

# Performance assessment of a multi-stage treatment system on Warnock's farm

A combined pond, constructed wetland and phosphorus sorption filter treatment system in the Waituna catchment

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# **Executive summary**

Treatment of drainage water from a permanently flowing, first-order stream on a Southland dairy runoff farm in the Waituna Catchment was assessed before and after passage through an existing duck pond supplemented with a constructed wetland and one of two parallel phosphorus sorption filters, a limestone rock filter and an oyster shell filter. The site was selected because the stream had high concentrations of total nitrogen (median 2.08 g m<sup>-3</sup>) and total phosphorus (median 0.415 g m<sup>-3</sup>).

The constructed wetland and phosphorus sorption filters were constructed in early 2015, and sampling started in September 2017 once emergent wetland plants were established. The combination of a constructed wetland and phosphorus sorption filter in series after a pond was anticipated to remove both nitrogen and phosphorus from drainage waters. The filter materials were chosen because of their ready local availability, low cost, non-toxic nature, and potential for safe re-use or disposal. Furthermore, the filter materials were naturally occurring and were reported in overseas studies to have a moderate to high affinity for phosphorus (by adsorption).

Although the duck pond was not constructed as part of the treatment system, as water passed through the duck pond there was a reduction in turbidity and suspended solids concentrations. Suspended solids concentrations were further reduced in downstream treatment modules (constructed wetland and lime rock filter), and visual clarity increased slightly.

The constructed wetland attenuated 64% of total nitrogen, which is higher than would be predicted based on performance of other constructed wetlands in New Zealand. Total organic nitrogen was the major form of nitrogen entering the wetland; the 47% reduction in total organic nitrogen accounted for most of the nitrogen attenuation. Attenuation of nitrate nitrogen was also high (97%), although wetland inlet concentrations were only a fifth of the total organic nitrogen concentration. It should be noted that limited performance data for this wetland at high flows mean it is not possible to determine whether these attenuation levels are typical of annual performance. There was no detectable total nitrogen removal in the duck pond, and negligible nitrogen removal in the phosphorus filters.

Phosphorus concentrations decreased in the duck pond – dissolved reactive phosphorus by 8%, and total phosphorus by 37%. These reductions were likely due to settling of particulate-associated phosphorus, sorption to sediment and uptake by plants and algae. Total phosphorus concentrations were reduced a further 75% in the wetland. Neither the limestone rock filter nor the oyster shell filter measurably reduced phosphorus concentrations.

The lack of detectable phosphorus removal by the filter media may have been due to:

- use of whole oyster shells rather than milled/ground shells (milling would have greatly increased the surface area of the medium and increased and made available many more phosphorus sorption sites)
- existing sorption sites may have become saturated in the first 2½ years of operation (prior to sampling and evaluation of phosphorus removal efficacy)
- lack of heat treatment of the filter media. Heat treatment would have converted some of the CaCO<sub>3</sub> in the filter media into CaO, which is much more effective for sorbing phosphorus and inducing phosphorus precipitation.

# 1 Introduction

Environment Southland is working with industry organisations such as DairyNZ to provide farmers with tools that they can use to mitigate nutrient losses from farming landscapes. Greater attention is directed at catchments that are highly sensitive to nutrient inputs. In this context, the Waituna catchment in Southland is very significant, because it drains into Waituna Lagoon, an 'intermittently closed open lake/lagoon (ICOLL)' (Scanes 2012; Schallenberg et al. 2017). ICOLLs are most sensitive to sediment and nutrient inputs of all estuary types due to long water residence times and limited interaction with the ocean when closed (Scanes 2012). Waituna Lagoon, a Ramsar wetland site of high ecological value,<sup>1</sup> is in a degraded condition because of excess inputs of nutrients and suspended solids over a prolonged period (Diffuse Sources and NIWA 2012). There has been a rapid decline in "high value seagrass" vegetation in Waituna Lagoon, and an increase in epiphytic and phytoplanktonic algae, along with sediment anoxia (Scanes 2012; Schallenberg et al. 2017).

Warnock's farm is a 424 ha. dairy runoff farm in the Waituna Lagoon catchment, drained by a nutrient-enriched stream (a tributary of Waituna Creek). In 2015, Environment Southland partnered with the landowner to construct an edge of field contaminant attenuation system. The aim was to reduce the concentrations of nitrogen and phosphorus in this stream. The 2,180 m<sup>2</sup> wetland has a catchment of 34 ha. (i.e., it is approximately 0.6% of the catchment area).

Sampling of the Warnock's farm treatment system began in September 2017, 2½ years after the system was constructed. In the study described in this report, the removal of suspended solids, nutrients (nitrogen and phosphorus, N and P respectively) and of faecal indicator bacteria (FIB) by the treatment system was assessed. This system comprised a constructed wetland and two phosphorus sorption filters – one containing untreated oyster shell and the other limestone rock chips. The constructed wetland was located downstream of an existing duck pond. It was uncertain how the duck pond would affect water quality, thus sampling was conducted up and downstream of the duck pond. Efficacy was determined in terms of capture of phosphorus, nitrogen, suspended solids and faecal indicator bacteria in farm drainage within the various components of the treatment system.

Suspended solids are attenuated primarily by settling and filtration. Reduction in suspended solids reduces turbidity and enhances visual clarity in the water.

FIB attenuation can occur though a number of processes. Solar inactivation occurs by exposure to ultra-violet (UV) radiation. Although FIB may also settle out of the water column, due to their small size (1-5  $\mu$ m) settling is very slow and not normally a major component of overall attenuation. FIB are also predated by protozoa and other microorganisms, either free-floating in the water column or on microbial biofilms onto which they adsorb.

Attenuation of nitrogen in polluted waters occurs by settling and mineralisation of organic forms, and microbial nitrification and denitrification of inorganic forms, or by their uptake into plant biomass. Nitrification requires aerobic conditions. In addition, nitrification rates are higher where nitrifiers have an attachment surface (e.g., plant stems or within a soil or gravel matrix); nitrifiers are slow growing and thus unattached nitrifiers can be washed out of a treatment system. Macrophytes

<sup>&</sup>lt;sup>1</sup> see <u>https://www.ramsar.org/wetland/new-zealand</u>

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assimilate dissolved inorganic nitrogen into their tissues, although this is typically at a lower rate than attenuation by microbes.

Attenuation of phosphorus occurs by plant uptake, precipitation, or by sorption onto minerals that bind negatively charged ions such as phosphate ( $PO_4^{3-}$ ). Plant uptake is considered a finite attenuation mechanism, as plants die and release assimilated nutrients. Precipitation requires the presence of elements such as calcium (Ca), iron (Fe), or aluminium (AI); typically precipitation only occurs under elevated pH conditions. Phosphorus also adsorbs onto materials containing these elements, however as sorption sites become occupied, phosphorus attenuation decreases. Indeed, treatment systems such as wetlands may become temporary sources of phosphorus as conditions within the sediments fluctuate between suitability for phosphorus capture or release. Phosphorus release is often associated with low oxygen conditions, and periods of elevated through-flow (Reddy et al. 1999; Monaghan 2008). Achieving consistently high levels of dissolved phosphorus removal in a constructed wetland often requires the addition of minerals, sorbents or filter materials which contain Ca, Fe or Al sites. These include bentonite, bauxite, limestone, oil shale ash, slags and light expanded clay aggregates (LECA) (Drizo et al. 1999; Ballantine and Tanner 2010; Vohla et al. 2011; McDowell and Nash 2012).

Both oyster shell and limestone rock chips contain calcium carbonate (CaCO<sub>3</sub>) and have been used in phosphorus sorption filters elsewhere (Hamester et al. 2012). While some direct binding of phosphorus to the calcium ions in CaCO<sub>3</sub> can occur, greater removal occurs when the pH of the incoming drainage water increases beyond about 10, due to calcium carbonate dissolution. Where this occurs, excess calcium ions will react with the phosphate, to precipitate as hydroxyapatite (a sparingly soluble precipitate), according to the reaction

## 10 $Ca^{2+}$ + 6 $PO_4^{3-}$ + 2 $OH^- \leftrightarrow Ca_{10}(PO_4)^*6(OH)_2 \downarrow$

This reaction indicates that the rate at which  $Ca^{2+}$  ions become available is important in controlling the rate of phosphorus removal by this mechanism – this is strongly determined by the pH of the water.

Crushed limestone is a relatively inexpensive medium for phosphorus sorption filters for use in surface flow wetlands (as in this study) and subsurface flow wetlands (Mateus et al. 2012). Crushed limestone has been used, along with the closely related dolomite (a calcium magnesium carbonate mineral<sup>2</sup>) in a number of constructed wetland studies to enhance attenuation of dissolved phosphorus (Johansson 1999; Hill et al. 2000; DeBusk et al. 2004). Mateus et al. (2012) used influent dissolved phosphorus concentrations of 2.3 - 20 g m<sup>-3</sup> (loading rates of 0.09 - 0.8 g m<sup>-2</sup>) to calculate effluent equilibrium concentrations of a limestone material (4.3-17.7 mm size range,  $d_{10}$  and  $d_{60}$  respectively<sup>3</sup>). At inlet concentrations of approximately 7–11 g m<sup>-3</sup>, removal efficacy ranged from 53–80%, although the authors noted that chemical precipitation associated with the calcium carbonate filter material may have contributed to the observed removal rather than sorption. Roques et al. (1991) reported attenuation of 20 g of P kg<sup>-1</sup> of dissolved reactive phosphorus by half-burnt dolomite<sup>4</sup>. In a review paper, Johansson Westholm (1999) reported dissolved phosphorus attenuation associated with limestone treatment ranging from 0.003–20 g kg<sup>-1</sup> of filter material, with

<sup>&</sup>lt;sup>2</sup> Limestone is a somewhat generic term, embracing mineral deposits that are composed of carbonates of calcium and magnesium and is sometimes used to refer to magnesian limestone, dolomitic limestone and dolomite. (MacIntire and Stansel 1953).

 $<sup>^3</sup>$   $d_{10}$  and  $d_{60}$  are the 10% and 60% sizes of the cumulative mass.

<sup>&</sup>lt;sup>4</sup> Dolomite is heat treated to induce partial decomposition to magnesium oxide and calcium carbonate with subsequent dissociation of calcium carbonate to calcium oxide.

sorption as the removal mechanism at low inflow concentrations, whereas precipitation was considered to be the main removal mechanism at higher concentrations.

Oyster shells have been used in phosphorus sorption filters and subsurface-flow constructed wetlands to adsorb phosphorus. Seo et al. (2005) found that the efficacy of phosphorus adsorption increased as the particle size of ground oyster shell media was reduced, observing a maximum phosphorus absorption capacity of 16 g kg<sup>-1</sup> for 0.1–2 mm medium, whereas Park and Polprasert (2008) calculated absorption capacities of 24.5 and 26 g P kg<sup>-1</sup> for oyster shells crushed to >0.6 mm and 0.3–0.6 mm respectively.

