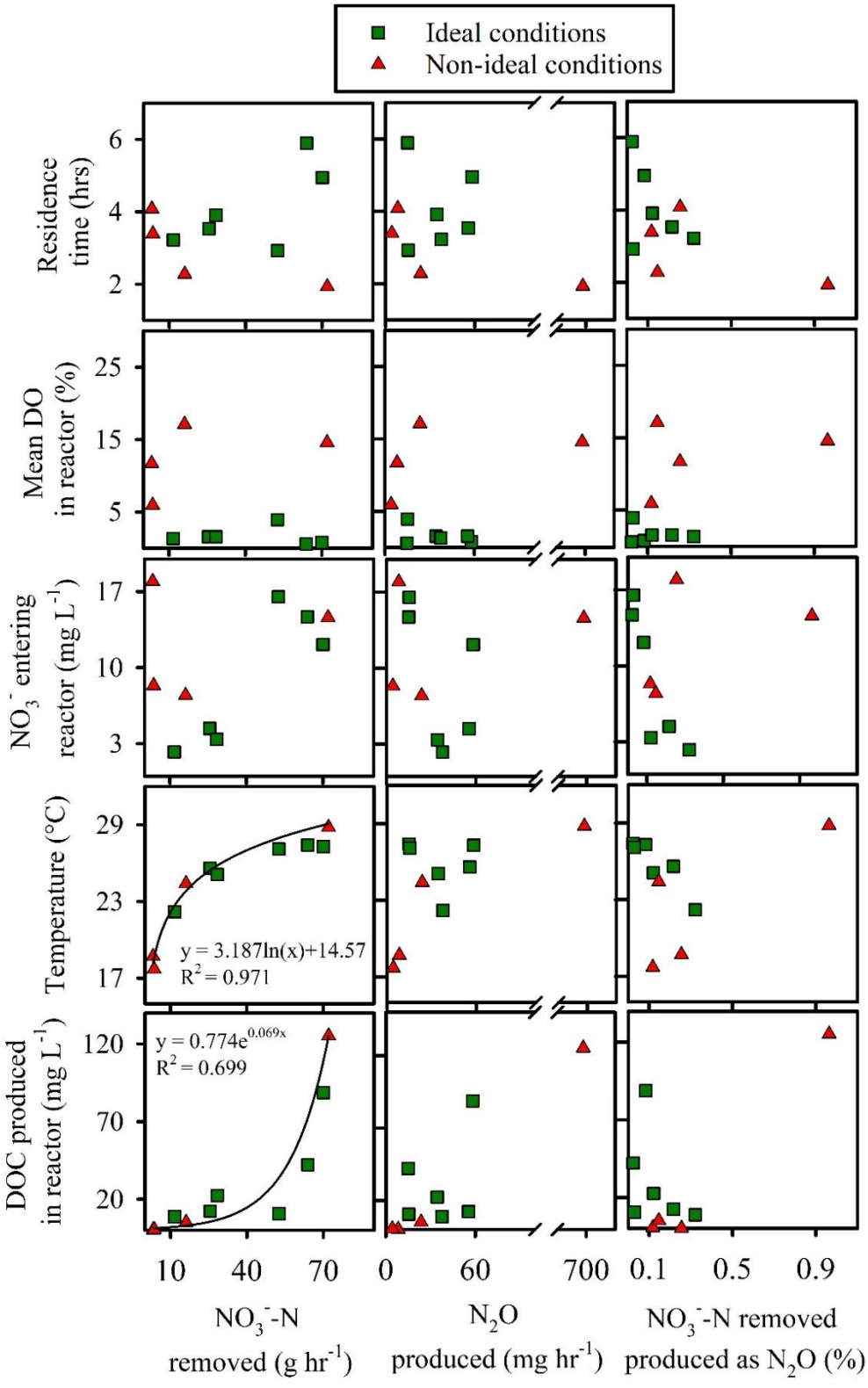

Figure 4: Data plots of results from 10 sampling campaigns in an edge-of-field surface-flow bioreactor near blueberry crops. Red triangles indicate sampling campaigns with <50% NO_3^--N removal efficiency (non-ideal conditions) and green squares indicate sampling campaigns with >50% NO_3^--N removal efficiency (ideal conditions).

4.3. N_2O gas production

Upstream values of N_2O close to the blueberry rows (12.6±5.3 µg $N\text{-}N_2O_{(aq)}$ L^{-1}) were within the same range as samples exiting the bioreactor (13.3±6.5 µg $N\text{-}N_2O_{(aq)}$ L^{-1}), indicating that the bioreactor was not a major source of N_2O. Inlet concentrations of N_2O varied between 1.23 (sample 2) and 33.73 (sample 5) µg $N\text{-}N_2O_{(aq)}$ L^{-1} and outlet concentrations varied between 2.72 (sample 2) and 64.45 (sample 5) µg $N\text{-}N_2O_{(aq)}$ L^{-1}. N_2O production in the bioreactor (outlet minus inlet) was highest in sample 5 (695 mg $N\text{-}N_2O_{(aq)}$ hr^{-1}), an order of magnitude higher than N_2O production in the other nine samples (27.9±6.6 mg $N\text{-}N_2O_{(aq)}$ hr^{-1}). This survey had a higher flow rate (22.6 m^{-3} hr^{-1}) than the other nine surveys (6.5±0.8 m^{-3} hr^{-1}). Sample 5 was also almost an order of magnitude higher when calculating NO_3^--N removed converted to N_2O (0.96%) than the other nine samples (0.15±0.03%).

