Processes of nutrient removal in riparian zones in sandy soils

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Executive Summary

The Ellen Brook catchment is a major contributor of nutrients to the Swan Canning river system and the use of riparian vegetation has been identified as a potential best management practice (BMP) to reduce this nutrient input. A previous report by O'Toole *et al.* 2013 highlighted the differences in nutrient dynamics between agricultural and riparian soils and investigated the appropriateness of riparian vegetation as a BMP on flat sandy soil systems. The aim of this report was to assess how water and nutrients interacted with soils from a riparian zone and a paddock in a controlled column experiment. The study focussed on how vertical movement of groundwater in paddock and riparian soil columns affected the export of nutrients with and without nutrient enrichment (fertiliser and cow manure). The experiment investigated whether riparian soils exported fewer nutrients than paddock soils due to improved soil characteristics.

The experiment used a soil column apparatus, which was able to mimic the rise and fall of groundwater, simulating two hydrological events (rainfall and groundwater rise and fall). After each event, the columns were drained and outflow water analysed for carbon, nitrogen and phosphorus. At the beginning and end of each experiment, the nutrient content of the soil was analysed. The outflow of water from the columns was timed after the last event, to determine flow rates in paddock and riparian soils.

The outflow of water was significantly slower from riparian columns compared to the paddock. This is a result of the input of organic matter to soils from riparian vegetation, which reduces pore size and increases the water holding capacity of the soil.

Slower flow increases the residence time of water in the soil allowing greater nutrient transformation processes, such as denitrification, to occur. This results in an increased loss of nitrogen from riparian soils. The increased residence time, coupled with the iron and carbon content of the soil and anoxic groundwater conditions, causes release of iron-bound phosphorus leading to higher concentrations in the riparian groundwater. Phosphorus export from the riparian columns was also higher as a result of phosphorus leaching from nutrient rich surface soils, following rainfall. The nutrient export described throughout this report refers to export from soil columns and does not refer to nutrient export from the riparian zone, which would depend on larger scale water movements through the landscape (see O'Toole *et al.* 2013).

The addition of superphosphate fertiliser to the paddock soil columns resulted in rapid export of phosphorus following rainfall, whereas in the riparian zone, this phosphorus was largely adsorbed due to the increased phosphorus binding capacity of the soil. In the riparian columns, cow manure resulted in the greatest phosphorus export.

The hypothesis that: *Riparian soils will export fewer nutrients than paddock soils due to improved soil characteristics* was shown to be partially correct. The higher carbon content of riparian soils slowed the rate of water movement, improved the phosphorus binding capacity of the soil and promoted denitrification. However, the increased carbon content also

supported a greater microbial community and the input of extra nutrients (including labile carbon from manure) increased microbial respiration leading to release of iron-bound phosphorus into the groundwater. Within riparian soils there is a balance between phosphorus uptake and loss governed by soil carbon and physico-chemical conditions. The greater storage of phosphorus and nitrogen in the riparian soils lead to greater export from the soil columns and potentially from riparian zones if not managed correctly.

Management recommendations based on the findings of this study are:

- Fence riparian zones to keep out stock, particularly cattle
- Ensure an adequate fertiliser action plan is in place on Bassendean sands
- Use soil remediation methods to improve the nutrient holding capacity of soils
- Maintain or improve the stores of carbon within riparian soils by limiting disturbance and planting native vegetation
- Native riparian vegetation must be protected where it exists and improved through appropriate management whenever possible (e.g. removal of weeds)
- Native riparian vegetation, providing a complex community of trees understorey, groundcover and streamside sedges, should be planted where it is lacking

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Introduction

Urbanisation and agricultural production in catchments are the primary causes of nutrient enrichment in waterways (Peters and Meybeck 2000). Nutrient enrichment has led to eutrophication of the Swan Canning river system and is a key environmental issue affecting the health of the system. The Ellen Brook catchment is a major contributor of nutrients to the Swan River. Farms and horticulture contribute approximately 31.6% of nitrogen to Ellen Brook, while farms, horticulture and viticulture contribute approximately 75.5% of the phosphorus (Swan River Trust 2009b). The poor soils within the catchment and large input of nutrients have contributed to the catchment contributing 39% of the total phosphorus and 28% of the total nitrogen load to the Swan Canning estuary annually (Swan River Trust 2009a).

The magnitude of nutrient loss from agricultural catchments is a function of nutrient loading (e.g. fertiliser rates and livestock density) and the capacity of the catchment to retain the nutrients added. The latter is often a function of soil type (Sims *et al.* 1998). Soils in the Ellen Brook catchment are largely comprised of Bassendean sands, which are nutrient poor and have a poor nutrient holding capacity (Summers *et al.* 1999; Barron *et al.* 2009). As a result, high application rates of fertilisers are required to make the soils viable for crop production. However, due to the leaching capacity of these sands, nutrients can be quickly mobilised by runoff leading to poor uptake by crop plants, enrichment of the underlying groundwater and increase in the nutrient enrichment of Ellen Brook and the Swan River. Leaching of nutrients from agricultural soils following fertiliser application is an international issue (Kang *et al.* 2011; Wang *et al.* 2013). Historically, fertiliser use has often been ineffective and poorly managed, leading to higher application rates than necessary to promote plant growth. It has also resulted in fertiliser being used in inappropriate areas (e.g. next to streams and in areas prone to inundation and nutrient leaching). The use of fertilisers coupled with livestock grazing has shown to greatly increase nutrient export.

The different forms of agriculture occurring within catchments can greatly affect nutrient export. As highlighted above, while fertilisers contribute directly to nutrient export, cattle farming can also result in considerable organic nutrient export from catchments. Often it is the density of cattle being farmed that dictate the magnitude of nutrient export. Cattle can be highly detrimental to the environment, contributing nutrients through defecation and destroying native riparian vegetation, which increases erosion and removes the beneficial nutrient retention properties this vegetation provides (Robertson and Rowling 2000).

Cattle farming is common practice in the Ellen Brook catchment and has been identified as a major contributor of nutrients (Kelsey *et al.* 2010). Urea and manure are high in organic nutrients (Yadvinder-Singh *et al.* 1995) and are delivered directly to the underlying soils. With the poor soils in Ellen Brook, urea provides a highly soluble source of nutrients that rapidly enters groundwater, whereas manure is slowly decomposed over time but also contributes nutrients to the groundwater (Chardon *et al.* 2007). Where cattle are confined in a small area, it can lead to a large pulse of nutrients into receiving waters (Robertson and Rowling 2000). Even where riparian vegetation is protected, if grazing occurs upslope of the stream and there is significant slope, manure can be washed directly into riparian zones.

When riparian vegetation is not fenced, like much of Ellen Brook, cattle can defecate in the riparian zone and stream, allowing rapid nutrient mobilisation (Kauffman and Krueger 1984).

Paddock and riparian soils are adjacent to one another in agricultural landscapes, yet the capacity of these soils to intercept nutrients can vary greatly. When comparing the nutrient removal capacity of these soils it is imperative to understand why they differ. The variation in soil dynamics is a result of a number of factors. Firstly, the location of soils in the landscape can strongly affect soil makeup. Soils in the riparian zone are likely to be more varied and complex due to the proximity to streams. Streams or rivers affect soil composition of riparian zones during flooding by scouring and adding silt to near stream sediments (Herron and Hairsine 1998). Secondly, riparian soils accrete nutrients over time from organic matter as a result of litterfall and from trapping nutrients from overland flow (Lyons *et al.*1998; Lyons *et al.* 2000). Paddock soils are often nutrient poor due to intensive farming practices and remain this way unless there are nutrient inputs from livestock or fertilisers. Finally, riparian soils have more carbon than paddock soils due to input of organic matter from riparian litterfall over time (Jobbagy and Jackson 2000).

Carbon in soils affects the hydrology and nutrient dynamics of paddock and riparian soils. Carbon in riparian soils affects both soil structure and the processes which occur within the soil. Soil carbon has the capacity to reduce pore size (which can limit the flow of water through soils) and absorb water, thereby increasing the water holding capacity of riparian soils (Rawls *et al.* 2003; Reddy and DeLaune 2008). This slow flow and input of carbon into riparian soils can influence underlying physico-chemical conditions (Reddy and DeLaune 2008). Carbon fuels microbial respiration and growth, which can contribute to anaerobic and highly reducing conditions in underlying soils (Richardson and Vepraskas 2001). While soil type and structure affect nutrient storage, the interaction between soil and water can have a strong influence on nutrient export.

For nutrients to be intercepted there needs to be interaction between soil and runoff. The movement of water through the riparian zone affects nutrient movement and removal. The movement of water through the Ellen Brook catchment is a function of the sandy soils and the flat landscape. The hydrology of Bingham Creek (the sandy soil site in Ellen Brook used in this study) is defined by the lack of slope, no impermeable subsurface layer and poor sandy soils. This has resulted in limited surface flow from the paddock to the stream as rainfall rapidly infiltrates into the sands and the hydrology is dominated by vertical, rather than horizontal, subsurface water movement (O'Toole *et al.* 2013). Water rises and falls through the soil column as a result of rainfall and recharge or decline of groundwater, however it has not risen above the soil surface over the time period of this study (Figure 1). This type of water movement occurs in both the paddock and riparian zone and is likely to be key factor influencing groundwater nutrient dynamics.