# 2 Project brief

NIWA was contracted by DairyNZ to "analyse flow, sediment, nutrient and *E. coli* data supplied by Environment Southland for the Warnock's constructed wetland". Data were supplied for the period September 2017 to June 2019. We analysed these data to describe how the values or concentration of various water quality variables changed as water flowed through the various units of the treatment system. We reported these changes as the difference in measured values between inflow to the duck pond and the outflow of each subsequent treatment unit. This provides removal efficacy values for each treatment unit sequentially, as well as the overall treatment system. We have expressed these differences as a proportion of the inflow value or concentration in the outflow. Where possible, we have included recommendations on how the performance of the system could be improved.

# 3 Methods

An open water wetland (2180 m<sup>2</sup>) planted with native emergent wetland plants was constructed at Warnock's farm in 2014/2015. The inflow to the constructed wetland passed through an existing duck pond (~4221.5 m<sup>2</sup>), which received drainage water from a permanently flowing first-order stream arising in a farm paddock (Figure 1). The wetland outflow was conveyed via an open channel into a simple flow splitter which divided the flow between two phosphorus sorption filters constructed downstream of the wetland (Figure 2). One filter contained limestone and the other contained oyster shell halves. Each filter comprised a 1 m deep, 25 x 5 m horizontal flow, geotextile lined bed. The first flow splitter did not divide flow evenly and was replaced with an advanced-design flow splitter in early 2017.



**Figure 1:** Location of Warnock's Farm wetland and phosphorus filters. The catchment boundary has been generated in ARC GIS (ESRI). The boundary of this catchment is outlined in teal. Flow paths have been shown with a light blue line. The constructed wetland location is outlined by a solid yellow line (satellite imagery taken before wetland construction). The duck pond is outlined in a dashed yellow line.

Monthly grab water quality samples were taken from five locations (Figure 2) in the treatment system.



**Figure 2:** Satellite image of Warnock's farm treatment site. Sampling locations are identified. (Credit: Google Earth).

The sampling locations in Figure 2 are:

- A Duck pond inlet (NZTM; 1261086 N, 4848990 E).
- B Duck pond outlet (NZTM; 1261257 N, 4848919 E) (Figure 3).
- C Wetland outlet (NZTM; 1261430 N, 4848954 E) (Figure 4).
- D Oyster shell filter outlet (NZTM; 1261453 N, 4848936 E) (Figure 5 & Figure 6).
- E Lime rock filter outlet (NZTM; 1261464 N, 4848940 E) (Figure 7).



Figure 3: Duck pond at outlet. Chris Owen, Southern Waterways. (Credit: Aquatech).



**Figure 4:** Constructed wetland looking from inflow end. Surface flow wetland planted with the native tall spike rush, kuta (*Eleocharis sphacelata*). (Credit: Aquatech/Environment Southland).



Figure 5: Oyster shell filter, with inlet in the foreground. (March 2015). (Credit: Chris Tanner, NIWA).



**Figure 6:** Oyster shell filter taken from the outlet end. The outlet is shown in the foreground. (February 2017). (Credit: Chris Tanner, NIWA). Note that the oyster shells are un-crushed.



Figure 7: Limestone rock filter, with inlet in the foreground. (March 2015). (Credit: Chris Tanner, NIWA).

Sampling was undertaken on 10 dates between September 2017 and June 2018. Sampling time varied between 7:00 a.m. and 1:45 p.m.

Samples were analysed at Hill Laboratories (Christchurch). Analyses undertaken on the samples are listed in Table 1 with methods and reported detection limits. Dissolved oxidised nitrogen refers to the sum of nitrate and nitrite. In most instances, nitrite is a small component of oxidised nitrogen, and the combined results are referred to as nitrate nitrogen throughout this report. Field observations included flow, clarity, odour, weather and wind speed. Figure 8 shows a water sample being collected from one of the outlets.

Where laboratory or field data were censored because they were greater or less than the analytical detection limits, they have been recorded with ">" or "<" respectively. Median values have been used throughout this report for assessing pollutant removal. For calculation of arithmetic mean<sup>5</sup> values, "less than" values have been assigned a value of half the analytical limit of detection. "Greater than" values have been assigned the maximum value for the analytical technique<sup>6</sup>.

Treatment efficacy was calculated using this equation:

$$Treatment \ efficacy \ (\%) = \frac{Inflow \ value - outflow \ value}{Inflow \ value} \times 100$$

where value may be concentration or some other physico-chemical metric, e.g., turbidity or visual clarity.

<sup>&</sup>lt;sup>5</sup> Arithmetic mean values are recorded in Appendix A to allow comparison with other studies which only report mean values.

<sup>&</sup>lt;sup>6</sup> This only occurred for visual clarity, where the black disc was still visible at the end of the measuring tube.

Variables	Method	Detection limit
Visual clarity	Black disc, 20 mm diameter.	Maximum of 0.98 m
Conductivity	Field meter.	
Escherichia coli	Membrane filtration, count on mFC agar, incubated at 44.5°C for 22 hours, confirmation. APHA 9222 G, 22nd ed. 2012.	1 colony forming unit (cfu) per 100 ml depending on dilution of sample.
Nitrate	Filtered sample. Total oxidised nitrogen. Automated cadmium reduction, flow injection analyser. APHA 4500-NO <sub>3</sub> - I 22nd ed. 2012 (modified).	0.002 g m <sup>-3</sup>
Ammonium	Filtered sample phenol/hypochlorite colourimetry. Flow injection analyser. (NH <sub>4</sub> -N = NH <sub>4</sub> <sup>+</sup> -N + NH <sub>3</sub> -N). APHA 4500-NH <sub>3</sub> H (modified) 22nd ed. 2012. (APHA 2012).	0.010 g m <sup>-3</sup>
Total nitrogen	Calculation: Total Kjeldahl N + nitrate-N + nitrite-N (unfiltered sample). Please note: The default detection limit of 0.05 g/m <sup>3</sup> is only attainable when the TKN has been determined using a trace method utilising duplicate analyses. In cases where the detection limit for TKN is 0.10 g/m <sup>3</sup> , the default detection limit for total nitrogen will be 0.11 g/m <sup>3</sup> .	0.11 g m <sup>-3</sup>
Dissolved reactive phosphorus	Filtered sample. Molybdenum blue colourimetry. Flow injection analyser. APHA 4500-P G (modified). 22nd ed. 2012.	0.004 g m <sup>-3</sup>
Total phosphorus	Total phosphorus digestion, ascorbic acid colorimetry (unfiltered sample). Discrete Analyser. APHA 4500-P B & E (modified from manual analysis) 22nd ed. 2012. Also modified to include the use of a reductant to eliminate interference from arsenic present in the sample. NWASCA, Water & Soil Miscellaneous Publication No. 38, 1982.	0.004 g m <sup>-3</sup>
Total suspended solids	Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2 - 1.5μm), gravimetric determination. APHA 2540 D 22nd ed. 2012.	3.0 g m <sup>-3</sup>
Turbidity	Field meter.	0.1 NTU
Temperature	Field meter.	
Dissolved oxygen (% saturation and g m <sup>-3</sup> )	Field meter.	

## Table 1:Laboratory and field analyses.



Figure 8: Sample collection from one of the outlets. (Credit: Aquatech/Environment Southland).

A temporary hydrometric station was installed downstream of the duck pond prior to the beginning of sampling (just below site B, see Figure 9). Stage height at this station was recorded every 10 minutes. Flow was gauged at this location on 8 occasions. The continuous stage record was converted to a continuous flow record by applying the stage-flow relationship developed from the 8 gaugings. The shallow depth at this and other flow monitoring sites introduced unavoidable uncertainty to the accuracy of the flow estimates, particularly at lower flows. Flow was also gauged at the inflow to the filter beds (Site C) and at the outlet of the duck pond on 3 occasions at both sites.



**Figure 9: Water depth monitoring location.** Dianne Elliotte, Aquatech. (Credit: Aquatech/Environment Southland). Note iron floc in the water.

# 4 Results

Median values for water quality variables are presented in Table 2 for each stage of the treatment system. The table shows percent change in median values for key variables within each stage, as well as overall percentage change from the inflow to the duckpond to the outflows of the two phosphorus filters. Raw data for all field and laboratory measurements are presented in Appendix A along with median and mean values. Time series graphs of concentrations of key water quality variables are presented in Appendix B, while time series graphs of loads of DRP, TP and TN are presented in Appendix C.

 Table 2:
 Summary table of median values and percent changes for water quality variables. Note that a positive percentage change indicates an increase in the median value of a variable (net production or export), and a negative change percentage indicates a reduction in the median value of a variable (net removal). Reductions have been shaded green (representing improvements), except for black disc clarity and dissolved oxygen, where increases are shaded green.

Variable		Duck Pond		Wetland		Total % change (Pond & Wetland)	Lime Rock	< Filter	Oyste	er Filter	Total % change from duck pond inlet		
	Inlet value	Outlet value.	% change	Outlet value	% change	, and the second s	Outlet value.	% change	Outlet value	% change	Pond, Wetland & Pond, Wetland Lime Rock Oyster		
Temperature (°C)	11.6	13.2		13.4			13.6		13.0				
Turbidity (NTU)	5.1	1.8	-64%	2.8	+51%	-46%	<0.1	>-99%	0.4	-85%	>-99%	-92%	
Black disc clarity (m)	0.65	0.67	+3%	0.83	+24%	+28%	0.90	+8%	0.85	+2%	+38%	+31%	
Dissolved oxygen (g m <sup>-3</sup> )	4.78	7.80	+63%	7.63	-2%	+60%	4.23	-45%	3.68	-52%	-3%	-23%	
Suspended solids (g m <sup>-3</sup> )	18	3.0	-83%	<3.0	-50%	>-83%	<3.0	0%	<3.0	0%	>-83%	>-83%	
Nitrate-N (g m <sup>-3</sup> )	0.62	0.29	-53%	0.009	-97%	-99%	0.116	+1189%	<0.002	-78%	-81%	>-99%	
Ammoniacal-N (g m <sup>-3</sup> )	0.079	0.072	-8%	<0.010	-93%	-87%	<0.010	0%	0.115	+2200%	-87%	+46%	
Total organic nitrogen (g m <sup>-3</sup> )	0.76	1.015	+33%	0.534	-47%	-30%	0.447	-16%	0.528	-1%	-42%	-31%	
Total-N (g m <sup>-3</sup> )	2.08	2.30	+11%	0.83	-64%	-60%	0.63	-25%	1.11	+33%	-70%	-47%	
DRP (g m <sup>-3</sup> )	0.084	0.077	-8%	0.010	-87%	-88%	0.037	+265%	0.035	+250%	-57%	-58 %	
Total phosphorus (g m <sup>-3</sup> )	0.415	0.260	-37%	0.065	-75%	-84%	0.081	+26%	0.118	+83%	-80%	-72%	
<i>E. coli</i> (cfu 100 ml <sup>-1</sup> )	650	130	-80%	17	-87%	-97%	8	-52%	20	+21%	-99%	-97%	

## 4.1 Flow

There was continuous flow throughout the sampling period (Figure 10). Flow was generally low over the spring/summer-early autumn period, with 65% of flows at or below 2 L s<sup>-1</sup> and 85% at or below 7 L s<sup>-1</sup> (Figure 11). Flows increased from April 2018 onwards (late autumn-winter period), with a median daily flow of 6 L s<sup>-1</sup> and peaks close to 70 L s<sup>-1</sup>. Hydraulic loading rates (HLR) and retention times (HRT) for the wetland and phosphorus filters are presented in Table 3.