Our N_2O CO_2-eq 20yr potential emissions show large variations between sites (upstream and downstream of the bioreactor) as well as between sampling events (Figure 5). We omit samples taken inside the bioreactor from this analysis because these sample locations are not exposed to the atmosphere and do not apply to emission analysis. We report data from open to air sites, i.e. Field - site US1 at the bottom of blueberry rows, Channel - site US2 in the drainage channel between the field and the bioreactor, Inlet - site 1 in the bioreactor infiltration zone, Outlet - site 6 at the outlet of the bioreactor and Stream - site 7 located 10 m downstream of the bioreactor in a forested natural drainage channel. Our mean N_2O contributions to total CO_2-eq emissions from all open to air sites were 19.5±7.9% (189.1±42.8 g CO_2-eq emissions d^{-1}), 32.8±7.9% (572.9±77.2 g CO_2-eq emissions d^{-1}), 16.8±5.1% (288.7±85.3 g CO_2-eq emissions day^{-1}) and 69.9±8.4% (11970.6±1168.3 g CO_2-eq emissions d^{-1}), in Dry, $High_{inf}$, Low_{inf} and $Peak_{inf}$ respectively. CH_4 CO_2-eq contribution was negligible across all open to air sites, with the highest contribution of 0.04% at the bioreactor outlet during the Dry samples.

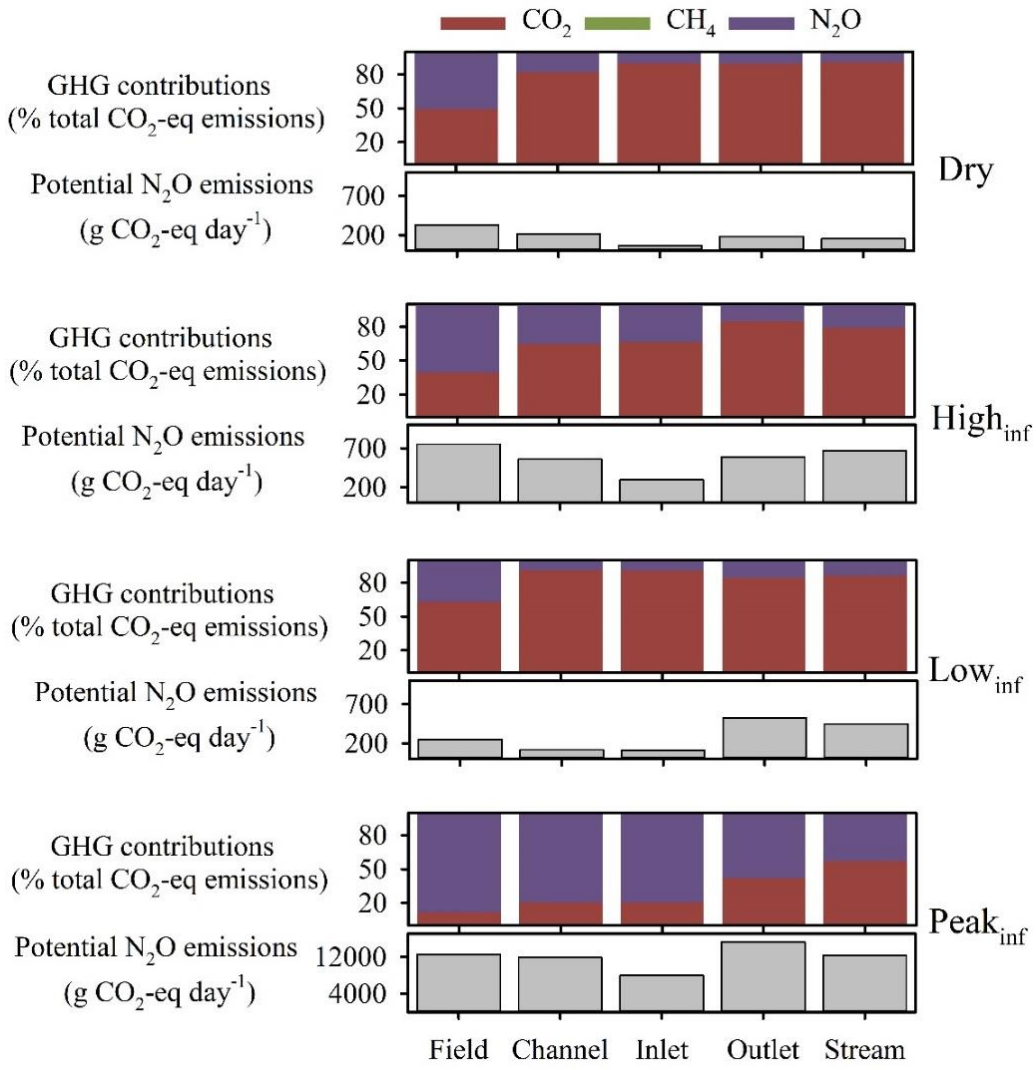

Figure 5: Calculated potential CO_2-eq N_2O emissions across the sampling period at open channel sites on 20 year sustained global warming potential timescales and the percentage contribution to total CO_2-eq emissions per greenhouse gas (N_2O, CH_4 and CO_2) determined using Neubauer and Megonigal (2015). Classifications are based on Dry (samples 1, 2 and 7), $High_{inf}$ (samples 3, 4 and 6) $Peak_{inf}$ (sample 5) and low_{inf} (samples 8, 9 and 10). Sites are depicted as Field (Site US1 at the bottom of blueberry rows), Channel (site US2 in the drainage channel between the field and the bioreactor), Inlet (site 1 in the bioreactor infiltration zone), Outlet (site 6 at the outlet of the bioreactor) and Stream (site 7 located 10 m downstream of the bioreactor in a forested natural drainage channel). Note the scale change in $Peak_{inf}$ potential N_2O emissions. Maximum CH_4 emissions were 16.5 g CO_2-eq d^{-1} and are not visible in the plot.

5. Discussion

5.1. Nitrate removal

Our surface flow bioreactor is unique because it captures episodic runoff from rainfall rather than just constant irrigation flows. Nitrate removal efficiencies (NRE) reaching ~75% are commonly reported in the literature (Christianson et al., 2012a; Lepine et al., 2020), though removal efficiencies can be highly variable in different situations. Removal rates as low as 3% (David et al., 2016) in a tile draining open-to-air bioreactor and as high as 99% in laboratory-scale enclosed reactors (Damaraju et al., 2015) and a below-ground pastoral bed reactor (Rivas et al., 2020) have been observed. The samples taken during $High_{inf}$ (samples 3, 4 and 6) and Low_{inf} (samples 8, 9 and 10) were indicative of ideal conditions of this bioreactor operation reaching 73.0±10.4% of NO_3^--N inflows, indicating that future bioreactor designs and modifications should aim to simulate the conditions observed during these campaigns.