It is possible to simulate vertical groundwater movement and rainfall input into soil and determine the soil response and soil and groundwater nutrient concentrations. Column experiments provide a controllable tool that can mimic groundwater movement at Bingham Creek, providing insight into the nutrient interactions that occur. This information can

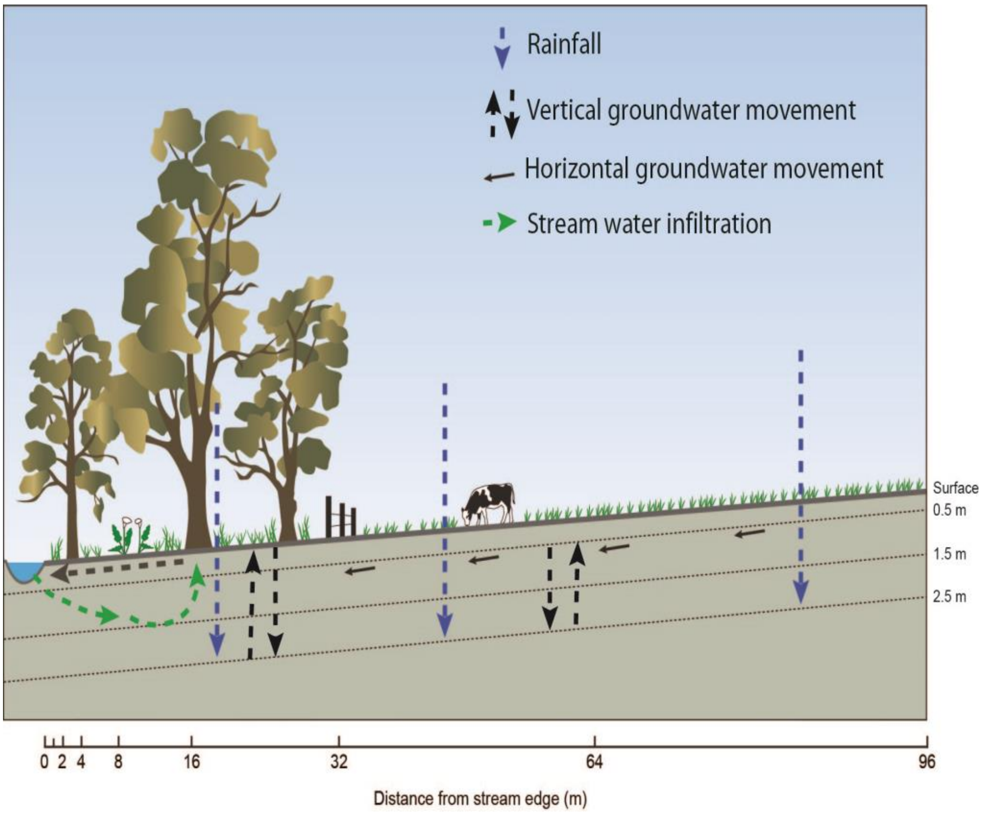


Figure 1- A conceptual model of the hydrology at Bingham Creek

provide insight into nutrient trends described in a previous study (O'Toole *et al.* 2013). The results from this report are experimental and the export of nutrients refers to columns only. The soil columns mimic natural conditions but only a small surficial portion of the landscape. For example, in the field the export of nutrients from 0.5 m soil profile represented in the columns would be intercepted by groundwater below and stored, or be subject to the prevailing hydrological conditions in the landscape. It is unlikely that this water would go directly into the stream. The hydrology of this site is described in O'Toole *et al.* (2013). Understanding the nutrient interactions between soil and water is crucial to successful management of nutrient enrichment in Ellen Brook. The key questions addressed in this report are:

- **Do riparian soils modify hydrology relative to paddock soils?**
- **How does water movement (downward from rainfall and upward from rising groundwater) influence nutrient movement and potential export from paddock and riparian soils?**
- **What effect do added nutrients (superphosphate fertiliser and cow manure) have on soil and groundwater nutrient concentrations?**

The hypothesis tested is:

Riparian soils will export fewer nutrients than paddock soils due to improved soil characteristics.

Methods

Experimental design

A column experiment was designed to assess how water movement up and down the soil profile affects water and soil nutrient concentrations. The experiment used nine intact soil columns collected from riparian and paddock zones to investigate whether riparian soils are more effective at taking up nutrients as water flows through them. Different hydrological events affect nutrient movement differently. Rain provides a mechanism for downward leaching of surface material to occur, whereas rising groundwater simulates the effect of saturation of a previously aerated soil profile.

Soil collection and experimentation occurred over two periods. Soil was collected in winter as the hydrological conditions that were replicated in the column experiment were winter rainfall events and the rise and fall of groundwater due to incoming water. Paddock soil was collected on 7 August 2013 and riparian soil on 2 September 2013, using a 10 cm diameter soil corer with a sharpened edge. Intact cores (0.5 m deep) were transferred directly to PVC columns in the field for transport to the laboratory. Soil columns were all collected from the same area in the paddock or riparian zone to reduce variations in soil structure and nutrient concentrations. Three additional 0.5 m soil columns were collected using a 5 cm corer to assess baseline soil nutrient concentrations.

Columns were constructed of 10 cm diameter PVC pipe. Two 60 cm lengths of PVC pipe were connected using a manifold, allowing water to move between columns (Figure 2). One column was filled with soil, while the other had water added, allowing the height of water in the soil column to be manipulated, as the relative height of water would equalise between the two columns. Water was drained via a tap beneath the manifold. The tap was positioned to allow the two columns to be separated (which prevented flow from the water column following saturation of the soil column) and for the soil column to be drained separately to the water column.

The nine columns were randomly assigned to three replicates each of a control, or treatments of cow manure or fertiliser. The control had nothing added, while the treatments had 100g of fresh cow manure and 0.14g of CSBP superphosphate (dosage rate of 100kg/ha) spread over the soil surface. The cow manure was analysed for total phosphorus and total nitrogen to determine the load of nutrients added (TN-1900 mg, TP-250 mg, C-33 g).

The columns were filled with distilled water over three days, from the bottom up to simulate a rise in groundwater level, to a maximum water level of 5 cm below the soil surface (the maximum groundwater height noted in the field - O'Toole *et al.* 2013). Once saturated, the soil column was isolated from the water column (so fresh water was not flowing in) and left to sit for three days. The soil column was then drained over the day and a water sample taken for nutrient analysis once draining was complete. The following day, water was added to mimic a rainfall event. A moderate rainfall event (20 mm) was simulated by adding 160 ml of distilled water to the soil surface over two hours using a watering can nozzle. The column

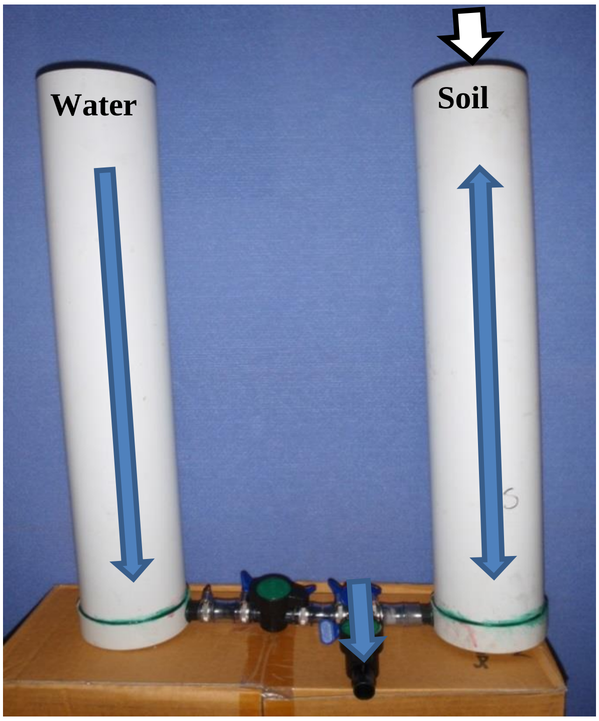


Figure 2- A photograph of the columns used, highlighting water movement from the water to soil column, which imitates the rise and fall of groundwater following rainfall

was then drained until it no longer flowed and a sample taken for nutrient analysis following the end of drainage. This process was the repeated the following day to simulate a second 20mm rainfall event. The soil column was then re-filled with water from the bottom up over three days until the column was saturated, to simulate a second groundwater rise after rainfall. The column remained saturated for three days before draining. The final drain was timed, with time taken for each 150 ml sample to drain from the soil core recorded. Each 150 ml sample was then processed separately for nutrient analysis. Drainage occurred for up to eight hours, whereupon flow from the columns became insignificant and three 150 ml water samples were collected for riparian and paddock columns.

After the final draining, a soil core the full length of the column (0.5m) of 5 cm diameter was removed and analysed for nutrients. The soil was split into three sections, the top 10 cm, 10-30 cm and 30-50 cm depths.

Nutrient analysis

Water

Following the collection of water, all samples were analysed by the Marine and Freshwater Research Laboratory (MAFRL, NATA accredited No. 10603) for total phosphorus (TP, Valderrama 1981), total nitrogen (TN, Valderrama 1981), filterable reactive phosphorus (FRP, Johnson 1982), nitrate-nitrite-nitrogen or oxidised nitrogen (NO_x-N, Johnson 1983), ammonium-nitrogen (NH_4-N, Switala 1993) and dissolved organic carbon (DOC, APHA 1995). Samples FRP, NO_X-N, NH_4-N and DOC were filtered through a 0.45μm millipore filter. Samples for TP and TN were not filtered.

Soil

Following the collection of the soil, the soils were air-dried and a sample was taken for nutrient analysis in the laboratory. Soils were analysed by MAFRL for total Kjedahl nitrogen (TKN; APHA 1995), total phosphorus (TP; Aspilla *et al.* 1976), total organic carbon (%C; Dean 1974).

Data analysis

All data analysis was done using SPSS 17©. Repeated measure ANOVAs were used to determine if there was significant difference between drainage times and nutrient concentrations over hydrological events. A one-way, repeated measures ANOVA was conducted for drainage time, which compared time across soil type. Where the sphericity assumption was violated (sig <0.05), Greenhouse-Gossier reading was used to assess significance. When the homogeneity test was failed (Levene's <0.05), data was transformed using Log_{10}.

To assess nutrient concentrations over hydrological events, a two factor repeated measures ANOVA was completed. The ANOVA compared nutrient concentrations over four time periods, two soil types and the three treatments. The interpretation of the results followed the steps outlined above. Residual plots were used to further assess the spread of the data.

Soil nutrient concentrations were compared between paddock and riparian columns for the top 10 cm of soil only. This was due to the number of zeros encountered in the deeper soils, preventing ANOVAs to be completed. Concentrations were compared using a one way ANOVA, where the homogeneity test was failed (Levene’s <0.05), data was transformed using Log_{10}.