Flow rates (L s <sup>-1</sup> )	Wetland HLR (m yr <sup>_1</sup> )	Wetland HRT (Days)	Filter HLR (m yr-1)	Filter HRT (Days)
2	29	3.6	505	0.72
7	101	1.0	1766	0.21
20	289	0.4	5046	0.07
70	1013	0.1	17660	0.02

Table 3:	Constructed wetland and phosphorus filter hydraulic loading rates and hydraulic retention
times. Estima	tes of HRT assume that the wetland vegetation occupied 5% of wetland volume, and that both
filters had a p	orosity of 0.32 – equivalent to medium gravel.

Only one sample date coincided with elevated flow conditions (20 L s<sup>-1</sup> on 21 June, 2018). Five sets of water quality samples were collected during baseflow conditions (when the flow was around 2 L s<sup>-1</sup>) and a further two sets were collected when the flow was approximately 5 L s<sup>-1</sup>.



Figure 10: Flow at flow recording station below site B (duck pond outlet). Sampling occasions are marked with an orange dot.





## 4.2 Turbidity and visual clarity

Turbidity data are summarised in Figure 12. There were decreases in median turbidity in the duck pond relative to inflow turbidity, and in the two phosphorus sorption filters, although not in the constructed wetland. Overall reductions in turbidity from the duck pond inlet to the outlets of the lime rock filter and in the oyster shell filter were >99% and 92% respectively (Table 2).



**Figure 12:** Box plots of turbidity for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

Visual clarity showed a general inverse relationship to turbidity as can be seen in Figure 13, although with high variability ( $R^2 = 0.37$ ). The median visual clarity at the inflow to the duck pond was 0.65 m, increasing slightly in the pond (median 0.67 m, Figure 14). Visual clarity was higher in the outlet of the wetland (0.83 m) and in the two filters (0.90 m in the lime rock filter and 0.85 m in the oyster shell filter) than in the inlet to either stage. Visual clarity sometimes exceeded the length of the black

disc viewing tube in the wetland (2 occasions), lime rock filter (2 occasions) and the oyster shell filter (1 occasion).

Overall improvement in median visual clarity (increase) from the duck pond inlet to the outlets of the lime rock filter and in the oyster shell filter were 38% and 31% respectively (Table 2).



**Figure 13:** Relationship between turbidity and visual clarity. One value was excluded on the basis of it being greater than 3.0 x interquartile range from the 75<sup>th</sup> percentile and therefore considered to be an extreme outlier.



**Figure 14:** Box plots of black disc clarity for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

## 4.3 Suspended solids

There was a weak positive relationship between suspended solids and turbidity (Figure 15,  $R^2 = 0.47$ ). At the inlet to the duck pond, the median concentration was 18 g m<sup>-3</sup>, while at the duck pond outlet it had reduced to 3 g m<sup>-3</sup> (83% attenuation, Figure 16). Minor reductions in median concentrations also occurred in the constructed wetland, although the constructed wetland outlet median value was below the detection limit of 3.0 g m<sup>-3</sup>, thus attenuation could not be accurately calculated. Similarly, median TSS concentrations in the outlets of both filters were <3.0 g m<sup>-3</sup>. Overall reduction in median suspended solids concentrations from the duck pond inlet to the outlets of both phosphorus filters was > 83% (Table 2). Although accumulation of solids must be occurring in the filters, this was not visible or sufficient to cause obvious clogging of the beds.



Figure 15: Relationship between suspended solids and turbidity.



**Figure 16:** Box plots of suspended solids for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

## 4.4 Dissolved oxygen

Median dissolved oxygen concentrations increased by 63% in the duck pond. The median oxygen concentration value of 7.63 g m<sup>-3</sup> in the outlet of the constructed wetland was little different to the inflow (7.80 g m<sup>-3</sup>). Median dissolved oxygen concentrations decreased to 4.23 g m<sup>-3</sup> and 3.68 g m<sup>-3</sup> in the lime rock filter and the oyster shell filter respectively.



**Figure 17:** Box plots of dissolved oxygen concentrations for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

## 4.5 Nitrogen

## 4.5.1 Nitrate nitrogen

Nitrate nitrogen comprised 30% of the inflow TN load to the duck pond with a median concentration of 0.62 g m<sup>-3</sup> (Figure 18), and a maximum of 3.9 g m<sup>-3</sup> on the date when inflow volumes were also the highest (see Table A1 in Appendix A for details). On this occasion, the wetland, limestone chip and oyster shell filter effluent concentrations were also the highest recorded, at 2.8, 3.1 and 3.2 g m<sup>-3</sup> respectively (Tables A4-A5). The median nitrate nitrogen concentration decreased to 0.29 g m<sup>-3</sup> in the duck pond outlet, a 53% reduction. Further attenuation occurred in the wetland, reducing the median nitrate nitrogen concentration to 0.009 g m<sup>-3</sup> (97% reduction in this module, or 99% overall). However during the winter months when flows were higher and temperatures were lower, values in the wetland outlet exceeded those in the wetland inlet. The median nitrate nitrogen concentration increased in the lime rock filter (median 0.116 g m<sup>-3</sup>) but decreased in the oyster shell filter (median outlet concentration of <0.002 g m<sup>-3</sup>). However, it should be noted that these filters were not designed to remove nitrate nitrogen, and that the increase was relatively small compared with the ranges of nitrate recorded throughout the system (Figure 18). Overall median concentration reduction of nitrate nitrogen from the duck pond inlet through to the lime rock filter outlet was 81%, and to the outlet of the oyster shell filter was >99%.



**Figure 18:** Box plots of nitrate-N concentrations for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

## 4.5.2 Ammoniacal nitrogen

In the duck pond inflow, ammoniacal nitrogen was generally a smaller component (<5%) of total nitrogen than nitrate nitrogen, although maximum values in each component of the treatment system exceeded 1 g m<sup>-3</sup> (Figure 19). An increase in the maximum values occurred in the duck pond (to 5.50 g m<sup>-3</sup>). The median concentration in the constructed wetland outlet was below the laboratory detection limit (<0.010 g m<sup>-3</sup>), as it also was after the lime rock filter. There was however an increase in the median ammoniacal nitrogen concentration in the oyster shell filter (increasing from <0.010 g m<sup>-3</sup> at the inlet to 0.115 g m<sup>-3</sup> at the outlet). Overall ammoniacal nitrogen was





**Figure 19:** Box plots of ammoniacal nitrogen concentrations for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars. Note the y-axis has a log<sub>10</sub> scale as the data ranged over several orders of magnitude.

## 4.5.3 Total organic nitrogen

Total organic nitrogen (37% of TN in the inflow to the duck pond) is shown in Figure 20. As noted above, an increase in total organic nitrogen is apparent in the duck pond, increasing from a median of 0.76 g m<sup>-3</sup> at the inlet to 1.015 g m<sup>-3</sup> at the outlet (33% increase). Attenuation of total organic nitrogen occurred mainly in the constructed wetland (47% reduction in the median concentration from the constructed wetland inlet). Some additional attenuation occurred in the lime rock filter (16% reduction), but minimal change occurred in the oyster shell filter (1% reduction). Overall attenuation from the duck pond inlet to the lime rock filter outlet was 42%, while from the duck pond inlet to the lime rock 31%.





## 4.5.4 Total nitrogen

The median total nitrogen concentration in the inlet to the duck pond was 2.08 g m<sup>-3</sup>. This concentration increased to 2.30 g m<sup>-3</sup> (11%) at the outlet, primarily due to an increase in total organic nitrogen. Substantial TN attenuation was measured in the constructed wetland, largely due to a 47% reduction in total organic nitrogen, the highest nitrogen removal observed in this system. Nitrate nitrogen decreased by 97%. At the wetland inlet the relative contribution of nitrate nitrogen to total nitrogen was much lower than at the inlet to the duck pond. Thus, even though 97% of nitrate entering this module was removed (~0.28 g m<sup>-3</sup>), this reduction in total organic nitrogen (~0.48 g m<sup>-3</sup>). The median total nitrogen concentration at the constructed wetland outlet was 0.83 g m<sup>-3</sup> (64% reduction across all sampling points). Attenuation of total nitrogen was reduced during the winter months when temperatures were lower and flows were higher (Appendix B).

Further attenuation of total nitrogen occurred in the lime rock filter, with a median of 0.63 g m<sup>-3</sup> in the outlet. In contrast, there was a 33% increase in median total nitrogen in the outlet of the oyster shell filter (median of  $1.11 \text{ g m}^{-3}$ ). Overall removal through the system – from the duck pond inlet to the outlets of the lime rock filter and the oyster shell filter – were 70% and 47%, respectively (Table 2).





## 4.6 Phosphorus

#### 4.6.1 Dissolved reactive phosphorus

The median concentrations of DRP in the inlet and outlet of the duck pond were 0.084 g m<sup>-3</sup> and 0.077 g m<sup>-3</sup> respectively (8% attenuation). Attenuation within the wetland was 87%, with the median DRP concentration in the wetland outlet decreasing to 0.010 g m<sup>-3</sup>. Median outflow concentrations from the filters were higher than at their inlets – 0.037 g m<sup>-3</sup> and 0.035 g m<sup>-3</sup> in the lime rock filter and oyster shell filter, respectively. Overall DRP attenuation through the system – from the duck pond inlet to the outlets of the lime rock filter and the oyster shell filter – were 57% and 58% respectively (Table 2).



**Figure 22:** Box plots of dissolved reactive phosphorus concentrations for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

## 4.6.2 Total phosphorus

Total phosphorus concentrations through the treatment system are shown in Figure 23. Median total phosphorus concentrations in the inlet and outlet of the duck pond were 0.415 g m<sup>-3</sup> and 0.260 g m<sup>-3</sup>, respectively (37% attenuation). Further attenuation occurred in the constructed wetland, with a median concentration at the outlet of 0.065 g m<sup>-3</sup> (75% attenuation in the wetland, rising to a total of 84% when combined with the duck pond attenuation).

