

Evaluation of AQUAL-P for removal of phosphorus from tile drainage

Revision 2

Prepared for DairyNZ

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Prepared by:
Neale Hudson
Evan Baddock
Greg Olsen

For any information regarding this report please contact:

Neale Hudson
Environmental Chemist/Group Manager
Catchment Processes
+64-7-856 1772
neale.hudson@niwa.co.nz

National Institute of Water & Atmospheric Research Ltd
PO Box 11115
Hamilton 3251

Phone +64 7 856 7026

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Executive summary

NIWA was engaged to assess the performance of a phosphorus (P) removal device (“P-filter”), where the active ingredient was a bed of Aqual-P, a modified zeolite. The efficacy of the P-filter depends on the affinity between the filter matrix and dissolved reactive phosphate (DRP). Dissolved P is adsorbed to active sites on the surface of the filter bed and within the bed material, through a range of physico-chemical binding processes.

Use of similar filter materials has demonstrated environmental benefits in several situations, including improving lake and stream ecological conditions. Removal of DRP reduces the amount of readily available P, which in turn helps reduce nuisance plant growth (particularly phytoplankton in lakes).

The field trial was intended to determine the P-removal efficacy of Aqual-P under field conditions. A suitable site was selected in the Waituna Lagoon catchment, Southland, where soil conditions favoured release of P (principally in dissolved form) in tile drainage. The trial design involved delivery of DRP-containing drainage water to the surface of a filter bed. Samples were collected from the inflow and outflow of the filter bed for measurement of P concentration. The volume and timing of water applied was also measured. Samples of bed materials were collected at the end of the trial and the P content, P-binding capacity and concentrations of P in pore water were measured.

Using the measured inflow and outflow concentrations, and available flow records, the removal efficacy of the filter bed summarised in Table i was observed over the 27-month trial period. These values indicate the proportion of influent P (as either DRP or TP, with the latter comprising all forms of P not present as *ortho*-phosphate, PO_4^{3-}).

Table i: Summary of phosphorus removal performance.

Water quality variable	Removal efficacy (removal as proportion of inflow, %)	
	Concentration	Flux
Dissolved reactive phosphate	99.3	99.2
Total phosphorus	80.3	81.3

Removal efficacy also requires determination of the mass of P retained on the filter bed per mass of filter material. In an earlier trial involving the same equipment design, a pump malfunction had caused underloading of the filter bed. The second trial (this report) was commissioned primarily to overcome the loss of information caused by poor equipment performance in the earlier trial. The necessary adjustments to flow were implemented, but unfortunately similar pump-related issues caused smaller than designed volumes of drainage water to be applied to the filter bed during the second trial as well. In addition, as a consequence of the small discharge volumes, much of the drainage water applied was unmetered.

NIWA and the Project Manager acknowledge that this was something that should have been detected and remedied as part of normal project management/ operation activities.. This situation led to failure to meet the contract conditions over the trial period, and did not allow the performance of the bed material to be assessed as agreed. The trial therefore falls short of delivering the services that were commissioned by DairyNZ.

The bed was underloaded in terms of DRP and TP, and also made estimation of the actual mass of material applied impossible for approximately two thirds of the trial period. As a consequence, performance efficacy under realistic field nutrient loading rate conditions could not be fully estimated. Despite this limitation, we were able to determine the P removal capability of this material.

Laboratory assessments of the bed material at the end of the trial indicated that P removal capacity in the upper two thirds of the bed was almost 30% of the original material (0.11 mg/g for a DRP concentration of 0.2 mg/L), which increased to approximately 40% in the lower third of the bed (0.42 mg/g for a DRP concentration of 0.2 mg/L).

Using the theoretical P sorption capacity of the material used to construct the P filter, the bed could retain approximately 210 g P. At the nominal average flow in the tile drain (0.21 L/s) and the median DRP concentration (86 µg/L) from a drainage area of approximately 1 ha, the flux is approximately 1.5 g/d, and the yield is approximately 570 g/ha/y. The as-built filter bed could theoretically retain all the DRP in the tile drain discharge for a period of approximately 134 days. This performance is unlikely to be achieved because the hydraulic loading rate is too large to provide adequate contact time for the binding of P to the bed matrix to be effective.

The trial has demonstrated that provided the mass loading rate and the hydraulic loading rate do not exceed the capacity of the filter bed, the concentrations of DRP in the discharge are likely to deliver ecological benefits. In this trial, discharge DRP was consistently at or near the analytical detection limits (1 µg P/L).