Results

Groundwater drainage rates

The flow of water through the paddock columns was significantly (Greenhouse-Geisser, df= 1.474, error df= 23.588, f= 5.77, P= 0.015) faster than riparian columns (Figure 3a). The flow rate of water (ml/min) from the paddock soil column was more than twice that of the riparian zone for each 150 ml aliquot (Figure 3b).

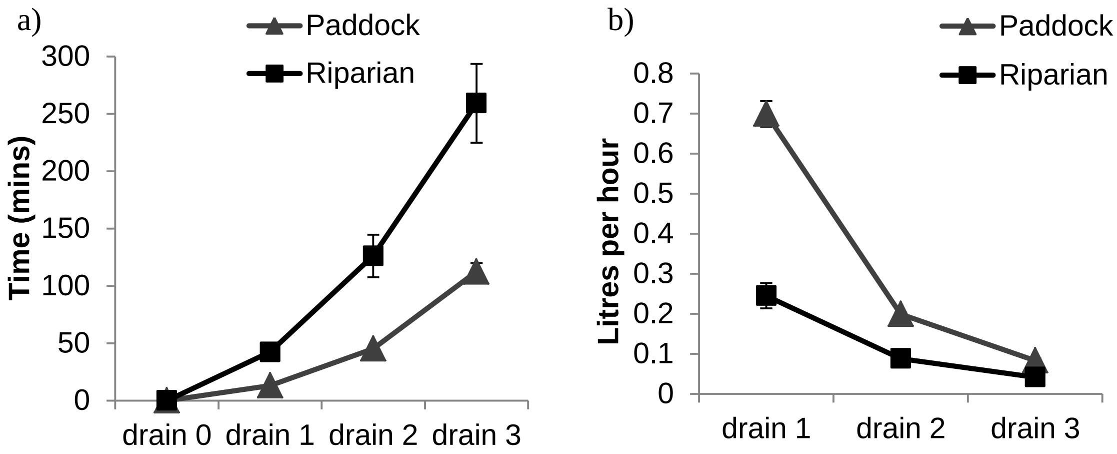


Figure 3- a) Comparison of drainage time of 150ml of water from the paddock and riparian columns b) Comparison of the rate of drainage (ml per minute) from the paddock and riparian columns over three drainage periods

Nutrient release following hydrological events

Trends in dissolved organic carbon (DOC) concentrations of water drained from the paddock and riparian columns (hereafter called outflow) were similar, with the highest concentrations occurring after the second rainfall event (Figure 4). Outflow concentrations were lowest after the rising groundwater events. DOC concentrations were substantially higher in riparian columns, particularly in the cow manure treatment (max~200 mg C/L), whereas the highest concentration in the paddock columns was approximately 40 mg C/L (Figure 4).

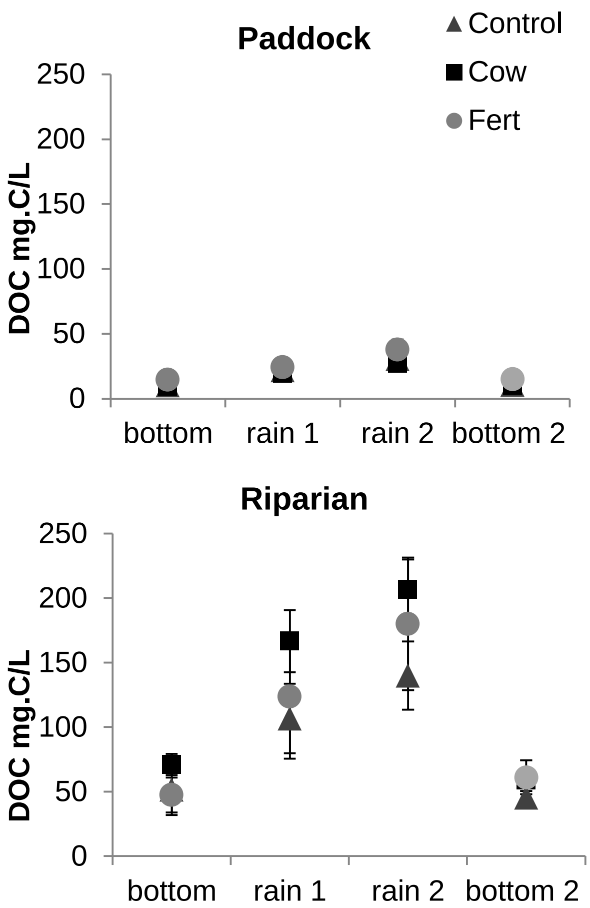


Figure 4- A comparison of DOC concentrations between paddock and riparian soil columns based on four hydrological events and three treatments

The variability in the outflow concentration of DOC between the two soil types and the three treatments was not significant, however there were significant differences between hydrological events (Greenhouse-Geisser df=1.82, error df= 21.86, F= 2.558, P <0.000). This pattern was consistent across both soil types, with concentrations highest after rainfall events and lowest after the second groundwater event (Figure 5).

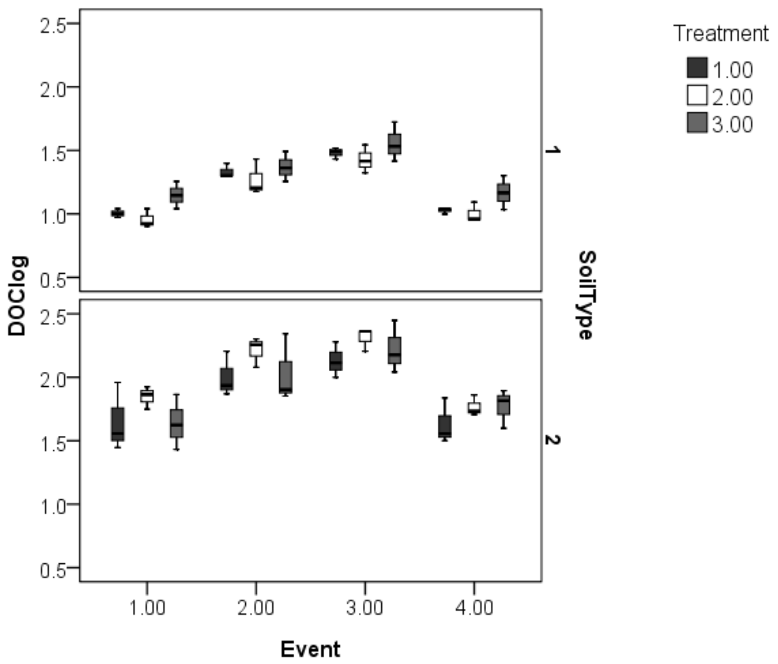


Figure 5- Box plots comparing Log_{10} DOC concentrations of soils water across soil type (1. Paddock 2. Riparian), treatments (1. Control 2. Cow manure 3. Fertiliser) and four hydrological events

Phosphorus (both filterable reactive phosphorus (FRP) and total phosphorus (TP)) concentrations of the outflow from the paddock and riparian columns varied considerably, being highest after the second rainfall event and lowest after the second groundwater event (Figure 6). Phosphorus concentrations in the paddock outflow were consistently lower than the riparian columns. In the paddock, the fertiliser treatment caused the highest export of phosphorus, which was most evident after the last two hydrological events (Figure 6). Riparian columns showed no clear trend over the hydrological events. However, phosphorus concentrations were clearly highest in the outflow from the cow manure treatment, whereas concentrations were similar in the control and fertiliser treatments (Figure 6).

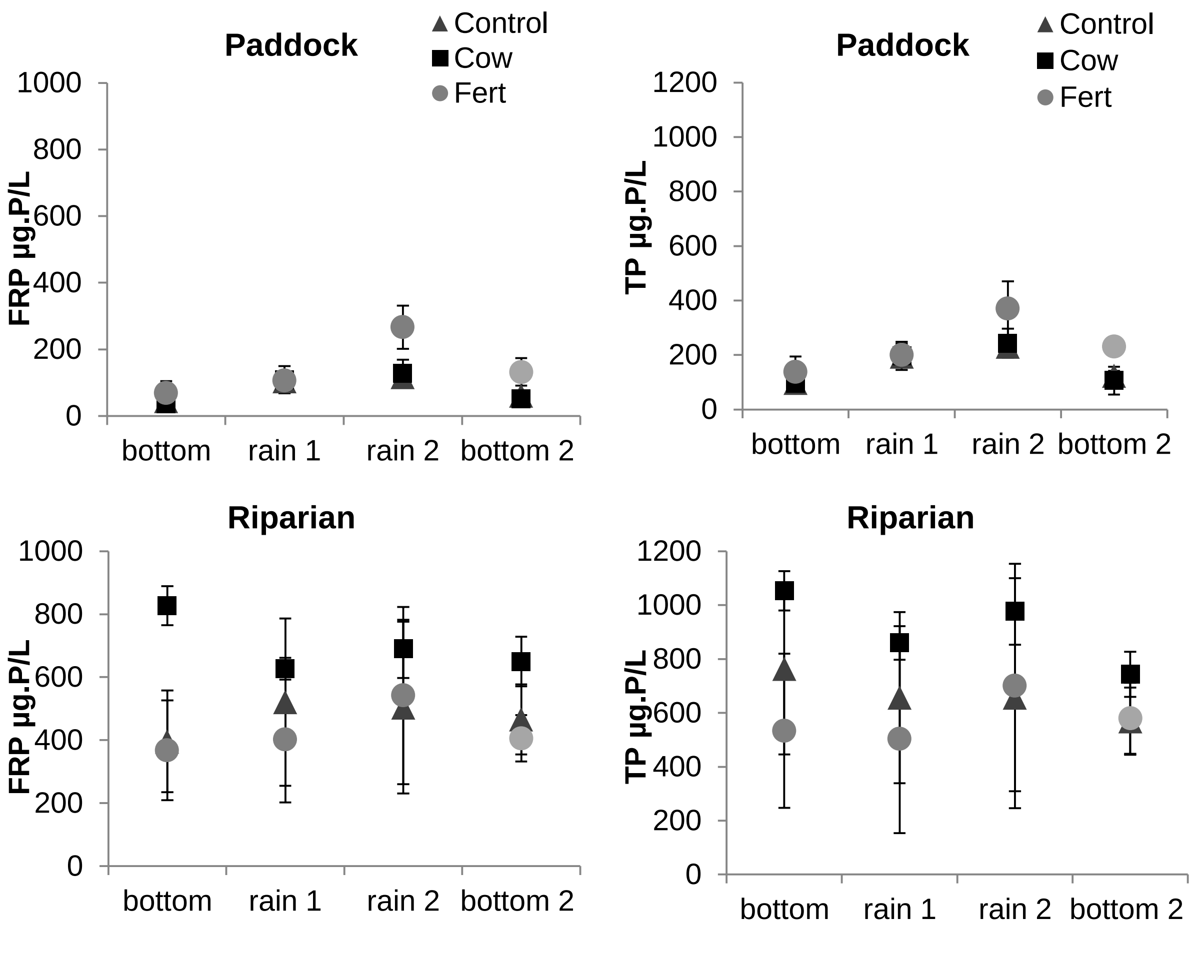
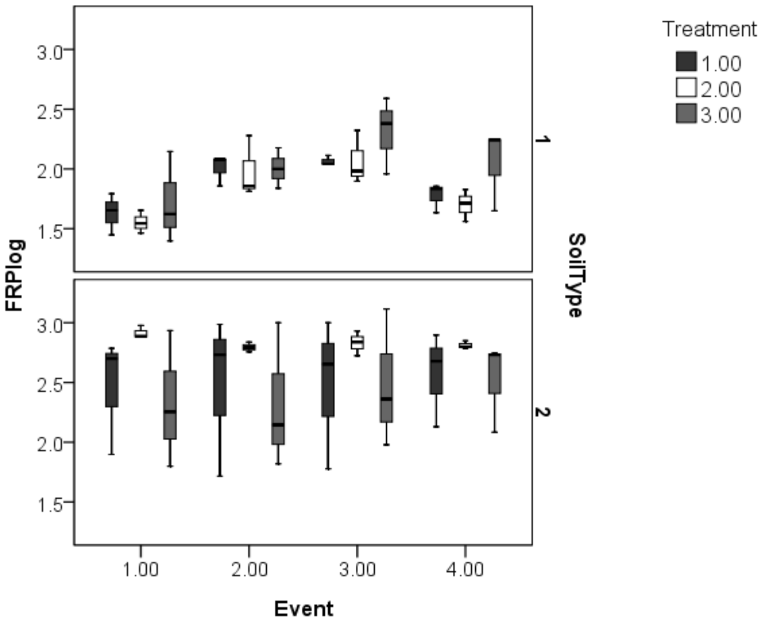