The median total phosphorus concentration in the outlet of the lime rock filter was 0.081 g m<sup>-3</sup>, a 26% increase from its inlet value. The median total phosphorus concentration in the outlet from the oyster shell filter was 0.118 g m<sup>-3</sup>, an 83% increase. Overall reduction within the combined systems from the duck pond inlet to the lime rock and oyster shell filter outlets was 80% and 72%, respectively. As noted for DRP, none of the removal is attributable to the phosphorus filters.



**Figure 23:** Box plots of total phosphorus concentrations for the five monitoring sites. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars.

## 4.7 Faecal bacteria

The median concentration of the faecal indicator bacterium *Escherichia coli* (*E. coli*) at the inflow to the duck pond was 650 colony forming units (cfu) 100 mL<sup>-1</sup>, which decreased to 130 cfu 100 mL<sup>-1</sup> at the duck pond outlet (80% reduction in concentration) (Figure 24). The median *E. coli* concentration in the outflow from the constructed wetland was 17 cfu 100 mL<sup>-1</sup>, equivalent to an 87% reduction, or a 97% reduction between the duck pond inlet to the wetland outlet. The median *E. coli* concentration in the outflow from the lime rock filter was 8 cfu 100 mL<sup>-1</sup> (52% removal from the filter inlet). The median outflow concentration from the oyster shell filter increased to 20 cfu 100 mL<sup>-1</sup>, equivalent to a 20% increase. Overall reductions were nearly two orders of magnitude (99% in the duck pond/constructed wetland/lime rock filter and 97% in the duck pond/constructed wetland/oyster shell filter). Overall DRP attenuation through the system – from the duck pond inlet to the outlets of the lime rock filter and the oyster shell filter – were 99% and 97% respectively (Table 2). *E. coli* attenuation occurred both during low and high flow periods (Appendix B).



**Figure 24:** *E. coli* concentrations. Box and whisker plots show 25<sup>th</sup> and 75<sup>th</sup> percentiles (box), and maximum and minimum values (whiskers). Median values are shown with black bars. Note log scale on y-axis.

## 4.8 Contaminant load estimation using regression modelling

We explored several options to create models to describe the relationship between the concentrations of water quality variables and discharge at key locations in the pond-wetland-filter treatment system. Should robust relationships be identified (indicated by statistical metrics such as the coefficient of determination), the models may be used to estimate the concentration of a water quality variable for each corresponding measured flow value. This would provide a continuous record of concentration. Multiplying the concentration estimate by the flow and adjusting the units provides estimates of load or flux, expressed as mass/time. Comparing loads or fluxes estimated for the inlet and outlet of a treatment unit (e.g., the duck pond, or a filter bed), provides more realistic estimates of the efficacy of the treatment unit. Examples of models at key locations in the treatment wetland complex are provided in Appendix D.

Even though the number of grab samples for which a flow estimate exists was low, in some cases, the relationship was reasonably strong (e.g., for nitrate nitrogen in the duck pond inflow, the  $R^2$  value was 0.94). For the duck pond outlet however, the relationship was weaker ( $R^2 = 0.7$ ). The time-series of loads calculated with these two models is shown in Figure 25, along with instantaneous loads estimated using the grab sample values.

Points to note:

- Under low flow conditions the models overestimate nitrate nitrogen loads in both the inflow and outflow.
- Under baseflow conditions, the model estimates indicated that the duck pond is a net exporter of nitrate nitrogen (i.e., inflow loads and smaller than outflow loads).
- Under slightly higher flow conditions, however, the inflow load always exceeded the outflow load (all of the periods of elevated flow).
- Under high flow conditions, the models predict that the duck pond reduced the nitrate nitrogen load by up to two orders of magnitude.

The number of data points used to develop these models was very limited, and there are very few data points for periods of elevated flow. These factors limited the conditions under which the models would provide realistic estimates. For example, in Figure 25, the grab samples illustrate that the amount of nitrate nitrogen entering and leaving the duck pond was underestimated by the model. Further, in February and March of 2018 the duck pond was a source of nitrate N, but the model was not able to replicate this. Both is these issues are due to the limited number of calibration data points upon which the model is based.



Figure 25: Modelled and grab sample values of nitrate/nitrate nitrogen (NNN) loads.

In the case of the phosphorus sorption filters, it was not possible to compare modelled estimates of inflow and outflow mass, because there was no apparent relationship between discharge and DRP concentrations in the inflow to the filter beds.

These prediction difficulties indicate that additional calibration data are required to provide realistic estimates of inflow and outflow loads. At this time we have limited our assessment of the contaminant removal efficacy to comparing inflow and out flow concentrations and instantaneous loads derived from grab sample concentrations and flows at time of sampling.

# 5 Discussion

## 5.1 Duck pond water quality

As noted in the introduction, the duck pond was not constructed to treat stream water, and it was unclear prior to commencing the study whether it would impair water quality due to phytoplankton growth (increasing suspended solids and turbidity and reducing visual clarity). However, improvements in almost all of the water quality variables occurred in the duck pond e.g. increased median dissolved oxygen concentration and visual clarity (while reducing turbidity), and reduced median concentrations of suspended solids, nitrate nitrogen, ammoniacal nitrogen, total nitrogen, DRP, total phosphorus and *E. coli*. It appears the duck pond was acting like a sedimentation pond, settling out particulate material and reducing turbidity.

It is likely that attenuation of dissolved nutrients (nitrate nitrogen and DRP) was due to uptake by marginal macrophytes, planktonic algae and submerged macrophytes. As there were improvements in visual clarity, turbidity and suspended solids, any growth of planktonic algae within the duck pond must have been offset by settling of solids. In addition, attenuation of nitrate nitrogen may be occurring at the base of the duck pond due to denitrification in anoxic sediments.

Photosynthesis by macrophytes and planktonic algae may explain the increase in median dissolved oxygen concentrations in the duck pond, in addition to diffusion from the atmosphere.

TN concentrations increased by 11% in the duck pond (primarily due to increase in total organic nitrogen – median concentration increased by 33%). Although this increase may have been due to growth of planktonic algae, there was no increase in the median suspended solids concentration.

Mechanism which may contribute to the attenuation of FIB such as *E. coli* in the duck pond are solar inactivation from UV in solar radiation, as well as microbial predation.

## 5.2 Constructed wetland water quality

At a median flow rate of 2 L s<sup>-1</sup>, the wetland had an HLR of 29 m yr<sup>-1</sup>. This is close to, but a little below the median for New Zealand constructed wetlands of 34 m yr<sup>-1</sup> (Woodward et al. 2020). The constructed wetland improved water quality overall, increasing the median visual clarity, while decreasing median suspended solids, nitrate nitrogen, ammoniacal nitrogen, total organic nitrogen, DRP, total phosphorus and *E. coli* concentrations. The increase in turbidity in the outlet of the constructed wetland does not match the reduction in suspended solids or increase in visual clarity. We believe this is due to the weakness of the relationship between these variables, evident in Figure 13 and Figure 15.

Surface flow constructed wetlands remove pollutants through several processes. Suspended solids may settle out in the water column and dissolved nutrients are taken up by emergent macrophytes. Plants provide other important functions in constructed wetlands. Their stems provide an attachment surface for microbes such as nitrifiers, allowing conversion of ammoniacal nitrogen to nitrate. The plants also contribute oxygen into the soil at the base of the wetland, providing additional sites for nitrification. In addition, during colder months, plants die back and drop their leaves and stems into the water. This accumulates at the base of the wetland and forms a layer of organic matter which acts as an energy source for denitrification. Where plant densities are high, they shade the water surface, reducing the potential for planktonic algal growth. We note that in Figure 4,

plants occupy no more than half of the available area. Despite this, there is little evidence that algal biomass increased in the wetland.

Tanner et al. (New Zealand Guidelines for Constructed Wetland Treatment of Tile Drainage, 2010) have developed a relationship between the area of a wetland as a proportion of the catchment delivering drainage water, and wetland performance in terms of nitrate removal. As can be seen in Figure 26, nitrate nitrogen removal is greater in wetlands which are large relative to their catchment size. This graph indicates that the majority of constructed wetlands occupying 1% of a catchment would be expected to remove between 12% and 32% of incoming nitrate nitrogen. The apparent observed attenuation in this wetland approached 97%, However, nitrate nitrogen concentrations were higher in the wetland outlet than the wetland inlet during the colder winter months when flow rates were also higher. The scarcity of samples at higher flows suggest the apparent high percentage removal based on median values is probably an overestimate.

TN reduction was 64%, compared with a range of 16 to 30% reported by Woodward et al. (2020) for New Zealand constructed wetlands receiving surface runoff and drainage water. Thus the TN removal performance of this wetland appears better than would be expected from guideline predictions, and may be a reflection of lower than usual hydraulic loading rates. However, the combination of limited data collected during high flow events and a single flow monitoring location means it is not possible to state whether the high TN attenuation level represents typical annual performance of this wetland.



**Figure 26:** Relationship between constructed wetland size relative to it contributing catchment and nitrate-N removal for New Zealand constructed wetlands. Taken from the New Zealand Guidelines for Constructed Wetland Treatment of Tile Drainage (Tanner et al. 2010).

Woodward et al. (2020) report a range of mass reductions of total phosphorus in New Zealand constructed wetlands of 20 to 59%. Thus the 75% reduction reported in this study is somewhat higher than expected. While some phosphorus will be taken up by plants, and some may end up in the layer of organic matter at the base of the wetland, these are considered finite sinks, with phosphorus released into the overlying water, as organic matter is degraded under anoxic conditions.

As more than half of the constructed wetland surface was unshaded, similar *E. coli* attenuation processes considered to have occurred in the duck pond are likely to have occurred in the constructed wetland; solar inactivation and microbial predation.

## 5.3 Lime rock filter

Median input concentrations of DRP and total phosphorus to the phosphorus sorption filters were 0.010 g m<sup>-3</sup> and 0.065 g m<sup>-3</sup> respectively. Median outlet concentrations from the lime rock filter were 0.037 g m<sup>-3</sup> and 0.081 g m<sup>-3</sup>, increases of 265% and 26% respectively. As noted in the introduction, for phosphorus precipitation to occur with CaCO<sub>3</sub>, pH needs to exceed 10 (e.g. Vohla et al. 2011). In a review paper, Vohla et al. (2011) reported pH levels ranging from 7.2 to 8.9 in five phosphorus sorption studies using limestone without heat pre-treatment. pH was not measured during the assessment of Warnock's wetland; but it appears unlikely that conditions within the filters would have provided pH values that would have enabled phosphorus precipitation by CaCO<sub>3</sub>. In addition, the filter had been in place for over 2½ years prior to this period of sampling, and readily available sorption sites may have become saturated. Based on the apparent release of phosphorus from the lime rock filter, it appears likely that phosphorus which had previously been attenuated within the filter was being released during this study.