Our nitrate removal rates (NRR) varied between 5.4 and 76.2 g NO_3^--N m^{-3} wetted woodchip d^{-1} with a mean of 30.3±7.3 g NO_3^--N m^{-3} wetted woodchip d^{-1}, and our upper NRR is in the upper limits of NRRs reported in the literature. NRR between 2 and 20 g NO_3^--N m^{-3} are commonly reported in tile-drained fed underground bed bioreactors (Gottschall et al., 2016; Hassanpour et al., 2017). However, NRR of 0.56 g N m^{-3} d^{-1} from a 25.3 m^3 bioreactor with low N influent in Virginia, USA (Bock et al., 2018) up to 79.3 g N m^{-3} d^{-1} from a 30 m^3 pasture tile drain bioreactor in New Zealand (Goeller et al., 2019) have been reported in recent years.

Our low NRE and NRR during Dry sample campaigns are possibly due low DOC and high DO. The combined effects of a depleted denitrifier community during the Dry period, low DOC and available oxygen as an electron acceptor may have reduced the capacity of the denitrifier community to remove NO_3^--N. Denitrifiers can be negatively influenced by drying events. Moisture provides microorganisms with increased liquid diffusion capacity and the ability to access NO_3^--N and soluble carbon (Blagodatsky & Smith, 2012). As the bioreactor had been active for >1 year, labile and available DOC commonly seen in the start-up phases of bioreactors had been flushed, so essentially, our bioreactor goes through re-start phases

after each dry event, when high biological oxygen demand, lack of available DOC and aerobic conditions may reduce NRE (Hellman et al., 2020; Schmidt & Clark, 2012).

The $Peak_{inf}$ sample showed the highest NRR (72.1 g NO_3^--N m^{-3} hr^{-1}); however, the NRE was 21.8%, and conditions during this sample were considered to be sub-ideal. The high flow rates and high DO contributed to low NRE. Even though there was a high NRR, the untreated mass of NO_3^--N lost to the stream was likely high. High-intensity episodic rainfall events occur in eastern Australia, rather than the seasonal rainfall expected in northern hemisphere temperate regions (Dey et al., 2019). The current projection for future rainfall with climate change indicates that, overall, yearly rainfall will decrease and short extreme intensity rainfall events will become more common in subtropical eastern Australia (Dey et al., 2019).

Results indicate the woodchip bioreactor, with proposed modifications is an effective denitrifying tool. However, wastewater still exceeds the ANZECC water quality guidelines for discharge into waterways by ~138 fold overall. Additional management tools, such as reduction of fertiliser use and incorporation of other reduction techniques, are required to improve water quality to meet ANZECC guidelines.

5.2. N_2O production and implications to greenhouse gas emissions

Previous investigations have examined NO_3^- to N_2O pollution swapping in bioreactors report between 0.003 and 9.7% of removed NO_3^- is converted to N_2O (rN_2O) (David et al., 2016; Elgood et al., 2010; Feyereisen et al., 2016; Greenan et al., 2009; Moorman et al., 2010). The IPCC default EF_5, which is the emission factor expected for indirect N_2O emissions from waterways downstream of agricultural nitrogen sources, is currently set at 0.75% (Syakila & Kroeze, 2011). If emissions from a bioreactor are above 0.75% of NO_3^--N converted to N_2O, we have evidence of pollution swapping.

In our sample transects, pollution swapping (rN_2O >0.75%) only occurred during sample 5 when HRT was only 2.0 hours. Our bioreactor produced a rN_2O of 0.17±0.04%, 0.05±0.02% and 0.22±0.06% in Dry (3.3±0.5 hrs HRT), $High_{inf}$ (4.6±0.9 hrs HRT) and Low_{inf} (3.6±0.2 hrs HRT) respectively. The $Peak_{inf}$ sample generated a rN_2O of 0.96%, which is evidence of pollution swapping. Incomplete denitrification and low HRT (2.05 hr) was likely the source of increased N_2O production; however, it should be noted that this condition would only be expected <1% of the year when the bioreactor is at full capacity or overflowing. Overall, the bioreactor reduced N_2O pollution that would naturally occur from streams and waterways,

with a *r*N_2O mean of 0.23±0.09%. Our *r*N_2O percentage is below much of the literature. *r*N_2O values of 9.7% (Feyereisen et al., 2016) and 0.49 to 3.48% (Warneke et al., 2011b) from laboratory scale (0.009 and 0.2 m^3 respectively) woodchip bioreactors, 1 to 6% from a field woodchip bioreactor (250 to 1250 m^3) treating aquaculture effluent (Aalto et al., 2020), 0 to 1.5% from a field bioreactor (78 m^3) under pasture (Rivas et al., 2020) and 0.35 to 5.19% in experimental (68 m^3) bioreactors with three HRTs (Davis et al., 2019) have been previously observed. Our bioreactor did not show evidence of pollution swapping, as our overall mean *r*N_2O was ~3.3 fold lower than the expected 0.75% IPCC default EF_5.

N_2O fluxes were highly variable depending on conditions, calculated using similar methods to White et al. (2018a) and Reading et al. (2020). Mean N_2O fluxes across all conditions were 4.3% higher at the bioreactor outlet than the field site, though there was high variability in conditions, i.e. the field site was 46.1% and 31.3% higher than the bioreactor outlet during Dry and $High_{inf}$ conditions; however, the bioreactor outlet was 21.9% and 9.4% higher than the Field site during Low_{inf} and $Peak_{inf}$ conditions. N_2O fluxes in the field site (Figure 2) were 845.9±142.3, 1234.7±517.4, 1580.7±1266.1 and 17990.2 µmol m^{-2} d^{-1} in Dry, $High_{inf}$, Low_{inf} and $Peak_{inf}$ respectively, whilst N_2O fluxes in the field site were 456.1±12.0, 847.8±356.0, 2024.0±1260.6 and 19855.5 µmol m^{-2} d^{-1} in Dry, $High_{inf}$, Low_{inf} and $Peak_{inf}$ respectively. Overall mean N_2O fluxes were 3.1±1.9 mmol m^{-2} d^{-1} at the field site and 3.3±2.1 mmol m^{-2} d^{-1} at the bioreactor outlet. Schipper et al. (2010) reported that N_2O fluxes were ~6 fold higher in the bioreactor than in a nearby pasture, highlighting that under certain circumstances, bioreactors may be a significant source of N_2O to the atmosphere. However, this does not appear to be the case in our study, as overall N_2O fluxes from the field site were similar to N_2O fluxes from the bioreactor outlet.