Figure 6- A comparison of FRP and TP concentrations between paddock and riparian soil columns, based on four hydrological events and three treatments

Filterable reactive phosphorus and total phosphorus concentrations of the outflow were highly variable in the riparian columns, with a significant difference between event*soil type (FRP Greenhouse-Geisser df= 2.08, error df= 4.18, F= 11.57, P <0.000, TP Greenhouse-Geisser df= 1.83, error df= 21.98, F= 14.66, P <0.000). This illustrates the outflow concentrations were significantly higher in riparian columns and there were significant differences over hydrological events (Figure 7).



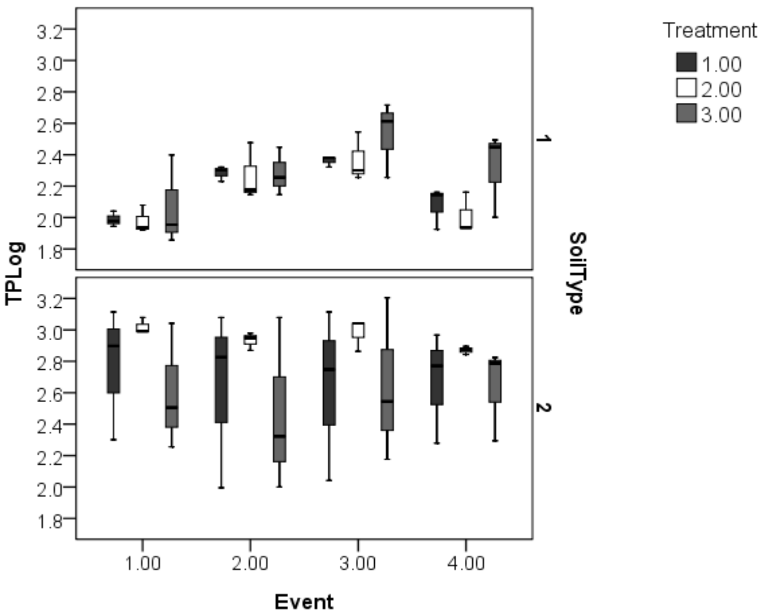


Figure 7- Box plots comparing Log_{10} FRP and TP concentrations across soil type (1. Paddock 2. Riparian), treatments (1. Control 2. Cow manure 3. Fertiliser) and four hydrological events

Outflow concentrations of nitrogen (in all forms) were typically lower in paddock columns, while there was greater variability in riparian columns (Figure 8). For both ammonium (NH_4-N) and total nitrogen (TN), in both paddock and riparian columns, the highest outflow concentrations occurred after the second rainfall event and the lowest occurred after a rising groundwater event. The greatest nitrogen export occurred in the fertiliser treatment with the exception of TN in riparian columns (Figure 8). Oxidised nitrogen (NO_x-N) concentrations of the outflow from paddock columns decreased with each subsequent hydrological event in all treatments. In the riparian columns, outflow concentrations of NOx-N decreased over hydrological events in the cow manure and fertiliser columns, however NO_x-N outflow concentrations from the riparian control columns were considerably higher and peaked after rainfall events (Figure 8).

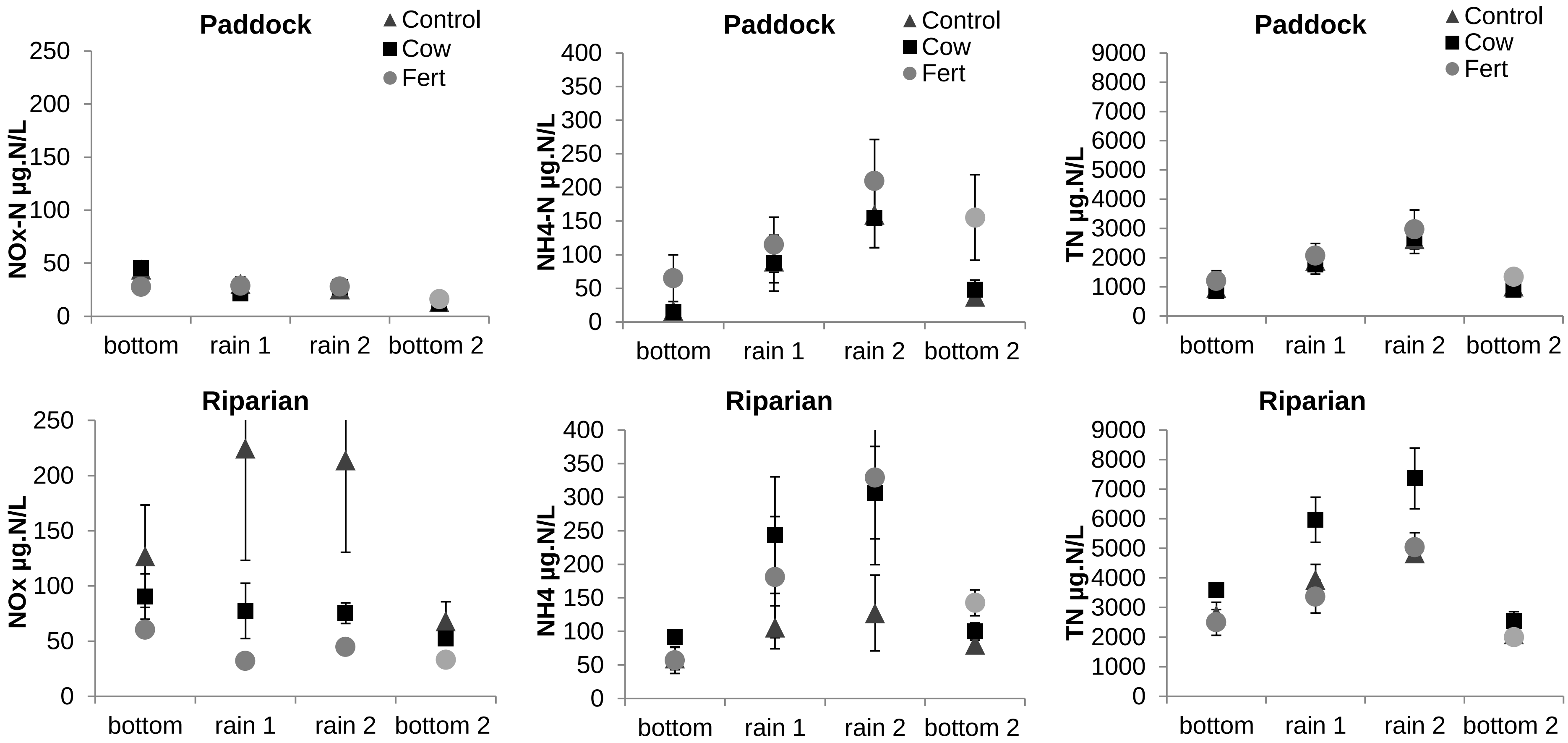


Figure 8- A comparison of NO_x-N, NH_4-N and TN concentrations between paddock and riparian soil columns, based on four hydrological events and three treatments

Oxidised nitrogen concentrations (NO_X-N) showed considerable variability, particularly in the riparian columns (Figure 9). There was a significant difference for the interaction event*soil type* treatment (Sphericity assumed df= 6, error df= 36, F= 2.74, *P*= 0.027). This illustrates there are significant differences occurring in the interaction between soil type, treatments and hydrological events. NO_X-N outflow concentrations from the riparian control columns were significantly higher than the other two treatments.