In addition, overseas trials showing substantial phosphorus removal using minerals containing calcium tend to have used much higher inlet concentrations of phosphorus than those recorded in drainage water at Warnock's farm. For example, Vohla et al. (2011) noted that natural (i.e., without heat pre-treatment) products with CaO content up to 37% were able to reduce phosphorus levels down to 2 g m<sup>-3</sup>, but they did not observe phosphorus removal below these concentrations. Similarly, Mateus et al. (2012) tested a planted subsurface flow wetland filled with fragmented limestone which naturally contained up to 55% CaO; they recorded P removal of up to 80% for over two months. However, the average concentration in their influent solution was 9 g m<sup>-3</sup> with an average effluent concentration of 1.8 g m<sup>-3</sup>. Both of these values were much higher than the maximum phosphorus concentration in the inlet to the filters recorded in the Warnock's trial (0.260 g m<sup>-3</sup> at the wetland outlet).

In the Warnock's farm study, factors which may have combined to limit phosphorus removal include:

- influent phosphorus concentrations below a minimum concentration for effective phosphorus removal
- insufficient CaO in the limestone<sup>7</sup>
- sorption sites may have become saturated in the 2½ year interval before testing began, and

<sup>&</sup>lt;sup>7</sup> While limestone may naturally contain some CaO, to increase its content, CaCO<sub>3</sub>-containing minerals are subjected to heat treatment in a furnace in air (referred to as calcination or lime-burning). The resultant product is referred to as "burnt lime". A similar procedure can be applied to materials composed of CaCO<sub>3</sub> such as oyster shells.

 while it is conjecture, pH concentrations are unlikely to have exceeded 10, the value at which untreated limestone has been shown to effectively cause phosphorus coprecipitation with Ca ions.

## 5.4 Oyster shell filter

Similar to the lime rock filter, phosphorus release was recorded from the oyster shell filter with median outlet values of DRP and total phosphorus of 0.035 g m<sup>-3</sup> and 0.118 g m<sup>-3</sup>, respectively (250% and 83% increases). There are many factors that could have influenced the performance of the oyster shell filters used in this system.

The international literature presents contrasting outcomes from assessments of phosphorus attenuation in oyster shell filters. Kwon et al. (2004) found phosphorus removal did not occur with crushed (but otherwise unaltered) oyster shell filters, whereas after heat pre-treatment, high rates of removal (68–98%) were recorded. These results differ from those of both Seo et al. (2005) and Park and Polprasert (2008), where up to 98% of total phosphorus was removed by crushed oyster shell material (0.1-2.0 mm by Seo et al. 2005, and 0.3–0.6 mm by Park and Polprasert, 2008) **without** heat pre-treatment. Crushing substantially increases available surface area. It should be noted that Park and Polprasert (2008) recorded release of phosphorus from their filter (up to 5 g m<sup>-3</sup>) during shock loading, demonstrating the reversable binding of phosphorus in these filters. This behaviour may explain the increase in phosphorus concentrations recorded in the outlet of the Warnock's farm oyster shell filter.

As was the case in the international limestone rock trials summarised in the preceding section, influent wastewater phosphorus concentrations were notably higher in the studies of Park and Polprasert (2008) at 17.9 g m<sup>-3</sup>, and Seo et al. (2005) at 2.5–320 g m<sup>-3</sup> than in the inlet to the Warnock's farm system (median concentration of 0.415 g m<sup>-3</sup>).

The lifetimes of phosphorus attenuation estimated for the filter materials used in the Park and Polprasert (2008) and Seo et al. (2005) studies differed markedly – seven months versus 8–23 years, respectively. In addition, pre-treatment of the filter materials differed considerably. It is difficult to use the results from these studies to estimate for how long the oyster shells used in the Warnock farm study may have retained sorption capacity. It may be that no sorption capacity remained in the "uncrushed" oyster shells used in the Warnocks study after 2½ years of operation prior to commencement of water quality monitoring.

The lack of measurable phosphorus removal by the oyster shell filter medium tested in the Warnock's filter may have been due to a combination of:

- the relatively low phosphorus concentration of the influent (relative to influent P in published trials which did show removal)
- the large particle sizes of the oyster shell filter medium (it was not crushed crushing would have increased the number and availability of adsorption sites), and
- absence of heat pre-treatment of the medium (which would have increased the CaO content).

# 5.5 Potential methods for enhancing the performance of the trialled media in the Warnock's phosphorus sorption filters

International research indicates that the phosphorus removal performance of Ca-rich filter media can be enhanced by heating, to increase proportions of CaO relative to CaCO<sub>3</sub> (Vohla et al. 2011). For instance, Brogowski and Renman (2004) demonstrated that heating Opoka (a silica-calcite sedimentary rock similar to limestone which contains Ca primarily as CaCO<sub>3</sub>) increased its sorption capacity from 0.1 g P kg<sup>-1</sup> up to 39.0 g P kg<sup>-1</sup>. The CaO content and phosphorus removal capability also increased as the temperature at which the material was treated increased (up to 1000°C).

Kwon et al. (2004) assessed the phosphorus-sorption capacity of crushed oyster shells. As noted previously, the untreated oyster shell (composed primarily of CaCO<sub>3</sub>, considered relatively non-reactive), showed no ability to remove phosphorus even at influent phosphorus concentrations of 30 g m<sup>-3</sup>. However, pyrolyzed shell (heated to at least 750°C in a nitrogen atmosphere) had lower CaCO<sub>3</sub> content (following conversion to CaO); following heat treatment, phosphorus-removal increased to 98% of dissolved phosphate at inlet concentrations of 30 g m<sup>-3</sup>, and a dosing rate of 1 L of solution to 5 g of oyster shell. Oyster shells heated to 750°C (in air) removed up to 68% of influent phosphorus at the same dosing rates. In the study of Kwon et al (2004), the shells were crushed before adding them to the filters to create a much greater surface area for interaction with the wastewater and thereby improve attenuation.

# 6 Recommendations

## 6.1 System monitoring

Improved characterisation of treatment system performance would be achieved if the monitoring programme were redesigned. Firstly, the monthly sampling regime did not capture any high flow samples. More frequent sampling specifically targeting high flow periods or, alternatively, use of flow proportional sampling would better characterise inlet and outlet concentrations over the range of flow conditions they experienced. Monitoring of the inflow to the wetland was valuable, enabling flow and contaminant loadings to be quantified. However, systems such as this are open to rainfall inputs, losses or gains due to seepage, and losses from evapotranspiration. Performance assessment should ideally be undertaken using mass loads (the product of concentration and flow), not just concentration data and account for flows in and out of the system (Howard-Williams 1985).

## 6.2 Phosphorus-sorbing media

While the two phosphorus filters at Warnock's farm did not attenuate phosphorus during the assessment period, further exploration of these filter media is warranted. Firstly, we note that the sampling did not start until 2½ years after the system was constructed and loading to the two systems during this period was not equal, meaning one of them likely received a much larger loading than the other. This delay and unequal loading may have led to under-estimation of the phosphorus sorption capability of one or other of the media, because it is possible that sorption sites in the trialled media may have become saturated prior to commencement of sampling. If this was the case it would suggest relatively short-term benefits for phosphorus remediation. We recommend that in the future such field assessments should be undertaken as soon as the filters start to receive drainage water.

When correctly pre-treated, both media (lime rock and oyster shell) have demonstrated effective phosphorus removal in overseas studies. The performance of these media may be improved by implementing some of the recommendations in section 5.5. We note however that the international studies involved much higher influent phosphorus concentrations. Therefore, we recommend laboratory pre-testing using drainage water from the Waituna Creek to determine the phosphorus-sorption potential of candidate filter materials at the concentrations they are likely to experience in field trials. Ultimately the cost-effectiveness of such systems will depend on the costs of such modifications and how this affects their long-term efficacy.

# 7 Summary

Drainage waters containing nitrogen, phosphorus, suspended sediment and faecal indicator bacteria were passed through an on-farm treatment system comprising an artificial duck pond, and a constructed wetland followed by two phosphorus sorption filters (a limestone rock filter or an oyster shell filter). The trial site was at Warnock's farm, located on a tributary of Waituna Creek, which drains into the Waituna Lagoon.

## 7.1 Duck pond performance

Attenuation of suspended solids (83%) occurred in the duck pond, resulting in a 64% reduction in median values of turbidity but no measurable improvement in visual clarity.

*Escherichia coli*, a microbial indicator of faecal pollution, decreased from a median inlet value of 650 cfu 100 ml<sup>-3</sup> to a median outlet value of 130 cfu 100 ml<sup>-3</sup> (80% attenuation).

Although there was some attenuation of nitrate nitrogen in the duck pond, median total nitrogen concentrations increased by 11%.

Median dissolved phosphorus concentrations were attenuated by 8%, whereas total phosphorus concentrations were attenuated by 37%. Attenuation processes are likely to be a combination of settling of particulate-associated phosphorus along with some plant uptake of dissolved phosphorus.

## 7.2 Constructed wetland performance

The constructed wetland reduced median total nitrogen concentrations by 64% (from 2.30 to 0.83 g  $\,m^{\text{-}3}$ ).

Substantial reductions in median dissolved (87%) and total phosphorus (75%) concentrations occurred in the wetland.

A reduction in median suspended solids concentrations was unable to be determined as the inlet concentration was at the laboratory detection limit. In addition, the median visual clarity value was largely unaffected.

Median turbidity values increased marginally from 1.8 NTU at the inlet to 2.8 NTU at the outlet.

## 7.3 Phosphorus sorption filters performance

Neither the limestone rock filter nor the oyster shell filter demonstrated measurable removal of phosphorus, with some release of phosphorus during the experimental period. The lack of phosphorus removal efficacy was attributed to:

- Calcium probably being present primarily as CaCO<sub>3</sub>, which has lower sorption of DRP compared with CaO, and
- neither media was finely ground to increase availability of reaction sites.
- Sampling of the system did not begin until 2½ years after the filters were constructed and received drainage water. It is possible that available sorption sites may have become saturated during this intervening period.

Enhanced removal would be expected if these media were heat treated prior to deployment (converting some of the CaCO<sub>3</sub> to CaO), and if they were ground up to create finer particle sizes, thereby creating more reaction and binding sites. A potential adverse effect of converting CaCO<sub>3</sub> to CaO is the increase in pH this causes in the drainage water flowing out of the filters. This may need to be mitigated.