Here, we calculate SGWP on 20-year timescales and put N_2O emissions in perspective to the other GHGs, CO_2 and CH_4. SGWP is the preferred radiative forcing estimation, rather than global warming potential (GWP). GWP considers emissions as a one-time pulse of a GHG, whereas SGWP assumes that the emission contributes to sustained warming potential on a 20-year timescale (Myhre et al., 2013). On a global scale, 6.2% of the annual CO_2-eq anthropogenic GHGs is estimated to come from N_2O (Pachauri et al., 2014). Across all our sampling campaigns, mean N_2O emissions contributions to total CO_2-eq emissions from the field site (59.1±11.0%) and the bioreactor inlet (33.1±16.6%) were ~2.4 and ~1.3 fold higher than the outlet (24.7±11.2%) respectively. These contributions are far higher than the expected 6.2% N_2O contribution in natural streams surrounding agriculture (Pachauri et al.,

2014). The $Peak_{inf}$ sample contained the highest N_2O CO_2-eq contribution of 88.6%. These high potential CO_2-eq emissions of N_2O during the $Peak_{inf}$ are influenced by extremely high flow situations that drive bioreactor overflow events during <1% of the year. Mean N_2O CO_2-eq emissions at the outlet of the bioreactor (431.9±125.4 g CO_2-eq emissions day^{-1}) and the Field site (443.1±156.9 g CO_2-eq emissions day^{-1}) were similar, indicating that the bioreactor did not contribute higher N_2O emissions than what naturally occurs if the bioreactor was absent.

5.3. Drivers of denitrification

Due to the lack of NH_4^+-N production in our bioreactor, we suggest that heterotrophic denitrification is the primary NO_3^--N reduction mechanism (Schipper et al., 2010), though we acknowledge that dissimilatory nitrate reduction to ammonium (DNRA), N immobilisation into organic matter and anammox may also be occurring (Burgin & Hamilton, 2007). Any microbial process that out-competes denitrifiers for available carbon can potentially reduce NRR. Available oxygen may give aerobes the competitive advantage over denitrifiers for available carbon, as may have occurred in surveys 1, 2 and 7, when we observed low DOC production and DO at the bioreactor outlet was 5.9 to 17.1% (Rivett et al., 2008). Higher DO at the bioreactor outlet may be due to low HRT, high flow rates, the variability of flow rates and episodic nature of the surface runoff in our bioreactor. DO in bioreactors can be depleted in as little as ~1 h in both laboratory and field bioreactor tests, (Robertson, 2010; Robertson et al., 2009), however, our bioreactor did not always achieve DO saturations <5% sat (Figure 4). Our bioreactor reduced DO by 97.5±0.8% from inlet to outlet in sample campaigns with >50% NO_3^--N removal efficiency but only 81.0±5.9% in sample campaigns with <50% NO_3^--N removal efficiency. This suggests that there was available oxygen for aerobes to utilise available C, possibly reducing denitrification capacity and NRR.

Water temperature exiting the subtropical bioreactor (24.4±1.2 °C) was higher than reported from bioreactors in the literature, dominantly in temperate America (~4 to ~20 °C), contributing to increased NRR in our study (Addy et al., 2016). Of the campaigns with >50% NO_3^--N reduction, the average temperature was 25.7±0.8 °C (Figure 4). Temperature increases have a positive influence on denitrification rates (Addy et al., 2016; Dawson & Murphy, 1972). We saw a significant logarithmic correlation between temperature and NO_3^--N removal in g hr^{-1} (R^2 = 0.97, p <0.001) as well as between temperature and NRR (R^2 =

0.80, p <0.01). Q_{10} is the factorial increase in NRR for every 10 °C increase in temperature. Q_{10} is a valid expression only when NO_3^--N is always available and is not a limiting factor (Davidson & Janssens, 2006), and caution is advised when NO_3^--N concentrations are low (Ghane et al., 2015). Various Q_{10} factors have been reported throughout the literature. For example, Q_{10} values of 1.3 - 1.4 between 9.6 and 23.9 °C (Bock et al., 2015), 0.8 - 5.7 between ~1 and ~20 °C (Christianson et al., 2012a), 2.0 between 17 and 24 °C (Warneke et al., 2011a), 1.2 between 16.8 and 27.1 °C (Warneke et al., 2011b) and 3.8 between 6 and 16 °C (David et al., 2016). Here, we calculated a Q_{10} value of 7.63 ($y = 0.1569e^{0.2032x}$) between 17.7 and 28.8 °C.

5.4. Nitrate removal cost-benefit analysis

We estimate the cost of removing 1 kg of NO_3^--N in a similar way to Christianson et al. (2013) and Schipper et al. (2010). We model the estimated NO_3^--N removed in the experimental period and predicted the total removal over the bioreactor lifetime. We assume that prolonged dry periods and dry-wetting cycles cause aerobic breakdown and wood-loss, and our bioreactor woodchips will likely need to be replaced every ten years, with a half-life of 5 years (Moorman et al., 2010). NO_3^--N removal is mostly a function of temperature (Q_{10}) and rainfall, allowing us to use historical climate parameters to predict annual nitrate removal.