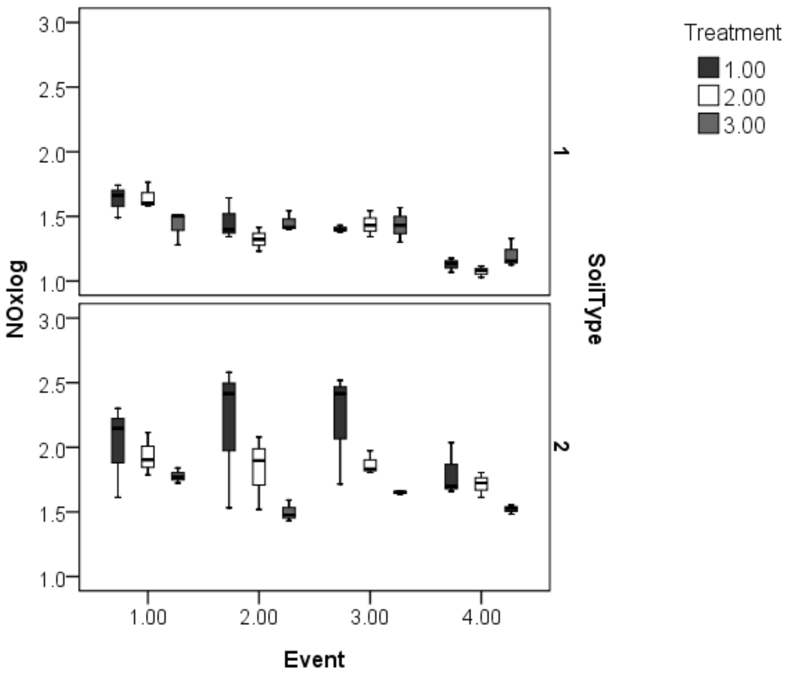


Figure 9- Box plots comparing Log_{10} NOx-N concentrations across soil type (1. Paddock 2. Riparian), treatments (1. Control 2. Cow manure 3. Fertiliser) and four hydrological events

There was a similar trend for ammonium concentrations in the paddock and riparian soils and there was a significant difference between hydrological events (Greenhouse-Geisser df= 1.45, error df= 17.37, F= 24.41, *P* <0.000). Ammonium concentrations of the outflow were highest after the second rainfall event for both soil types and the greatest variability occurred in riparian cow manure columns (Figure 10).

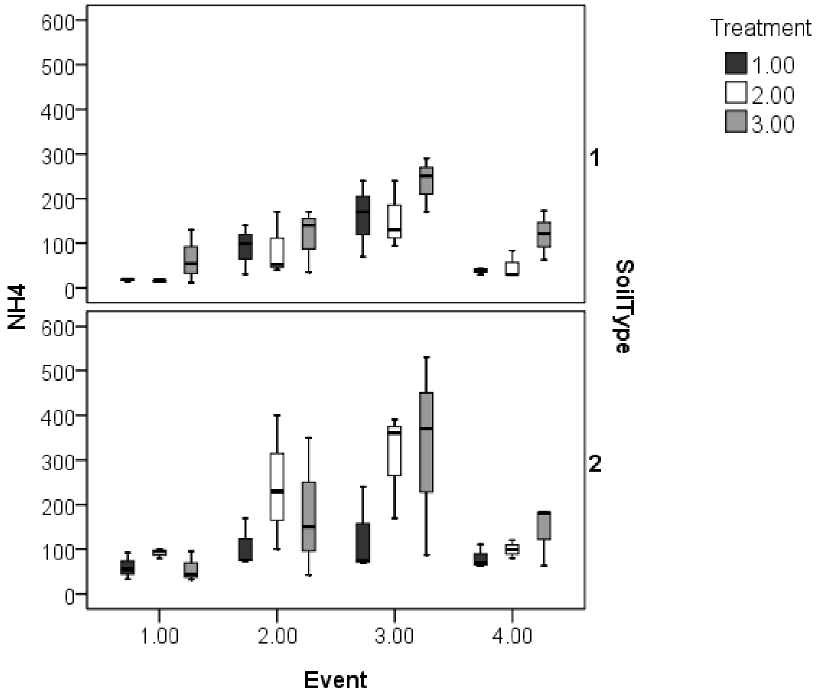


Figure 10- Box plots comparing NH_4-N concentrations across soil type (1. Paddock 2. Riparian), treatments (1. Control 2. Cow manure 3. Fertiliser) and four hydrological events

Total nitrogen concentrations showed a similar pattern to ammonium with highest outflow concentrations after the second hydrological event and lowest at the last groundwater rising event (Figure 11). Concentrations were higher and more variable in riparian soils and there was a significant difference for event*soil type (Greenhouse-Geisser (df= 1.65, error df= 19.74, F= 11.16, *P*= 0.001). Concentrations were significantly higher in riparian columns and there were significant differences of the hydrological periods.

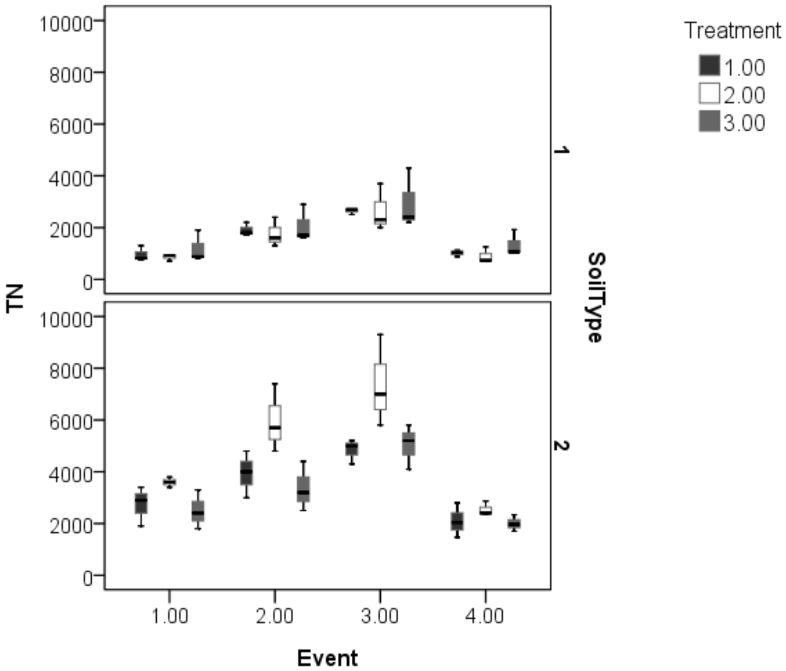


Figure 11- Box plots comparing TN concentrations across soil type (1. Paddock 2. Riparian), treatments (1. Control 2. Cow manure 3. Fertiliser) and four hydrological events

Nutrient export from soil columns with increasing time

The following data describes the changes in nutrient concentrations of the outflow after the last hydrological event. The final drain comprised three 150 ml water samples (Drain 1, 2 and 3 in graphs below) representing the first, middle and last sample taken over the timed period of drainage (see Figure 3). These three aliquots are likely to represent water flowing from the bottom of the column first and then further up the column with each subsequent aliquot.

Dissolved organic carbon concentrations of the outflow increased from the first to last drain for both the paddock and riparian columns (Figure 12), however the concentrations were higher in the riparian columns which peaked at approximately 80 mg.C/L compared to the paddock (~20 mg.C/L).

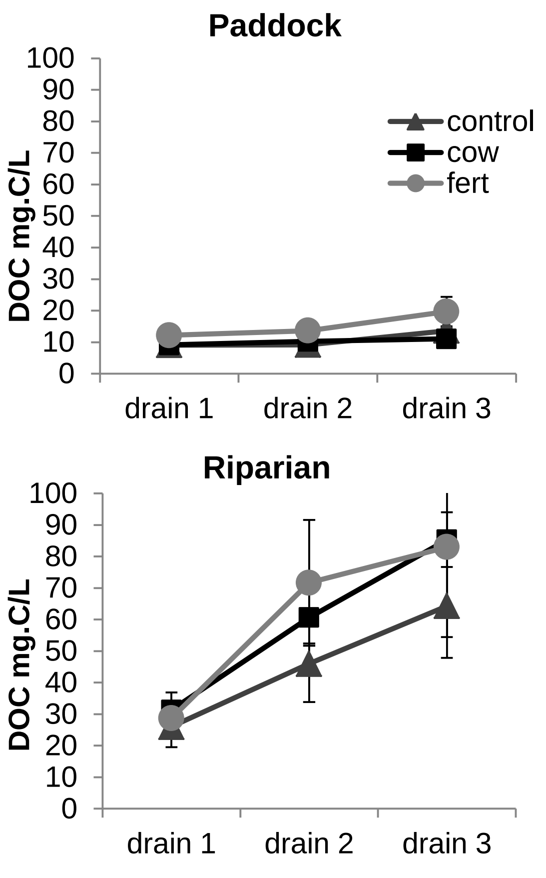


Figure 12- Comparison of dissolved organic carbon concentrations between paddock and riparian columns over three timed drainage periods

Phosphorus (FRP and TP) concentrations of the outflow increased over the drainage period, with the exception of the fertiliser treatment in the riparian soil column (Figure 13). Phosphorus was primarily in inorganic form in riparian columns (~77%), compared to paddock columns (~60%). In the paddock, concentrations were highest in water released from the fertiliser columns but in the riparian columns they were highest in the cow manure treatment. Overall phosphorus concentrations of the outflow were higher, and showed greater variability, in the riparian zone (Figure 13).