## 7.4 Overall performance

Overall removal efficacy for the combined duck pond/constructed wetland/limestone rock filter system for median values was 80% for total phosphorus and 70% for total nitrogen. In addition, >83% of suspended solids were removed and 99% of *E. coli* based on median values.

Similar performance was seen for the duck pond/constructed wetland/oyster shell filter for median concentrations of suspended solids (>83%) attenuation, total phosphorus attenuation (72%) and *E. coli* attenuation (97%). However, median total nitrogen removal efficacy was lower in this system at 47%. The differences in flow the two filters experience prior to sampling beginning is likely to have influenced overall system functioning which may make these comparisons of overall performance somewhat unreliable.

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## Appendix A Data summary

Where a value was less than the detection limit, it has been assigned a value of half the detection limit for calculation of mean values. Where measurements were greater than the detection limit (e.g., visual clarity), the maximum value has been used to calculate means. Flow at the gauging station on each sampling occasion is presented in Table A2.

	Waituna Treatment System at Duck Pond Inlet																
	Date	Water Temperature (Field)	Turbidity (Field)	Clarity (Black Disc, Field)	Conducti vity (Field)	Oxygen (Dissolved Sat, Field)	i Oxygen ad (Dissolved, d) Field)	kygen Suspended ssolved, Solids ∹ield) (Total)	nded Nitrogen ids (Nitrate al) Nitrite)	Nitrogen (Total Ammoniacal)	Nitrogen (Total Kjeldahl)	Nitrogen (Organic)	Nitrogen (Total)	Phosphorus (Dissolved Reactive)	DIN:DRP	Phosphorus (Total)	E. coli
		(°C)	(NTU)	(m)	(µS cm-1)	(%)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )		(g m <sup>-3</sup> )	(cfu 100 ml-1)
Median		11.6	5.1	0.65	274.1	44.90	4.78	18	0.62	0.079	0.85	0.76	2.08	0.084	11.8	0.415	650
Average		11.3	9.5	0.68	278.6	40.82	4.60	20	1.08	0.210	1.17	0.96	2.27	0.144	53.8	0.438	398
Max		15.4	32.9	0.95	353.5	69.10	7.89	48	3.90	1.340	3.30	1.96	4.50	0.510	231.0	1.210	3300
Min		7.8	0.4	0.40	226.0	6.85	0.72	<3.0	0.02	0.027	0.53	0.49	0.75	0.014	0.5	0.036	30
	27-Sep-17	9.5		0.59	240.8	65.00	7.39	48	1.62	0.035	1.41	1.38	3.00	0.027	61.3	0.50	160
	27-Oct-17	9.6		0.44	231.5	69.10	7.89	6	0.93	0.039	0.53	0.49	1.46	0.051	19.0	0.128	1200
	29-Nov-17	13.0		0.75	242.5	39.20	4.17	37	0.31	0.059	0.88	0.82	1.20	0.117	3.2	0.35	1000
	20-Dec-17	13.0	11.8	0.40	278.0	6.85	0.72	36	0.02	0.230	1.63	1.40	1.65	0.510	0.5	1.21	700
	25-Jan-18	15.4	32.9	0.50	305.6	12.51	1.24	30	0.02	1.340	3.30	1.96	3.40	0.300	4.5	0.87	3300
	21-Feb-18	12.3	13.2	0.65	226.0	18.40	1.95	6	0.02	0.112	0.73	0.62	0.75	0.250	0.5	0.48	700
	22-Mar-18	11.5	5.1	0.65	270.2	34.98	3.87	30	0.04	0.098	1.07	0.97	1.11	0.122	1.1	0.63	600
	16-Apr-18	11.6	1.4	0.95	353.5	50.59	5.38	<3.0	1.79	0.042	0.75	0.71	2.50	0.014	130.9	0.106	90
	15-May-18	9.0	1.4	0.95	318.5	52.66	6.08	<3.0	2.20	0.114	0.82	0.71	3.10	0.027	85.7	0.073	30
	21-Jun-18	7.8	0.4	0.95	319.1	58.94	7.32	<3.0	3.90	0.027	0.62	0.59	4.50	0.017	231.0	0.036	200

#### Table A1: Duck pond inlet.

#### Table A2:Duck pond outlet.

	Waituna Treatm	ent Sys	stem at Duck	Pond Outlet														
	Date	Flow	Water Temperature (Field)	Turbidity (Field)	Clarity (Black Disc, Field)	Conductivity (Field)	Oxygen (Dissolved Sat, Field)	Oxygen (Dissolved, Field)	Suspended Solids (Total)	Nitrogen (Nitrate Nitrite)	Nitrogen (Total Ammoniacal)	Nitrogen (Total Kjeldahl)	Nitrogen (Organic)	Nitrogen (Total)	Phosphorus (Dissolved Reactive)	DIN:DRP	Phosphorus (Total)	E. coli
		(L s <sup>-1</sup> )	(°C)	(NTU)	(m)	(µS cm <sup>-1</sup> )	(%)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )		(g m <sup>-3</sup> )	(cfu 100 ml <sup>-1</sup> )
Median			13.2	1.8	0.67	310.5	73.35	7.80	3.0	0.29	0.072	1.18	1.015	2.30	0.077	16.12	0.260	130
Average			12.9	4.0	0.66	298.7	70	7.46	4.1	0.78	0.79	2.12	1.33	2.90	0.096	40.6	0.247	108
Max			18.0	15.0	0.95	418.1	118	11.15	11.0	3.00	5.50	8.00	2.50	8.60	0.220	180.7	0.480	340
Min			6.4	0.1	0.20	237.6	23	2.21	<3.0	0.00	<0.010	0.76	0.69	1.03	0.017	0.1	0.052	10
% change Median (from inlet)				-64%	3%	13%	63%	63%	-83%	-53%	-8%	39%	33%	11%	-8%		-37%	-80%
% change Average (from inlet)				-58%	-3%	7%	72%	62%	-79%	-28%	277%	80%	38%	28%	-33%		-44%	-73%
	27-Sep-17	9	13.5		0.84	242.7	99	10.23	<3.0	0.76	0.054	0.81	0.76	1.57	0.041	19.9	0.110	10
	27-Oct-1/	2	13.2		0.67	240.3	92	9.68	3.0	0.29	0.068	0.92	0.85	1.21	0.078	4.6	0.142	160
	29-Nov-17	2	17.8		0.78	246.8	23	2.21	<3.0	0.02	<0.010	1.02	1.02	1.03	0.197	0.1	0.260	340
	20-Dec-1/	2	18.0	2.9	0.60	237.6	118	11.15	5	0.00	<0.010	1.47	1.4/	1.4/	0.220	0.1	0.380	90
	25-Jan-18	4	42.4	10	0.50	220.2	74	7.00		0.00	0.477	2.20	2.42	2.20	0.420	4.5	0.400	240
	21-Feb-18	4	13.4	4.6	0.50	320.3	/1	7.33	11	0.02	0.177	2.30	2.12	2.30	0.130	1.5	0.480	340
	22-Mar-18	4	12.8	0.8	0.60	310.5	49	5.30	5	0.06	0.990	2.60	1.61	2.70	0.065	16.1	0.340	2/0
	10-Apr-18	6	0.1	15.0	0.95	419.1	24	2.04	-3.0	0.62	5.50	2.10	2.50	9.60	0.039	70.6	0.102	110
	21-Jun-18	20	6.4	0.4	0.80	320.1	74	9.50	<3.0	3.00	0.072	0.76	0.69	3.80	0.017	180.7	0.052	30

#### Table A3: Constructed wetland outlet.

	Waituna Treat	ment System	at Wetland	Outlet (	5m upstream	n of Filter B	eds)										
	Date	Water Temperature (Field)	Turbidity (Field)	Clarity (Black Disc, Field)	Conductivity (Field)	Oxygen (Dissolved Sat, Field)	Oxygen (Dissolved, Field)	Suspended Solids (Total)	Nitrogen (Nitrate Nitrite)	Nitrogen (Total Ammoniacal)	Nitrogen (Total Kjeldahl)	Nitrogen (Organic)	Nitrogen (Total)	Phosphorus (Dissolved Reactive)	DIN:DRP	Phosphorus (Total)	E. coli
		(°C)	(NTU)	(m)	(µS cm <sup>-1</sup> )	(%)	(g m-3)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m-3)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m- <sup>3</sup> )		(g m <sup>-3</sup> )	(cfu 100 ml <sup>-1</sup> )
Median		13.4	2.8	0.83	230.4	73.2	7.63	<3.0	0.009	<0.010	0.57	0.534	0.83	0.010	3.645	0.065	17
Average		13.7	2.1	0.74	256.1	68.41	7.22	3.9	0.53	0.42	1.15	0.73	1.68	0.011	92.6	0.072	21
Max		20.4	4.7	>0.98	361.4	109.00	11.07	17.0	2.80	3.80	5.70	1.90	6.70	0.025	404.2	0.163	100
Min		6.2	0.0	0.57	200.7	30.28	2.79	<3.0	<0.002	<0.010	0.36	0.36	0.36	<0.004	0.4	0.024	10
% Change median (from duck pond outlet)			51%	24%	-26%	0%	-2%	0%	-97%	-93%	-52%	-47%	-64%	-87%		-75%	-87%
% Change average (from duck pond outlet)			-48%	12%	-14%	-3%	-3%	-5%	-32%	-47%	-46%	-45%	-42%	-89%		-71%	-81%
% Change of medians (from duck pond inlet)			-46%	28%	-16%	63%	60%	-83%	-99%	-87%	-33%	-30%	-60%	-88%		-84%	-97%
	27-Sep-17	14.3		0.96	229.7	109.00	11.07	<3.0	0.37	<0.010	0.63	0.63	1.00	0.016	23.8	0.068	10
	27-Oct-17	12.8		0.57	226.5	75.60	8.03	17.0	0.003	0.018	1.36	1.34	1.37	0.007	3.0	0.163	90
	29-Nov-17	20.4		0.80	228.4	62.00	5.64	5.0	0.014	0.087	0.65	0.56	0.66	0.025	4.0	0.065	100
	20-Dec-17	17.7	0.4	0.85	200.7	80.42	7.64	<3.0	< 0.002	<0.010	0.50	0.50	0.50	0.008	0.8	0.064	20
	25-Jan-18	19.1	0.1	0.80	252.7	30.28	2.79	3.0	< 0.002	<0.010	0.51	0.51	0.51	0.017	0.4	0.080	10
	21-Feb-18	13.8	2.8	>0.98	231.0	49.73	5.10	<3.0	0.003	<0.010	0.41	0.41	0.41	< 0.004	3.3	0.036	10
	22-Mar-18	12.9	3.4	>0.98	228.4	70.87	7.61	<3.0	<0.002	<0.010	0.36	0.36	0.36	< 0.004	3.0	0.024	30
	16-Apr-18	11.0	0.0	0.95	305.2	81.91	8.85	<3.0	1.09	0.230	0.99	0.76	2.10	0.016	82.5	0.060	20
	15-May-18	8.4	4.7	0.70	361.4	48.80	5.70	3.0	1.05	3.80	5.70	1.90	6.70	0.012	404.2	0.129	10
	21-Jun-18	6.2	3.2	0.85	296.8	75.53	9.75	3.0	2.80	<0.010	0.38	0.38	3.20	0.007	401.4	0.034	13