We predict NO_3^--N removal using our Q_{10}, and limit model NO_3^--N removal using our NO_3^--N and runoff correlation. Our model was unable to estimate runoff NO_3^--N concentrations above 65 mm m^{-2} d^{-1}, which only occurred once during our modelling period (70.2 mm m^{-2} d^{-1}), and we instead used the upper limit of 65 mm m^{-2} d^{-1}. We use available rainfall-runoff data from the AWRA-L model and temperature data (Australian Bureau of Meteorology, 2020a) (Australian Bureau of Meteorology, 2020b) during the sampling period as model inputs. Our model estimates agree with our measured results during our sampling period (Figure 6; R^2 = 0.9, p <0.001). Based on the assumption that previous climate conditions in the past five years can be considered similar to climate conditions in the next ten years, we estimate NO_3^--N removal over the bioreactor lifetime below.

The cost to install the bioreactor was AUS$6500, incorporating construction, labour, delivery of woodchip, delivery of rock, excavator use, and incidental expenses. However, this estimate excludes design, project conception and research. The estimated total NO_3^--N removal from

the bioreactor based on our *in-situ* measured Q_{10}, current climatic conditions and the expected lifetime of the bioreactor (10 years) was 36.4 kg NO_3^--N yr^{-1}, representing a cost of AUS$17.83 for each kg NO_3^--N removed.

To put those values in perspective, we compare the bioreactor costs to the cost of applying fertilisers. We estimate the cost of fertiliser application based on calculations after Rose (2004), nitrogen contents in White et al. (2020), assumed fertilisation rates of 121 kg N $ha\ yr^{-1}$ (Doughty et al., 1988; Ireland & Wilk, 2006) and estimated fertiliser prices of calcium nitrate (AUS$600 tonne, 13% N, AUS$558.50 $ha\ yr^{-1}$), urea (AUS$600 tonne, 44% N, AUS$165 $ha\ yr^{-1}$), di-ammonium phosphate (AUS$700 tonne, 18% N, AUS$470.60 $ha\ yr^{-1}$), mono-ammonium phosphate (AUS$700 tonne, 12% N, AUS$705.80 $ha\ yr^{-1}$) and ammonium sulphate (AUS$500 tonne, 21% N, AUS$288.1 $ha\ yr^{-1}$). While we do not have data on the recipes applied on this or other farms, we assume that a combination of these fertilisers is used and, therefore, use the mean cost of application (AUS$437.60 $ha\ yr^{-1}$, AUS$3.60 kg N). Using these assumptions, the cost to remove 1 kg of N via the bioreactor is about five times higher than the fertiliser application cost. Therefore, while the bioreactor represents a new tool to minimize effluent NO_3^--N, better on-farm fertiliser management is likely to provide better value for money to prevent nitrogen pollution in waterways. However, even with best management practice, 100% fertiliser use efficiency is unlikely to be achieved, and NO_3^--N losses are commonly reported from 10 to 50% of applied fertiliser in horticulture (Cameron et al., 2013). Thus, some nitrogen losses to the atmosphere, groundwater and surface water will likely continue (Jayasundara et al., 2007; Majumdar et al., 2013). Hence, a suite of management practices, including better on-farm fertiliser management, increased fertiliser use efficiency as well as loss prevention devices, such as bioreactors, is recommended.

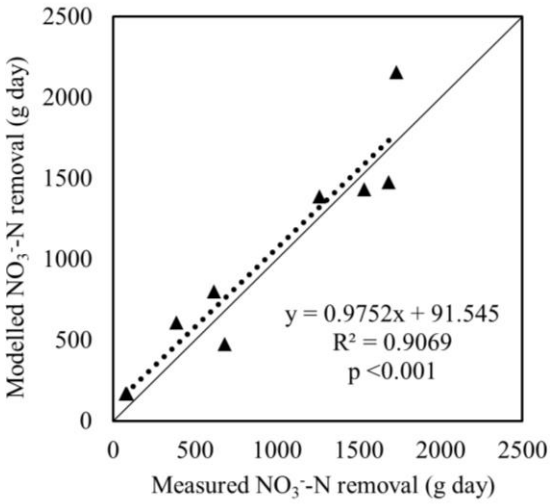

Figure 6: Plot of modelled and measured NO_3^--N removal based on climatic data (Australian Bureau of Meteorology, 2020a, 2020b). The black diagonal line indicates a 1:1 relationship between model and measured results. The relationship between model and measured results (dotted line) indicates a good calibration ($p < 0.001$).

Based on our modelled results using current climatic conditions over the past five years, we estimate that 32.6 kg NO_3^--N ha^{-1} yr^{-1} is lost via surface runoff at this site, representing 27.2% of applied nitrogen fertiliser lost via surface runoff (Doughty et al., 1988; Ireland & Wilk, 2006). Data on the amount or timing of fertilisers is not available; therefore, we assume that adherence to industry fertiliser application recommendations occurs. Our modelled NO_3^--N loss rates are similar to calculations during previous investigations in this catchment (14%; White et al. (2018a) and 18% White et al. (2020)) based on in-stream denitrification processes. These previous studies used observations further from the blueberry farms, and instream processes likely attenuated N loads more than this study, with samples taken before water entered the creek. Natural cycling of nitrogen and the transformational role of soil bacteria dictate that 100% plant uptake of applied fertiliser is unlikely to be achieved in field studies. Hence, some fertiliser loss, even in best management practice, is still likely to occur. When the bioreactor is overflowing during heavy rain events, untreated water bypasses the bioreactor and contributes to overall NO_3^--N losses. However, as this scenario is expected <1% of the year, the bioreactor's overall benefits on an annual scale are still significant. We estimate that under current climate conditions, 9.9 kg NO_3^--N ha^{-1} yr^{-1} is removed via the bioreactor from runoff, representing an overall 30.3% NO_3^--N removal rate when incorporating all flow and overflow events.

6. Implications

Our observed experimental bioreactor conditions were not always conducive to complete denitrification or high NRE; therefore, we recommend modifications to the current design to

improve the overall denitrification capacity. We also recommend increased efforts to reduce existing NO_3^- concentrations in fertigated water and associated watering regimes, especially prior to prolonged or intense rain events. The efficiencies and costs of further nutrient management methodologies recommended here are not assessed in detail; however, each approach is likely to be site-specific.