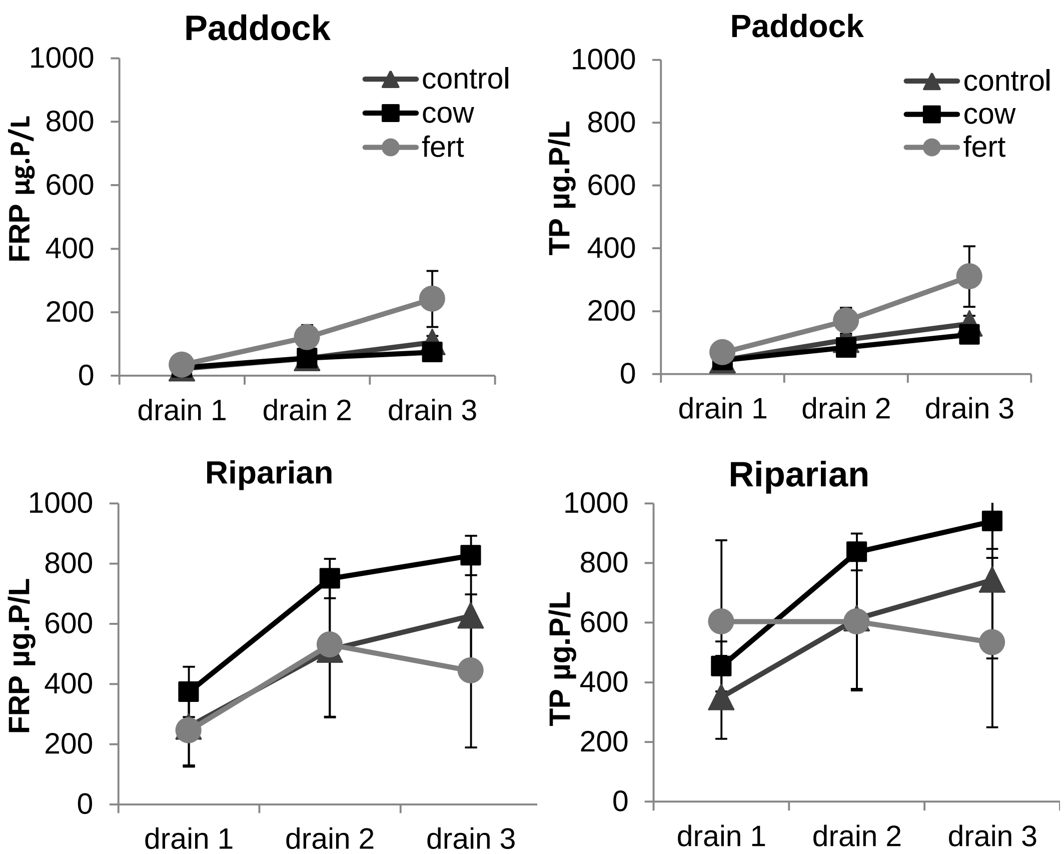


Figure 13- Comparison of filterable reactive and total phosphorus concentrations between paddock and riparian columns over three timed drainage periods

Outflow concentrations of nitrogen (in all forms) increased over the drainage period, with the exception of oxidised nitrogen and total nitrogen in the fertiliser treatment in the riparian soil columns (Figure 14). In the paddock, concentrations were highest in water released from the fertiliser columns but no trend was evident in the riparian columns. Overall nitrogen concentrations were higher and more variable in the riparian zone columns (Figure 14).

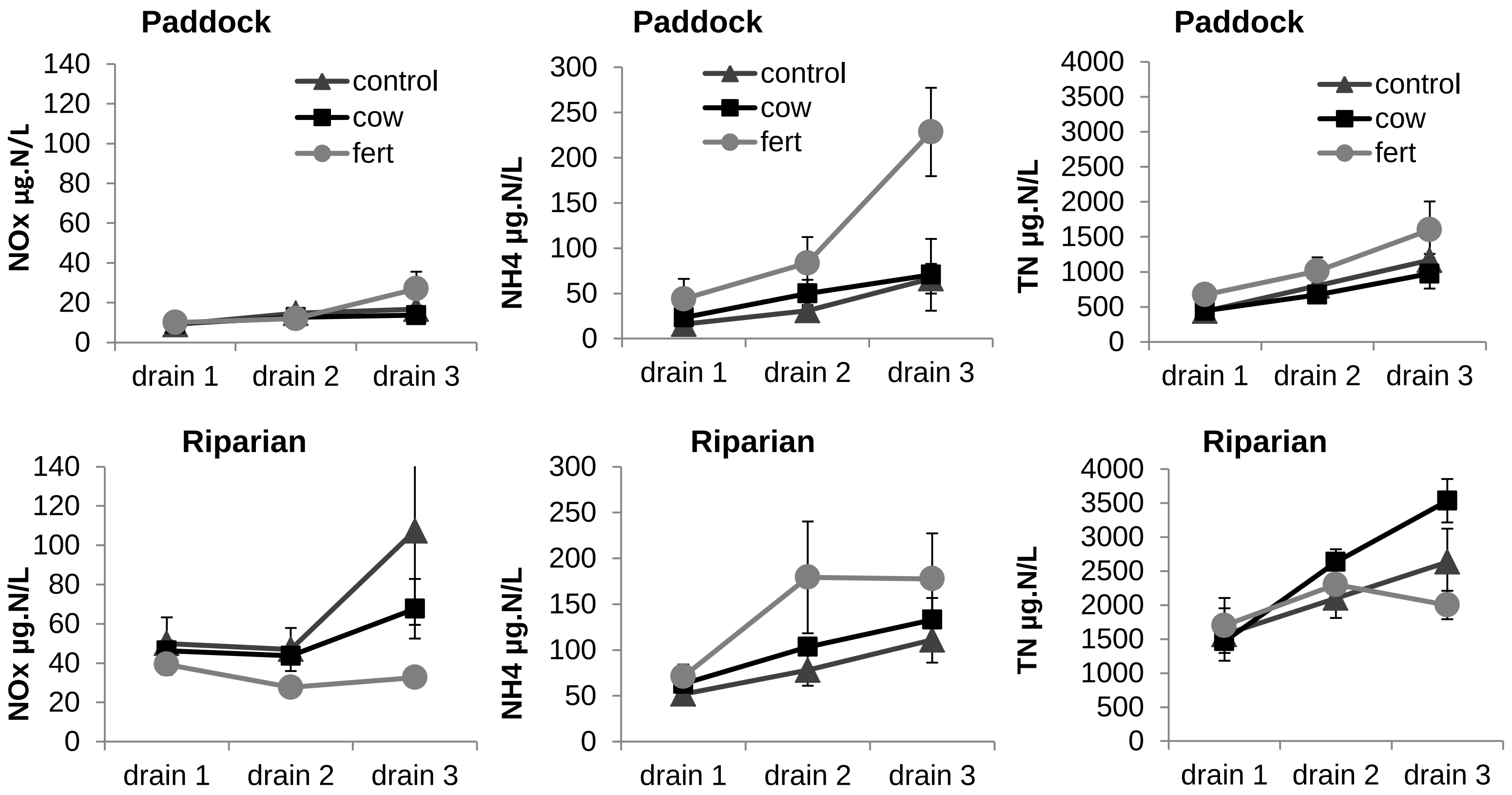


Figure 14- Comparison of oxidised nitrogen, ammonium and total nitrogen concentrations between paddock and riparian columns over three timed drainage periods

Nitrogen:Phosphorus ratios

The nitrogen to phosphorus ratios in outflow water from the paddock and riparian columns were similar for both total and inorganic nutrients (Table 1). The TN:TP ratio of 10 for paddock and riparian columns is ideal for macrophyte growth (Duarte 1992), indicating a balanced nutrient profile. The ratio for inorganic nutrients was roughly a tenth of the TN:TP ratio indicating that the system is limited by inorganic nitrogen (Duarte 1992).

Table 1- Comparison of TN:TP and (NOx-N+NH_4-N):FRP ratios in column water from paddock and riparian soils, values in brackets represent standard error

	TN:TP	**(NOx-N+NH_4-N):FRP**
Paddock	10:1 (0.4)	1.4:1 (0.1)
Riparian	10.3:1 (2)	1.1:1 (0.3)

Nutrient content of the soils

Total phosphorus concentrations of paddock soils were significantly lower (df= 1, F= 176, P<0.000) than riparian soils. The highest concentrations occurred in the top 10 cm for both soils and decreased with depth (Figure 15). However, phosphorus concentrations were significantly higher in deeper riparian soils in cow manure and fertiliser treatments compared to the base and control samples.

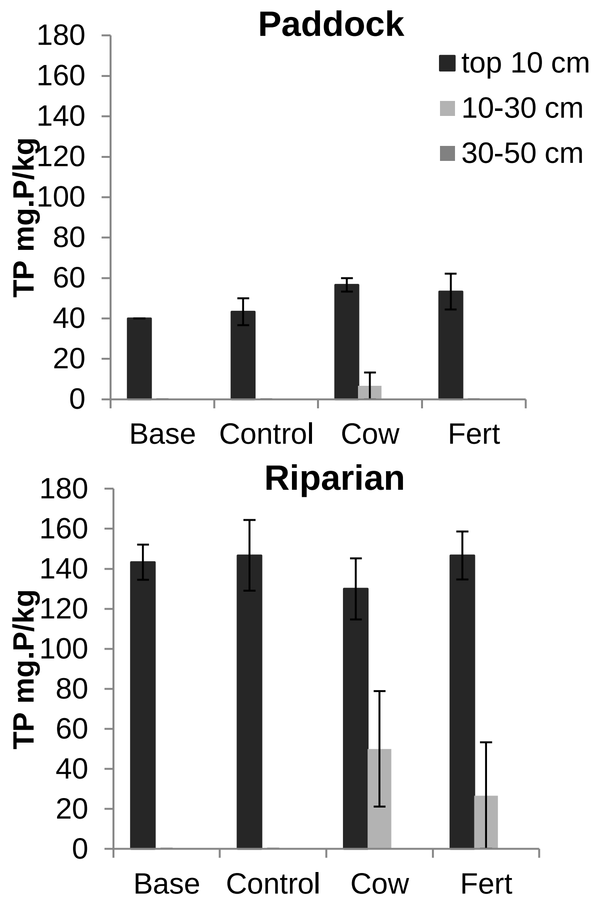


Figure 15- Soil TP concentrations for three depths comparing baseline concentrations with the three different treatments

Total Kjeldahl Nitrogen concentrations were highest in the top 10cm of soil and concentrations were significantly (df= 1, F= 104.41, P= <0.000) higher in surface riparian soils compared to paddock soils (Figure 16). The highest soil nitrogen concentration in the paddock columns was in the cow manure treatment, but in the riparian soils the baseline samples were highest, however, they were not significant. The reduction in nitrogen concentrations suggests nitrogen was mobilised during the experiment.