#### Table A4:Lime rock filter outlet.

	Waituna Treat	ment System a	t Lime Rock	Filter Ou	tlet												
	Date	Water Temperature (Field)	Turbidity (Field)	Clarity (Black Disc, Field)	Conductivity (Field)	Oxygen (Dissolved Sat, Field)	Oxygen (Dissolved, Field)	Suspended Solids (Total)	Nitrogen (Nitrate Nitrite)	Nitrogen (Total Ammoniacal)	Nitrogen (Total Kjeldahl)	Nitrogen (Organic)	Nitrogen (Total)	Phosphorus (Dissolved Reactive)	DIN:DRP	Phosphorus (Total)	E. coli
		(°C)	(NTU)	(m)	(µS cm <sup>-1</sup> )	(%)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m-3)	(g m <sup>-3</sup> )		(g m <sup>-3</sup> )	(cfu 100 ml-1)
Median		13.6	<0.1	0.90	358.1	43.72	4.23	<3.0	0.116	<0.01	0.525	0.447	0.63	0.037	5.48	0.081	8
Average		13.7	0.5	0.82	409.7	50.46	5.40	<3.0	0.690	0.346	0.95	0.60	1.63	0.041	70.1	0.073	10
Max		19.0	2.0	>0.98	999.5	81.52	10.53	3.0	3.10	3.100	5.00	1.90	6.70	0.072	322.7	0.110	30
Min		6.3	<0.1	0.86	272.0	35.3	3.7	<3.0	< 0.002	<0.01	0.30	0.30	0.39	0.011	0.9	0.028	4
% Change median (from wetland outlet)			>-99%	8%	55%	-40%	-45%	Unable to be calculated	1189%	0%	-8%	-16%	-25%	265%		26%	-52%
% Change average (from wetland outlet)			-77%	11%	60%	-26%	-25%	-23%	30%	-18%	-17%	-18%	-3%	268%		1%	-52%
% Change of medians (from duck pond inlet)	,		>-99%	38%	31%	-3%	-12%	>-83%	-81%	-87%	-38%	-42%	-70%	-57%		-80%	-99%
	27-Sep-17	12.4		>0.98	279.9	65.70	6.98	<3.0	0.51	<0.010	0.41	0.41	0.91	0.022	23.6	0.052	<10
	27-Oct-17	13.0		0.95	999.5	35.30	3.73	<3.0	0.116	< 0.010	0.39	0.39	0.51	0.023	5.5	0.041	<10
	29-Nov-17	19.0		0.86	360.3	40.00	3.75	<3.0	0.003	0.085	0.68	0.60	0.68	0.066	1.3	0.088	30
	20-Dec-17	17.5	<0.1	0.90	272.0	44.51	4.24	<3.0	0.056	<0.010	0.46	0.46	0.52	0.072	0.9	0.094	5
	25-Jan-18	18.7	1.4		372.4	39.53	3.68	<3.0	< 0.002	0.131	0.57	0.44	0.57	0.070	<1.9	0.097	20
	21-Feb-18	15.9	<0.1	0.90	346.0	42.92	4.20	<3.0	0.043	0.118	0.51	0.39	0.56	0.055	2.9	0.074	<10
	22-Mar-18	14.2	<0.1	0.90	293.6	49.93	5.20	<3.0	0.085	< 0.010	0.30	0.30	0.39	0.050	1.9	0.092	10
	16-Apr-18	10.9	<0.1	>0.98	356.0	68.72	7.44	<3.0	1.21	< 0.010	0.63	0.63	1.85	0.021	58.1	0.056	20
	15-May-18	9.1	2.0	0.95	456.7	36.48	4.21	3.0	1.74	3.10	5.00	1.90	6.70	0.015	322.7	0.110	20
	21-Jun-18	6.3	<0.1	0.87	360.1	81.52	10.53	<3.0	3.10	< 0.010	0.54	0.54	3.60	0.011	282.7	0.028	4

## Table A5:Oyster shell filter outlet.

	Waituna Trea	atment Syste	m at Oyste	Shell Fi	Iter Outlet												
	Date	Water Temperature (Field)	Turbidity (Field)	Clarity (Black Disc, Field)	Conductivity (Field)	Oxygen (Dissolved Sat, Field)	Oxygen (Dissolved, Field)	Suspended Solids (Total)	Nitrogen (Nitrate Nitrite)	Nitrogen (Total Ammoniacal)	Nitrogen (Total Kjeldahl)	Nitrogen (Organic)	Nitrogen (Total)	Phosphorus (Dissolved Reactive)	DIN:DRP	Phosphorus (Total)	E. coli
		(°C)	(NTU)	(m)	(µS cm <sup>-1</sup> )	(%)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m-3)	(g m <sup>-3</sup> )	(g m-3)	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )	(g m <sup>-3</sup> )		(g m <sup>-3</sup> )	(cfu 100 ml <sup>-1</sup> )
Median		13.0	0.4	0.85	343.0	36.75	3.68	<3.0	< 0.002	0.115	0.605	0.528	1.11	0.035	5.0	0.118	20
Average		13.5	0.8	0.77	356.7	40.98	4.40	4.3	0.69	0.46	1.10	0.64	1.78	0.052	46.3	0.150	18
Max		19.6	2.0	>0.98	472.4	73.28	9.45	5.0	3.20	3.10	4.90	1.80	6.70	0.157	188.8	0.400	600
Min		6.3	<0.1	0.65	305.1	30.00	2.91	<3.0	< 0.002	<0.010	0.32	0.29	0.33	0.017	1.7	0.036	1
% Change median (from wetland outlet)			-85%	2%	49%	-50%	-52%	0%	-78%	2200%	6%	-1%	33%	250%		83%	21%
% Change average (from wetland outlet)			-62%	4%	39%	-40%	-39%	23%	30%	9%	-5%	-13%	6%	372%		107%	-13%
% Change of medians (from duck pond inlet)			-92%	31%	25%	-18%	-23%	-83%	>-99%	46%	-29%	-31%	-47%	-58%		-72%	-97%
	27-Sep-17	12.5		>0.98	305.1	39.00	4.12	<3.0	0.58	< 0.010	0.43	0.43	1.01	0.04	16.4	0.070	20
	27-Oct-17	12.2		0.85	334.9	30.00	3.23	<3.0	< 0.002	0.118	0.58	0.46	0.58	0.07	1.7	0.114	<10
	29-Nov-17	19.6		0.84	351.0	36.00	3.33	<3.0	< 0.002	0.48	1.20	0.72	1.20	0.16	3.1	0.240	20
	20-Dec-17	17.3		0.90	309.4	35.49	3.40	5	< 0.002	0.129	0.67	0.54	0.67	0.04	3.0	0.220	28
	25-Jan-18	18.7	<0.1	0.80	399.6	31.23	2.91	5	< 0.002	0.59	1.25	0.66	1.25	0.09	6.7	0.400	600
	21-Feb-18	14.9	1.8	0.90	334.0	37.49	3.75	3	< 0.002	0.111	0.46	0.35	0.46	0.03	3.3	0.171	<10
	22-Mar-18	13.4	0.4		330.9	42.17	4.45	<3.0	0.019	0.027	0.32	0.29	0.33	0.02	2.0	0.062	100
	16-Apr-18	11.1	<0.1	0.95	361.8	53.92	5.80	<3.0	1.28	<0.010	0.63	0.63	1.92	0.02	56.1	0.062	10
	15-May-18	9.0	2.0	0.90	472.4	31.21	3.60	<3.0	1.80	3.10	4.90	1.80	6.70	0.03	181.5	0.122	20
	21-Jun-18	6.3	< 0.1	0.65	368.3	73.28	9.45	<3.0	3.20	< 0.010	0.52	0.52	3.70	0.02	188.8	0.036	1

Appendix B Concentration time series graphs of key water quality variables



Appendix C Time series graphs of load estimates of key water quality variables





- ▲ u/s Filter beds DRP load (g/d) grab samples
- ▼ Lime rock filter DRP load (g/d) grab samples
- Oyster shell filter DRP load (g/d) grab samples

- u/s Filter beds TP load (g/d) grab samples
- Lime rock filter TP load (g/d) grab samples
- Oyster shell filter TP load (g/d) grab samples

Duckpond inflow TN load (g/d) - grab samples
 Duckpond outflow TN load (g/d) - grab samples

## Appendix D Non-linear modelling

The NONLIN function of Systat 13.2 for Windows was used to identify nonlinear models that describe the relationship between water quality variable concentration and discharge.

The NONLIN function estimates parameters for several nonlinear models using several algorithms. In the estimates below, a Gauss-Newton algorithm was used.

In the examples that follow, a relationship of the form shown below was used:

Variable concentration  $(mg/L) = a^*(hourly average discharge (L/s))^(c)$ 

Where a and c are parameters for which the NONLIN function provides estimates.