In the setting of our bioreactor, under current climate change projections, we expect that high-intensity rainfall events will become more common (Dey et al., 2019). Thus, the ability to treat large volumes of water within a short period with limited land availability (without encroaching on productive land) presents challenges. During the $Peak_{inf}$ sample, and during bioreactor overflow, the greatest mass of NO_3^--N is presumed to be transported via flow, thus representing the greatest loss to downstream aquatic habitats. Our NRR during $Peak_{inf}$ (37.4 g NO_3^--N m^{-3} d^{-1}) was higher than commonly reported elsewhere, though far lower than the NRR during $High_{inf}$ samples (59.1±8.5 g NO_3^--N m^{-3} d^{-1}). Suggesting flow rates may be a significant component in NRR due to DO's influence on the denitrification process.

We suggest that land-use strategies that aim to attenuate water flow during high flow events should be encouraged, to increase denitrification, and also reduce rN_2O and CO_2-eq emissions from the bioreactor. Strategically placed contour banks and riparian zones within on-farm flow paths may provide an interception point for nitrogen uptake, whilst also attenuating flow rates in high-intensity rain events. Improved land-use planning may provide better nutrient management outcomes, such as locations and orientation of crops, the addition of water retention ponds and altered water flow paths, to better account for nutrient capture and retention. Provided upstream land space is not restricted and harvestable rights are not infringed, sequential hydraulic stormwater retention ponds that remain empty during dry periods and fill during high flow periods may attenuate high flows into the bioreactor, likely driving greater NRR and reduced rN_2O. In our specific case, upstream land space is restricted. Thus, possible solutions may be to periodically wet the bioreactor with fertigation water to increase DOC availability and increase the bioreactor's infiltration zone to allow more untreated water storage to attenuate high flows.

Our bioreactor was ~50 m upstream of the nearby creek and water travelled through a forested section of the drainage ditch before entering the creek. Low DO water can have negative impacts on downstream aquatic habitats. Mean DO at the outlet of the bioreactor was 6.44±2.04% sat. and mean DO at site 7, 10 m downstream of the bioreactor, was

34.92±2.11% sat., indicating that as water travels downstream and is exposed to atmospheric air, oxygen partial pressures have the opportunity to equilibrate and increase by ~3% per metre until reaching the stream. Therefore, if no other DO raising measures are implemented (e.g. cascade aeration), we suspect that >30 m between the bioreactor outlet and the nearby creek is needed to increase DO in outlet water to within guideline values (85 -110% DO sat.) (Australian and New Zealand Environment and Conservation Council, 2000). Therefore, this suggests that our ~50 m distance is sufficient to avoid low DO effluent entering the nearby creek, and a suitably long exit flow pathway should be included as a design feature for future bioreactor deployment.

Fertigation reduction strategies, such as fertigation recipe adjustments to better suit the needs of the crop on short timescales (1 week to 1 month), can reduce excess nitrogen storage in soils. Agricultural soils store between 68 and 191 g ha^{-1} day^{-1} (Van Meter et al., 2016; Worrall et al., 2015), and this stored nitrogen can be flushed via overland flow or groundwater seepage during rain events for years to decades after the cessation of agricultural activities (Grimvall et al., 2000; McCrackin et al., 2017; Santos et al., 2017). Emphasis on coupling crop needs to climatic conditions should be further investigated. Improved fertigation recipes that aim to reduce NO_3^- loss, and fertigation reduction before large rain events, particularly when soil moisture is high (White et al., 2020), should be implemented as a part of the nutrient management strategy suite.

DOC appeared to be a limiting factor for denitrification after Dry events upon re-start of the bioreactor. If the bioreactor was wetted periodically, such as when the plants in the field are fertigated (approximately bi-weekly), the dry-wetting cycles could be reduced and the woodchips would remain mostly saturated. This measure would enhance available DOC for denitrification and reduce the impact of dry-wetting cycles on bioreactor lifetime (Moorman et al., 2010). The cost associated with this change would likely be <AUS$2000. The infrastructure of fertigation is already in place and requires only extending a pipe ~50 m from the growing field to the bioreactor, feeding into a network of drip irrigation lines. An added benefit of this recommendation is that the fertigation water contains NO_3^--N, which could also provide a nutrient source to the denitrifying bacteria and sustain the bacterial community in dry periods, ready to be re-energised when the bioreactor next fills from natural rainfall. The bioreactor could be trickle fed from the top down (within the profile of the bioreactor), using a network of drip irrigation lines, similar to those already in use in the field. Overall, this enables the full capacity of the woodchips to be wetted and prevent periodic drying.

7. Conclusions

Our bioreactor is the first of its kind in Australia, with vastly different climatic, soil and crop conditions, to most global bioreactor studies.

- The samples taken during ideal conditions (n=6 transects) reduced NO_3^--N export to local waterways by ~73%, while samples taken during non-ideal conditions (n=4 transects) reduced exports by ~18%.
- During ideal and non-ideal conditions respectively, mean NO_3^--N inflows to the bioreactor were ~222 and ~302 fold higher than ANZECC guidelines, whilst outflows were from the bioreactor were ~60 and ~254 fold higher than ANZECC guidelines.
- Our model indicated that 9.9 kg NO_3^--N ha^{-1} farm yr^{-1} is removed via the bioreactor, representing a 30.3% NO_3^--N removal rate when incorporating overflow events. Overall, our NO_3^--N removal rates are very high compared to the literature.
- The estimated bioreactor NO_3^--N removal was 36.4 kg NO_3^--N yr^{-1}, representing a cost of AUS$17.8 for each kg NO_3^--N removed. We estimate the cost to remove 1 kg of N via the bioreactor is about five times higher than the fertiliser application cost.
- NO_3^--N to N_2O pollution swapping did not occur in 90% of observations, with a rN_2O mean of 0.23±0.09%, compared to the IPCC expected rN_2O of 0.75%. The bioreactor did not contribute to significantly higher N_2O emissions than naturally occur in the field or waterways.