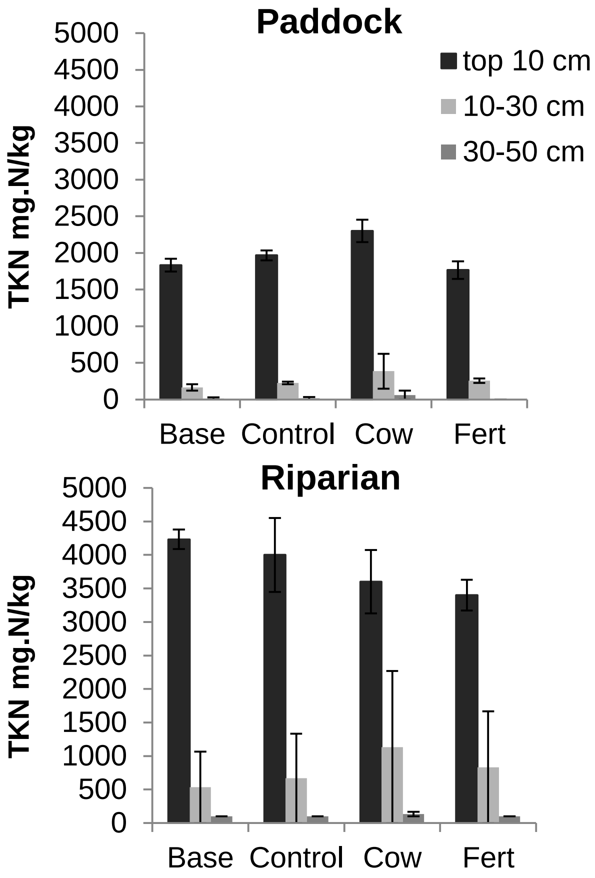


Figure 16- Soil TKN concentrations for three depths comparing baseline concentrations with the three different treatments

Total organic carbon concentrations of the riparian and paddock soils were both highest in top 10 cm of soils, and decreased with depth (Figure 16). Concentrations in the riparian soils were nearly twice as high as paddock soils across the top two soil depths. Soil carbon concentrations were significantly higher in surface riparian soils compared to paddock soils (df= 1, F= 64.82, *P*= <0.000). There was no significant difference in between treatments for either soil type. Furthermore, there was no detectable carbon at the lowest depth of the paddock soils, but it was present in low concentrations in riparian soils.

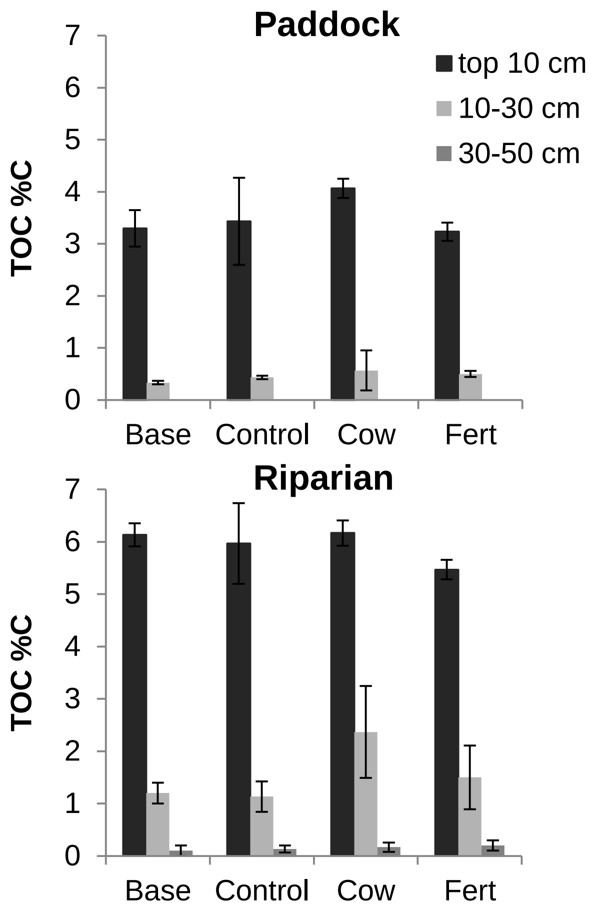


Figure 17- Soil TOC %C concentrations for three depths comparing baseline concentrations with the three different treatments

Discussion

Do riparian soils modify hydrology relative to paddock soils?

The difference in the hydrology of riparian and paddock soils highlights the effect riparian vegetation has on water movement. The outflow from riparian columns was significantly slower than paddock soils, with release of water taking twice as long. This is most likely the result of the higher carbon content of riparian soils. Carbon reduces the pore size of soil, which leads to slower movement of water through the soils (Rawls *et al.* 2003). Carbon also increases the water holding capacity of soils as it has the capacity to adsorb water as a result of textural complexity of carbon (Rawls *et al.* 2003; Richardson and Vepraskas 2001; Reddy and DeLaune 2008). Conversely, the large pore size of the sand in the paddock, which had little organic carbon, provided minimal impediment to flow. This is significant as in areas of sandy soils, riparian vegetation will reduce the rate of flow to streams.

The flow of water through soils influences the nutrient dynamics of riparian zones. Reduced flow of water increases residence time, enhancing the opportunity for nutrients to be intercepted by vegetation and soil, or transformed by microbial processes (Richardson and Vepraskas 2001; Reddy and DeLaune 2008). This can increase the likelihood of nitrogen and phosphorus uptake by plants, binding by sediment particles and nitrogen loss through denitrification (Groffman *et al.* 1992; Richardson and Vepraskas 2001). Slower flows also reduce the rate of input to receiving waters, whether surface streams or groundwater, and decrease the chance of a rapid pulse of nutrients. The differing flow rates from paddock and riparian columns were likely a key element in the different nutrient dynamics observed, primarily due to the increased residence time of water in the soil.

How does water movement (downward from rainfall and upward from rising groundwater) influence nutrient export from paddock and riparian soils?

The significantly higher carbon content of riparian soils (almost twice that of paddock soils) is due to organic matter accretion in the soil from decomposed riparian vegetation and possibly captured from throughflow from the catchment (Jobbagy and Jackson 2000). Riparian plant productivity fuels increased stores of both particulate and dissolved forms of carbon in the soil (Jobbagy and Jackson 2000). The accretion of carbon in sandy soils is slow, due to the larger pore size, poor binding capacity and tendency for carbon leaching to occur (Jobbagy and Jackson 2000; Reddy and DeLaune 2008). Riparian vegetation contributes labile and refractory carbon to underlying soils. Labile carbon represents bioavailable carbon and can be used to fuel microbial respiration, whereas refractory carbon is not bioavailable and is more likely to accumulate in riparian soils (Reddy and DeLaune 2008). Over time, carbon infiltrates to greater depths with the downward passage of water, increasing concentrations. As a consequence, dissolved organic carbon (DOC) concentrations in outflow water were significantly higher from riparian than paddock columns. However, the pattern of carbon export was similar in both soils, with greatest concentrations occurring after rainfall, highlighting the importance of downward flow transporting material from the surface and the potential for leaching in these sandy soils.

Like carbon, soil phosphorus concentrations were significantly higher in riparian than paddock soils, however, phosphorus was mainly restricted to surface layers (top 10cm). Sandy soils are often phosphorus deficient due to their susceptibility to leaching, large grain size and poor phosphorus adsorption capacity (Ritchie and Weaver 1993). However, the increased carbon content of the riparian soils, particularly in surface layers, improves the phosphorus binding capacity of the soil (Tan 2000). Riparian vegetation was shown to slightly improve the PRI of soils at Bingham Creek (O'Toole *et al.* 2013), as a consequence of increased soil carbon. This increase in soil PRI can reduce nutrient export from soils (Tan 2000). This, coupled with the continuous input of phosphorus from riparian litterfall and phosphorus rich groundwater, has led to higher surface soil phosphorus concentrations.

The combination of sandy soil, higher soil phosphorus and carbon concentrations helps explain why total phosphorus concentrations were significantly higher in the riparian column outflows. As groundwater and rainfall interacts with soils, nutrients can be leached into water within the soil (porewater or groundwater). In sandy soils, pore size is large and the sand usually has few binding sites (low PRI), so phosphorus is readily leached and mobilised (Reddy and DeLaune 2008). As a result Bassendean sands have low PRI values, contributing to the loss of phosphorus following rainfall (Barron *et al.* 2008). While the addition of carbon in the riparian zone reduces poresize and increases phosphorus binding potential of the soil, it also fuels microbial respiration (Chen *et al.* 2003; Reddy and DeLaune 2008). In a previous study, O'Toole *et al.* (2013) identified that groundwater in the Bingham Creek riparian zone was anoxic and highly reducing, evidence of the high soil carbon concentrations promoting microbial respiration.

Under reducing conditions phosphorus is released from bonds to iron, as reduction converts iron from an insoluble to a soluble form (Vought *et al.* 1994; Richardson and Vepraskas 2001; Kirk 2004). Riparian soils at Bingham Creek have high surface total iron concentrations (5500 mg.Fe/kg), compared to paddock soils (150mg.Fe/Kg; O'Toole *et al.* 2013) providing greater potential for phosphorus to be released from riparian soils under anaerobic conditions. Furthermore, the phosphorus in surface riparian soils at Bingham Creek was shown to be approximately 60% NaOH extractable (non-apatite, likely Fe-bound) phosphorus, compared to approximately 30% in the paddock (O'Toole *et al.* 2013). The greater the proportion of NaOH extractable phosphorus in soil means there is more available orthophosphate for plant uptake and consequently release into water (Doolette *et al.* 2011). The increased residence time of groundwater in riparian soils would result in the greater release of phosphorus into the porewater, due to a greater interaction time with microbes in the soil. When this water is mobilised through the soil column there is the potential for significant phosphorus export.

Phosphorus export from the soil columns was greatest following rainfall events. Passage of water can readily leach phosphorus from the Bassendean sands due to the poor phosphorus holding capacity (Summers *et al.* 1999; Barron *et al.* 2008). Even though riparian soils have improved soil structure, the high proportion of coarse sand still facilitates water movement making them prone to leaching (Franzluebbers 2002). Rainfall leaches the phosphorus-rich surface layers, transporting material to the more reducing conditions at depth (O'Toole *et al.* 2013), promoting phosphorus release. In contrast, rising groundwater passes only through already anoxic regions of lower phosphorus concentration and as the water did not intercept the phosphorus-rich, surface soils, export after a rising groundwater event was much lower. The upward movement of groundwater is a major component of the hydrology of these flat sandy systems and by not intercepting surface soils, phosphorus remains stored in the soil profile. This highlights that the key mechanism for phosphorus movement in the soil column is through downward leaching of surface-stored phosphorus.