#### > MODEL DI\_NNN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Inlet NNN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares									
Source	SS	df	Mean Squares						
Regression	23.333	2	11.667						
Residual	0.884	7	0.126						
Total	24.217	9							
Mean corrected	14.782	8							

Raw R-square (1-Residual/Total)	:	0.964
Mean Corrected R-square (1-Residual/Corrected)	:	0.940
R-square(Observed vs. Predicted)	:	0.940

Parameter Estimates									
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval				
				Lower	Upper				
A	0.050	0.034	1.494	-0.029	0.129				
С	2.422	0.394	6.143	1.489	3.354				

Asyr Para	Asymptotic Correlation Matrix of Parameters							
	а	с						
а	1.000							
с	-0.994	1.000						



#### > MODEL DO\_NNN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Outlet NNN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares									
Source	SS	df	Mean Squares						
Regression	11.887	2	5.944						
Residual	3.015	8	0.377						
Total	14.903	10							
Mean corrected	10.037	9							

Raw R-square (1-Residual/Total)	:	0.798
Mean Corrected R-square (1-Residual/Corrected)	:	0.700
R-square(Observed vs. Predicted)	:	0.703

Parameter	Parameter Estimates									
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Cont	idence Interval					
				Lower	Upper					
A	0.168	0.119	1.410	-0.107	0.443					
С	0.967	0.259	3.730	0.369	1.565					

Asymptotic Correlation Matrix of Parameters							
	a c						
а	1.000						
с	-0.968	1.000					





#### > MODEL LRF\_NNN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: u/s Lime rock filter NNN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares									
Source	SS	df	Mean Squares						
Regression	12.915	2	6.457						
Residual	1.473	8	0.184						
Total	14.387	10							
Mean corrected	9.676	9							

Raw R-square (1-Residual/Total)	:	0.898
Mean Corrected R-square (1-Residual/Corrected)	:	0.848
R-square(Observed vs. Predicted)	:	0.856

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Cont	idence Interval		
				Lower	Upper		
A	0.158	0.080	1.989	-0.025	0.342		
С	1.006	0.182	5.524	0.586	1.425		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	С			
а	1.000				
с	-0.971	1.000			





#### > MODEL OSF\_NNN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: d/s Oyster shell filter NNN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	13.710	2	6.855			
Residual	1.745	8	0.218			
Total	15.455	10				
Mean corrected	10.716	9				

Raw R-square (1-Residual/Total)	:	0.887
Mean Corrected R-square (1-Residual/Corrected)	:	0.837
R-square(Observed vs. Predicted)	:	0.847

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval		
				Lower	Upper		
A	0.156	0.085	1.840	-0.040	0.352		
С	1.021	0.196	5.209	0.569	1.473		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
a c		с			
а	1.000				
с	-0.973	1.000			





#### > MODEL DI\_TN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Inlet TN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	59.751	2	29.875			
Residual	5.008	8	0.626			
Total	64.759	10				
Mean corrected	13.366	9				

Raw R-square (1-Residual/Total)	:	0.923
Mean Corrected R-square (1-Residual/Corrected)	:	0.625
R-square(Observed vs. Predicted)	:	0.626

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval		
				Lower	Upper		
A	0.840	0.305	2.758	0.138	1.542		
С	0.862	0.246	3.502	0.294	1.429		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
a c		с			
а	1.000				
с	-0.959	1.000			





#### > MODEL DO\_TN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Outlet TN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares					
Source	SS	df	Mean Squares		
Regression	79.337	2	39.668		
Residual	40.354	8	5.044		
Total	119.691	10			
Mean corrected	51.674	9			

Raw R-square (1-Residual/Total)	:	0.663
Mean Corrected R-square (1-Residual/Corrected)	:	0.219
R-square(Observed vs. Predicted)	:	0.223

Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Cont	idence Interval	
				Lower	Upper	
A	1.577	0.845	1.866	-0.372	3.526	
С	0.397	0.266	1.494	-0.215	1.009	

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	с			
а	1.000				
с	-0.882	1.000			





#### > MODEL UFB\_TN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: u/s Filter beds TN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	38.562	2	19.281			
Residual	25.098	8	3.137			
Total	63.660	10				
Mean corrected	35.403	9				

Raw R-square (1-Residual/Total)	:	0.606
Mean Corrected R-square (1-Residual/Corrected)	:	0.291
R-square(Observed vs. Predicted)	:	0.298

Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Con	fidence Interval	
				Lower	Upper	
A	0.850	0.571	1.487	-0.468	2.168	
С	0.532	0.300	1.771	-0.161	1.224	

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	с			
а	1.000				
с	-0.906	1.000			





#### > MODEL OSF\_TN\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: d/s Oyster shell filter TN mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	44.022	2	22.011			
Residual	23.373	8	2.922			
Total	67.395	10				
Mean corrected	35.640	9				

Raw R-square (1-Residual/Total)	:	0.653
Mean Corrected R-square (1-Residual/Corrected)	:	0.344
R-square(Observed vs. Predicted)	:	0.350

Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval	
				Lower	Upper	
A	0.865	0.537	1.612	-0.373	2.104	
С	0.555	0.273	2.036	-0.073	1.184	

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	с			
а	1.000				
с	-0.910	1.000			





#### > MODEL DI\_DRP\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Inlet DRP mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares							
Source	SS	df	Mean Squares				
Regression	0.305	2	0.153				
Residual	0.141	8	0.018				
Total	0.446	10					
Mean corrected	0.240	9					

Raw R-square (1-Residual/Total)	:	0.685
Mean Corrected R-square (1-Residual/Corrected)	:	0.414
R-square(Observed vs. Predicted)	:	0.414

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval		
				Lower	Upper		
A	1.594	4.504	0.354	-8.792	11.981		
С	-2.826	4.036	-0.700	-12.132	6.480		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	с			
а	1.000				
с	-0.996	1.000			





#### > MODEL DO\_DRP\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Outlet DRP mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	0.087	2	0.044			
Residual	0.037	8	0.005			
Total	0.124	10				
Mean corrected	0.049	9				

Raw R-square (1-Residual/Total)	:	0.703
Mean Corrected R-square (1-Residual/Corrected)	:	0.251
R-square(Observed vs. Predicted)	:	0.251

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval		
				Lower	Upper		
A	0.205	0.137	1.502	-0.110	0.520		
С	-0.848	0.794	-1.068	-2.680	0.984		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	с			
а	1.000				
с	-0.938	1.000			





#### > MODEL UFB\_DRP\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: u/s Filter beds DRP mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares							
Source	SS	df	Mean Squares				
Regression	0.001	2	0.001				
Residual	0.000	8	0.000				
Total	0.002	10					
Mean corrected	0.000	9					

Raw R-square (1-Residual/Total)	:	0.721
Mean Corrected R-square (1-Residual/Corrected)	:	0.000
R-square(Observed vs. Predicted)	:	0.000

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Cont	idence Interval		
				Lower	Upper		
A	0.011	0.005	2.366	0.000	0.023		
С	-0.015	0.306	-0.048	-0.721	0.691		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	a	с			
а	1.000				
с	-0.854	1.000			





#### > MODEL LRF\_DRP\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: u/s Lime rock filter DRP mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	0.020	2	0.010			
Residual	0.002	8	0.000			
Total	0.022	10				
Mean corrected	0.005	9				

Raw R-square (1-Residual/Total)	:	0.920
Mean Corrected R-square (1-Residual/Corrected)	:	0.673
R-square(Observed vs. Predicted)	:	0.675

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval		
				Lower	Upper		
A	0.122	0.045	2.721	0.019	0.225		
С	-1.124	0.469	-2.394	-2.206	-0.041		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
а		С			
а	1.000				
с	-0.959	1.000			





#### > MODEL OSF\_DRP\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: d/s Oyster shell filter DRP mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	0.031	2	0.016			
Residual	0.012	8	0.002			
Total	0.044	10				
Mean corrected	0.017	9				

#### **R-squares**

Raw R-square (1-Residual/Total)	:	0.716
Mean Corrected R-square (1-Residual/Corrected)	:	0.264
R-square(Observed vs. Predicted)	:	0.265

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Cont	idence Interval		
				Lower	Upper		
A	0.128	0.085	1.506	-0.068	0.323		
С	-0.894	0.803	-1.113	-2.746	0.959		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
а		С			
а	1.000				
с	-0.942	1.000			



Scatter Plot

#### > MODEL DI\_TSS\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Inlet TSS mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares					
Source	SS	df	Mean Squares		
Regression	4,172.813	2	2,086.407		
Residual	2,674.937	8	334.367		
Total	6,847.750	10			
Mean corrected	2,947.125	9			

Raw R-square (1-Residual/Total)	:	0.609
Mean Corrected R-square (1-Residual/Corrected)	:	0.092
R-square(Observed vs. Predicted)	:	0.092

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Con	fidence Interval		
				Lower	Upper		
A	37.561	28.628	1.312	-28.456	103.577		
С	-0.648	0.837	-0.774	-2.578	1.282		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	С			
а	1.000				
с	-0.928	1.000			





#### > MODEL DO\_TSS\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: Duckpond Outlet TSS mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares					
Source	SS	df	Mean Squares		
Regression	141.413	2	70.707		
Residual	96.587	8	12.073		
Total	238.000	10			
Mean corrected	101.100	9			

Raw R-square (1-Residual/Total)	:	0.594
Mean Corrected R-square (1-Residual/Corrected)	:	0.045
R-square(Observed vs. Predicted)	:	0.045

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Con	fidence Interval		
				Lower	Upper		
A	5.078	3.074	1.652	-2.011	12.167		
С	-0.281	0.546	-0.513	-1.540	0.979		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	с			
а	1.000				
с	-0.876	1.000			





#### > MODEL UFB\_TSS\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: u/s Filter beds TSS mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	159.609	2	79.804			
Residual	192.641	8	24.080			
Total	352.250	10				
Mean corrected	204.025	9				

Raw R-square (1-Residual/Total)	:	0.453
Mean Corrected R-square (1-Residual/Corrected)	:	0.056
R-square(Observed vs. Predicted)	:	0.058

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Con	fidence Interval		
				Lower	Upper		
A	7.271	7.009	1.037	-8.892	23.433		
С	-0.614	1.054	-0.582	-3.045	1.818		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	С			
а	1.000				
с	-0.915	1.000			





#### > MODEL LRF\_TSS\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: u/s Lime rock filter TSS mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	27.359	2	13.679			
Residual	1.891	8	0.236			
Total	29.250	10				
Mean corrected	2.025	9				

Raw R-square (1-Residual/Total)	:	0.935
Mean Corrected R-square (1-Residual/Corrected)	:	0.066
R-square(Observed vs. Predicted)	:	0.066

Parameter	Parameter Estimates						
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Cont	idence Interval		
				Lower	Upper		
A	1.485	0.264	5.616	0.875	2.095		
С	0.087	0.117	0.738	-0.184	0.357		

Asyr Para	Asymptotic Correlation Matrix of Parameters				
	а	С			
а	1.000				
с	-0.853	1.000			





#### > MODEL OSF\_TSS\_MGL = a\*(FLOW\_LS\_H\_AVG)^(c)

Dependent Variable: d/s Oyster shell filter TSS mg/L Zero weights, missing data or estimates reduced degrees of freedom

Sum of Squares and Mean Squares						
Source	SS	df	Mean Squares			
Regression	59.284	2	29.642			
Residual	15.466	8	1.933			
Total	74.750	10				
Mean corrected	19.525	9				

Raw R-square (1-Residual/Total)	:	0.793
Mean Corrected R-square (1-Residual/Corrected)	:	0.208
R-square(Observed vs. Predicted)	:	0.210

Parameter Estimates								
Parameter	Estimate	ASE	Parameter/ASE	Wald 95% Conf	idence Interval			
				Lower	Upper			
A	4.113	1.748	2.353	0.083	8.143			
С	-0.526	0.446	-1.180	-1.554	0.502			

Asymptotic Correlation Matrix of Parameters					
	а	С			
а	1.000				
с	-0.905	1.000			