With minor design modifications, edge-of-field surface-flow bioreactors can be a cost-effective solution to reduce NO_3^--N runoff and pollution swapping. However, further studies that incorporate real-time and long-term monitoring of NO_3^--N in runoff and groundwater, as well as N_2O emissions and pollution swapping from bioreactors are needed. We strongly suggest further research of bioreactors in eastern Australia, to refine designs to function in various settings, enhancing the tools available for nutrient management to protect vital habitats such as protected aquatic habitats. Further investigation into each site-specific suite of management practices, including better on-farm fertiliser management, increased fertiliser use efficiency, and loss prevention devices, such as bioreactors, is recommended. These management options may also include methods not assessed here. We acknowledge the ongoing cooperation between researchers, farmers, industry bodies, and government authorities to improve nutrient management and retention on farms.

8. References

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9. Appendicies

Appendix 1: Raw data from 10 sampling campaigns along a transect of a surface flow bioreactor in northern NSW.

Site	Campaign	Sample date	Dissolved O_2 (% sat.)	Nitrate (mg N L^{-1})	Nitrite (mg N L^{-1})	Ammonium (mg N L^{-1})	Phosphate (mg P L^{-1})	$CO_{2\ (aq)}$ (mg L^{-1})	$CH_{4\ (aq)}$ (µg L^{-1})	$N_2O_{\ (aq)}$ (µg L^{-1})	$N_2O_{\ (aq)}$ (% sat.)	Dissolved organic carbon (mg C L^{-1})
1	1	28/06/2019 9:52	83.1	17.9	0.01	0.04	0.09	1.58	0.04	2.5	870.1	3.5
2	1		46.7	18.9	0.01	0.00	0.08	1.58	0.04	1.6	556.3	3.3
3	1		37.0	19.0	0.01	0.02	0.07	1.98	0.04	1.6	571.9	3.3
4	1		16.9	18.1	0.01	0.00	0.05	3.41	0.11	2.9	1113.9	3.3
5	1		6.0	18.6	0.01	0.05	0.04	3.12	0.40	3.9	1344.1	3.5
6	1		11.7	17.0	0.01	0.01	0.04	5.93	0.08	4.8	1694.3	3.5
7	1		37.8	17.1	0.01	0.00	0.07	4.43	0.06	4.7	1580.6	3.5
up1	2	5/07/2019 11:13	136.2	15.8	0.02	0.00	0.05	1.02	0.04	5.4	1853.7	0.0
up2	2		85.2	10.3	0.01	0.04	0.07	2.30	0.04	3.8	1286.0	6.4
1	2		87.2	8.3	0.01	0.02	0.10	3.45	0.04	1.2	422.9	4.8
2	2		31.8	9.0	0.01	0.01	0.08	5.80	0.05	2.1	724.6	5.2
3	2		22.2	8.4	0.01	0.00	0.07	8.24	0.23	1.6	550.1	5.0
4	2		12.6	8.3	0.01	0.00	0.05	5.28	0.04	1.9	642.4	5.2
5	2		5.9	7.8	0.01	0.00	0.03	6.82	0.05	2.5	856.9	5.2
6	2		11.2	7.1	0.01	0.01	0.03	2.05	0.07	2.7	927.4	4.9
7	2		47.0	8.0	0.01	0.00	0.08	2.20	0.04	1.8	608.3	4.9
up1	3	17/01/2020 11:40	92.1	23.8	0.09	0.85	0.35	0.41	0.03	10.7	4419.2	25.1
up2	3		81.1	22.5	0.01	0.08	0.13	1.63	0.03	5.5	2348.8	13.4
1	3		86.6	14.7	0.01	0.03	0.19	0.77	0.03	2.0	841.6	8.6
2	3		0.7	5.8	0.01	0.01	0.21	4.71	0.04	1.9	794.1	9.2
3	3		0.7	6.2	0.02	0.07	0.24	5.07	0.04	3.3	1387.0	10.1
4	3		0.7	6.8	0.02	0.09	0.22	6.07	0.23	5.0	2064.8	12.0
5	3		0.5	4.9	0.01	0.02	0.19	5.63	0.27	6.7	2786.5	15.9
6	3		0.6	2.2	0.02	0.00	0.15	7.82	0.34	4.9	2044.1	16.9
7	3		41.7	2.1	0.01	0.00	0.18	4.14	0.15	9.0	3763.5	19.1
up1	4	18/01/2020 15:20	76.0	23.0	0.09	0.14	0.33	2.92	0.03	17.6	7548.3	12.6
up2	4		76.6	12.9	0.04	0.00	0.31	2.35	0.03	14.0	6017.5	9.1
1	4		77.7	12.1	0.03	0.08	0.31	1.07	0.03	8.9	3672.6	7.9
2	4		1.7	9.5	0.06	0.05	0.22	2.88	0.04	15.4	6376.8	9.3
3	4		1.2	7.2	0.10	0.08	0.24	2.83	0.04	14.9	6145.1	15.8
4	4		0.7	4.6	0.09	0.03	0.11	3.98	0.05	14.9	6151.9	24.8
5	4		0.7	3.2	0.08	0.09	0.22	5.31	0.18	16.8	6933.1	28.5
6	4		0.8	2.2	0.03	0.01	0.09	5.63	0.05	17.1	7103.7	20.5
7	4		28.9	2.0	0.03	0.04	0.11	5.29	0.05	16.0	6698.0	18.9
up1	5	19/01/2020 16:00	106.7	23.2	0.26	0.10	0.18	0.91	0.03	53.1	26825.8	12.3
up2	5		60.7	22.8	0.11	0.03	0.07	1.58	0.03	50.1	24706.7	6.1
1	5		61.2	14.6	0.11	0.07	0.14	1.12	0.03	33.7	14957.4	6.0
2	5		26.5	14.7	0.21	0.08	0.13	2.60	0.04	20.9	9216.3	8.0
3	5		20.7	13.1	0.18	0.11	0.12	2.78	0.04	26.7	12643.2	9.1
4	5		11.4	11.8	0.14	0.06	0.09	3.53	0.04	45.3	21401.4	10.2
5	5		10.5	10.6	0.05	0.06	0.09	3.25	0.04	42.5	19511.3	9.5
6	5		14.6	11.4	0.14	0.05	0.07	5.35	0.17	64.5	30312.7	11.6
7	5		27.0	10.3	0.12	0.01	0.08	7.85	0.04	52.3	23452.4	11.0
up1	6	20/01/2020 8:45	113.8	19.5	0.10	0.00	0.10	0.97	0.03	9.7	4307.5	7.7
up2	6		70.2	18.4	0.03	0.03	0.07	1.89	0.03	8.3	3708.7	4.2
1	6		65.8	16.5	0.03	0.03	0.07	1.48	0.03	3.8	1626.1	4.7
2	6		6.9	10.6	0.04	0.02	0.07	2.96	0.03	3.8	1635.4	4.7
3	6		4.5	10.4	0.02	0.06	0.07	3.19	0.03	3.6	1580.8	4.8
4	6		4.0	10.2	0.04	0.05	0.06	4.12	0.05	5.3	2302.5	5.0
5	6		3.5	8.5	0.02	0.03	0.06	5.62	0.08	7.6	3128.0	4.9
6	6		3.9	7.2	0.02	0.02	0.06	5.17	0.06	6.5	2909.2	0.0
7	6		32.6	7.6	0.03	0.04	0.10	5.29	0.05	8.7	3733.5	6.5