The vertical movement of water up and down the soil columns influenced the species of nitrogen differently. Oxidised nitrogen (NO_x-N) concentrations in the outflow were not influenced by different hydrological events in the riparian and paddock columns but decreased over time. This is a result of the presence of labile carbon, which provides fuel for microbial respiration leading to anoxic conditions under prolonged wetted conditions (Kirk 2004; Reddy and DeLaune 2008). This is further influenced by the slow flow through riparian soil columns following rainfall and rising groundwater. This leads to greater residence times, which increases the potential for nitrogen transformations to occur. These conditions promote denitrification, transforming NO_X-N to N_2 gas, which can then be lost from the system (Naiman and DeCamps 1997; Richardson and Vepraskas 2001). This is consistent with the higher ammonium (NH_4-N) concentrations in outflow water after rainfall, as NH_4-N is the dominant form of soluble nitrogen under reducing conditions (Vought *et al.* 1994; Reddy and DeLaune 2008). Under anoxic conditions, when riparian vegetation contributes organic matter to surface soils, NH_4-N is released as a product of decomposition (Naiman and Decamps 1997). Total nitrogen concentrations in outflow water peaked after rainfall, while the vertical rise of groundwater in the columns intercepted limited nitrogen. This highlights that the greatest export of nitrogen is likely to occur when rainfall intercepts or leaches the nitrogen-rich surface soil. However, riparian soils reduce the speed of water movement, allowing for interception and denitrification to occur, reducing this nitrogen export.

What effect do added nutrients (superphosphate fertiliser and cow manure) have on soil and groundwater nutrient concentrations?

The input of two different nutrient sources resulted in different outcomes in the paddock and riparian columns. Cow manure contains organic phosphorus, which can be slowly released as the cow manure breaks down, whereas superphosphate fertiliser is a soluble form of inorganic phosphorus (Chardon *et al.* 2007; Wang *et al.* 2013). Phosphorus concentrations of the paddock outflow were highest from columns with fertiliser added. Phosphorus release from sandy soils following the application of superphosphate fertiliser is a common occurrence, due to the limited phosphorus binding and storage capacity (Ritchie and Weaver 1999). In the riparian columns, the cow manure treatment had the highest phosphorus concentrations in the outflow. Cow manure contributes both carbon and phosphorus to underlying groundwater and promotes microbial processes. As a result, phosphorus is added to the soil column as it is leached from the cow manure, while the carbon can promote further microbial release of phosphorus already present in the soil where it is bound to iron (Chadron *et al.* 2007; Reddy and DeLaune 2008). In contrast, the superphosphate fertiliser (where only P but not C was added) did not have a noticeable effect on the export of phosphorus from the riparian columns. In this case, the added phosphorus was able to be bound in the organically enriched soil, while the reduced availability of labile carbon limited the microbial release of phosphorus from iron bonds in the soil. The increased soil phosphorus concentrations at greater depth (10-30cm) in the riparian soils following cow manure and fertiliser application indicates that the riparian soils are capable of storing some additional phosphorus, due to their increased organic content (Svanback *et al.* 2013).

The input of cow manure and fertiliser to the riparian soils had a different effect on nitrogen dynamics than in paddock soils. It was apparent that the influx of nutrients to these soils provided fuel for microbial transformations to occur (Stutter and Richards 2012). This resulted in low NO_x-N concentrations and elevated NH_4-N concentrations relative to the control. The slow movement of water, presence of carbon and input of nutrients provide ideal conditions for denitrification, the reduction of NO_x-N and the loss of nitrogen (Naiman and DeCamps 1997; Kirk 2004; Reddy and DeLaune 2008). Comparing baseline results with the treatments showed there was a trend in decreasing soil nitrogen concentrations in riparian columns for each treatment. This reduction ranged from 200-800 mg.N/kg, indicating that nitrogen is being stripped from the soils, some of which may be lost through denitrification. This trend was not apparent in paddock soils, indicating that there was less nitrogen available for release in paddock soils. Further to this there was little variability in the nitrogen concentration of the paddock outflow following the input of superphosphate fertiliser and cow manure. This further highlights the importance of labile carbon in soils as its fuels microbial respiration and nitrogen transformations. The paddock soils had little carbon and therefore would not support a significant microbial community. As a result, addition of nutrients to the paddock soil would not enhance microbial respiration and nutrient transformations, including denitrification, and consequent loss of nitrogen would be minimal. Whereas the improved structure and higher carbon content of riparian soils, slows flows and improves the capacity of introduced nutrients to being intercepted or transformed.

Implications

The results from this study are experimental but do provide an indication of what may be occurring in the natural environment. The experiment was conducted over days and not weeks or months, thus providing a snapshot of the nutrient processing that occurs. It was identified by O'Toole *et al.* (2013) that the groundwater had a long very residence time and there was limited movement of groundwater to the stream. Therefore the increased rate of water movement in this experiment may have exacerbated the export of nutrients, nutrient transformations and trends that would occur in the riparian zone. Furthermore, only the top

0.5 m of soils were analysed and the processes and interactions occurring below this region are unknown. Groundwater flow to the stream was identified as being limited (O'Toole *et al.* 2013), reducing the potential for nutrient release to streams. However this experiment confirms that the paddock soils with Bassendean sands readily lose phosphorus following fertiliser application and rainfall, as noted in other studies (Summers *et al.* 1999; Barron *et al.* 2008).

The hypothesis that: *Riparian soils will export fewer nutrients than paddock soils due to improved soil characteristics* was shown to be partially correct. The higher carbon content of riparian soils slowed the rate of water movement, improved the phosphorus binding capacity of the soil and promoted denitrification. However, the increased carbon content also supported a greater microbial community and the input of extra nutrients (including labile carbon from manure) increased microbial respiration leading to release of iron-bound phosphorus into the groundwater. Within riparian soils there is a balance between phosphorus uptake and loss governed by soil carbon and physico-chemical conditions. The greater storage of phosphorus and nitrogen in the riparian soils lead to greater export from the soil columns and potentially from riparian zones if not managed correctly.

Key findings

- Water flow through riparian soils is nearly twice as slow as through paddock soils. This is due to the addition of organic matter from the riparian vegetation which reduces the pore size of the soil and increases its water holding capacity.
- Slower flow reduces the rate of nutrient input to streams.
- Slower flow increases residence time of water in the soil allowing greater nutrient transformation processes, such as denitrification, to occur. This results in an increased loss of nitrogen from riparian soils.
- There is greater release of nutrients from riparian and paddock columns following rainfall. Nutrients, primarily stored near the soil surface, are intercepted and leached following rainfall.
- Phosphorus export from riparian columns was greater than paddock columns. This is due to higher soil phosphorus concentrations in riparian soils and a result of high soil iron and carbon coupled with anoxic reducing conditions, which facilitates release of iron-bound phosphorus.
- The application of superphosphate fertiliser on paddock soils results in rapid mobilisation of phosphorus following rainfall.
- Input of fertiliser and cow manure has a priming effect in riparian soils, increasing microbial respiration. This contributes to the reduction, and loss, of nitrogen and the mobilisation of soluble phosphorus.

Recommendations

Management recommendations to improve nutrient uptake by riparian zones

- Fence riparian zones to keep out cattle
- Ensure appropriate fertiliser planning is in place through understanding soil types and fertilisation requirements and improve nutrient holding capacity of soils on agricultural land
- Maintain or improve the stores of carbon within riparian soils by protecting riparian vegetation from disturbance
- Native riparian vegetation must be protected where it exists and improved through appropriate management whenever possible (e.g. removal of weeds)
- Native riparian vegetation, providing a complex community of trees understorey, groundcover and streamside sedges, should be planted where it is lacking

Fence riparian zones to keep out cattle. Cattle are destructive in riparian vegetation (which plays a key role in nutrient uptake and adding organic material to the soil). Cattle urination and defecation add nutrients in close proximity to the stream and through the addition of both carbon and phosphorus can result in microbial release of stored phosphorus in the soil.

At Bingham Creek the soils are Bassendean sands, which have a poor phosphorus holding capacity. Therefore it is imperative to have an appropriate fertilisation plan in place (e.g using regular soil testing to inform appropriate fertiliser type and application rates) for these soils, as phosphorus readily leaches from fertiliser following rainfall. To limit phosphorus release from paddock soils, the binding capacity of the soil needs to be improved. This can be done through soil amendments which have shown to increase phosphorus adsorption of poor sandy soils (Summers *et al.* 1993).

Carbon plays an integral role in hydrology and nutrient dynamics of riparian soils. Improving soil carbon storage in the riparian zone could enhance nutrient interception and reduce the speed of water flow. The best way of doing this is through the protection of riparian vegetation and through planting more native vegetation. Increasing the carbon content of soils is a double-edged sword, as an increase in the labile fraction can potentially lead to nutrient release, however, the benefits outweigh the disbenefits. Increased carbon in the soil will further reduce the flow of water and increase residence times. Slower flows increase the opportunity for nutrient interception and promotes nitrogen removal through denitrification. Increased soil carbon improves soil structure and PRI of the soil, enhances the potential for phosphorus adsorption to occur and improves the riparian zone as a nutrient store. Carbon is of greater benefit in areas that are prone to nitrogen enrichment and not those that have soils high in iron-bound phosphorus. Microbial respiration is good for denitrification, however it can facilitate the release of iron-bound phosphorus in groundwater.

Riparian vegetation must be protected where it exists and be planted in regions where it is lacking. This will lead to slower surface and subsurface flows through the riparian zone, increase the storage potential of phosphorus and create conditions that are conducive to nitrogen removal. Riparian zones store significant nutrient loads which would be released to receiving waters if disturbed and soil is eroded. Healthy intact vegetation is required to maintain riparian nutrient uptake and storage.

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