Site	Campaign	Sample date	Dissolved O_2 (% sat.)	Nitrate (mg N L^{-1})	Nitrite (mg N L^{-1})	Ammonium (mg N L^{-1})	Phosphate (mg P L^{-1})	$CO_{2\ (aq)}$ (mg L^{-1})	$CH_{4\ (aq)}$ (µg L^{-1})	$N_2O_{\ (aq)}$ (µg L^{-1})	$N_2O_{\ (aq)}$ (% sat.)	Dissolved organic carbon (mg C L^{-1})
up1	7	8/02/2020 8:30	92.8	8.5	0.05	0.01	0.11	0.74	0.01	7.7	3206.3	9.0
up2	7		79.9	8.8	0.01	0.02	0.05	2.26	0.01	5.0	2115.3	5.7
1	7		67.9	7.4	0.02	0.02	0.08	1.48	0.01	1.6	669.4	5.6
2	7		25.1	8.0	0.01	0.02	0.05	2.50	0.01	1.5	635.7	5.1
3	7		19.3	5.2	0.01	0.02	0.06	2.62	0.03	1.5	640.6	0.0
4	7		11.1	5.2	0.02	0.01	0.04	3.98	0.21	3.3	1239.9	5.1
5	7		15.5	5.6	0.02	0.02	0.08	3.70	0.17	1.9	799.2	5.7
6	7		17.1	5.2	0.00	0.01	0.02	4.93	0.12	4.9	2060.1	6.3
7	7		28.6	4.7	0.01	0.01	0.09	4.54	0.10	4.1	1736.5	7.1
up1	8	9/02/2020 13:00	145.9	4.5	0.04	0.00	0.11	0.22	0.01	6.2	3142.5	7.5
up2	8		80.0	4.7	0.02	0.05	0.10	2.08	0.01	1.5	732.0	4.0
1	8		57.2	4.4	0.00	0.04	0.05	1.50	0.01	1.4	610.5	4.3
2	8		1.6	4.3	0.02	0.04	0.06	2.66	0.05	4.8	2121.9	4.2
3	8		2.7	3.3	0.03	0.10	0.08	3.84	0.05	8.1	3542.3	4.6
4	8		2.1	2.5	0.02	0.03	0.05	2.69	0.13	4.8	2074.5	5.0
5	8		2.6	1.2	0.01	0.00	0.05	2.62	0.20	1.4	602.7	5.1
6	8		1.6	1.4	0.03	0.03	0.04	3.36	0.05	7.9	3549.9	5.7
7	8		34.5	1.2	0.03	0.03	0.10	3.47	0.04	5.5	2450.1	5.5
up1	9	10/02/2020 16:00	95.6	2.9	0.03	0.02	0.14	1.35	0.01	2.2	1058.2	5.2
up2	9		80.1	2.8	0.01	0.02	0.05	1.20	0.01	1.2	606.1	4.8
1	9		67.3	3.4	0.03	0.05	0.07	1.47	0.01	1.4	627.2	4.5
2	9		1.8	3.2	0.03	0.05	0.08	2.23	0.02	3.0	1398.8	5.6
3	9		2.1	4.0	0.04	0.16	0.09	2.47	0.08	6.7	3108.5	5.2
4	9		2.4	2.2	0.02	0.04	0.07	3.15	0.13	7.1	3182.2	5.6
5	9		1.0	0.9	0.02	0.05	0.09	3.77	0.58	2.1	918.2	5.7
6	9		1.6	0.5	0.02	0.05	0.05	4.11	0.10	4.8	2172.7	6.8
7	9		40.8	0.4	0.02	0.05	0.07	3.30	0.06	4.0	1785.9	6.1
up1	10	10/02/2020 19:20	46.1	3.5	0.04	0.02	0.05	1.60	0.04	0.8	328.9	8.2
up2	10		65.9	2.6	0.01	0.04	0.06	1.96	0.04	1.9	784.0	5.7
1	10		71.7	2.2	0.01	0.03	0.07	1.48	0.03	1.6	683.8	5.3
2	10		1.8	2.4	0.01	0.07	0.07	1.82	0.03	1.5	617.1	5.3
3	10		1.2	1.7	0.02	0.10	0.09	2.37	0.08	1.4	579.0	4.9
4	10		1.4	1.9	0.02	0.08	0.06	2.43	0.16	2.6	1087.4	4.9
5	10		1.3	1.1	0.02	0.06	0.09	3.34	0.52	1.4	588.1	5.3
6	10		1.3	0.9	0.03	0.02	0.04	4.07	0.09	6.1	2513.4	6.4
7	10		30.3	1.0	0.02	0.01	0.07	4.78	0.12	6.6	2757.8	6.6