Achieving the desired ecological benefits will require some degree of maintenance and management of the filter system. Gravity supply to a filter system is unlikely to be achievable for most tile drain situations, which will require pumping of the drainage water to the head of the filter. The selection of pump and management of application rates are key requirements for effective reduction in tile drainage P load. Prior to establishing a P-filter, it would also be advantageous to characterise the tile drainage water chemistry, specifically the dissolved iron content, pH and dissolved oxygen status. Additional information derived from these measurements may indicate that inclusion of additional treatment units (e.g., a header tank) could improve the form in which the P is delivered to the bed material, or reduce the amount of other species entering the filter (e.g., dissolved iron). The latter may be adsorbed on the filter surface, either providing additional P-binding under oxic conditions or reducing the binding and hydraulic capacity of the filter bed with formation of iron/organic flocs.

1 Introduction

Phosphorus (P) is an element and an essential requirement for all life-forms. Adequate soil P content is necessary for profitable crop and livestock production, and P-containing fertilisers and soil amendments are applied to soils to maintain productivity. The availability of P in soils is subject to a range of factors and conditions, including parent soil characteristics, texture, oxygenation state, pH and tillage practices. In some circumstances excess P accumulates in soil surface layers, where it tends to become fixed. This P is not necessarily immobile however – P can move as a component of the particulate fraction transported by wind and water erosion processes (e.g., Abell et al. (2013)); P is also mobilised through uptake by plants and ultimately animals and crops, which may involve transport off site, or re-deposition onto the land surface (Sharpley and Beegle 1999).

In some circumstances (characterised by organic-rich soils, waterlogged or highly permeable soils), P is less well-fixed to soils, and may be lost in soluble form (dissolved reactive phosphate (DRP) or *ortho*-phosphate) to groundwater and ultimately to surface waters (Sharpley and Beegle 1999). P in this form is bioavailable, able to promote plant growth, particularly algae. If this soluble P is captured in sediments in streams and estuaries, it forms a source of potentially available P.

Avoiding nuisance algal growth is a key objective of the Resource Management Act 1991 (as amended (New Zealand Government 1991)), in the National Policy Statement for Freshwater Management (New Zealand Government 2017), and in Regional Policy Statements and Regional Plans. For example, Plan Change Six in Hawke’s Bay region had a focus on management of P inputs to the Tukituki River.

Penn and Bowen (2018) suggest that mitigation of P input to surface waters necessitates a two-pronged approach:

1. addressing the source of P (“legacy P”) – the P that already exists in the landscape, and which can be mobilised so that it enters surface waters in either soluble or dissolved form, and
2. addressing the fraction of P that is mobilised in soluble form.

The first approach requires long-term strategies that may take decades to achieve measurable success. It may involve altering land management practices; in the case of naturally P-rich soils, or organic-rich soils where P-binding capacity is naturally limited, it is unrealistic to anticipate that significant reduction of P inputs to surface waters can be achieved through land management practices alone. Deployment of customised “P-filters” may be required to directly address 2) above, and should be regarded as a component of the long-term strategy to address 1) as well.

In many catchments in New Zealand, conditions exist for transport of DRP into surface waters via tile drains (Monaghan et al. 2002; Monaghan and Smith 2004; McDowell et al. 2005; Wilcock et al. 2007). These drains exist to lower shallow water tables – saturated soils are one of the factors contributing to DRP mobilisation. These drains may therefore function as conduits for transporting DRP in shallow groundwater from farmland to the creeks and rivers into which they discharge. Reducing input of P from drains has been identified as one mechanism whereby receiving water quality objectives may be met. Mitigation strategies include constructed wetlands (Ballantine and Tanner 2010), as well as other devices that are engineered to facilitate contact between drainage waters and P- sorbent substrates (Lyngsie et al. 2014; Penn et al. 2017).

Penn et al. (2017) recently reviewed phosphorus removal structures. Four characteristics were identified for these mitigation tools:

1. The device contains sufficient mass of high capacity, P-retentive material.
2. The P-sorbent material is placed in a hydrologically active area, and receives DRP concentrations in excess of 0.2 mg/L.
3. The water flows through the bed of P-retentive material.
4. Ability to replace the P retentive material once P removal rates fall below an identified threshold.

Multiple designs that meet these criteria were identified, including: surface runoff beds, subsurface beds for wetlands, subsurface tile drainage filters, drainage ditch filters, and modular perforated boxes. The term “retentive” is used above to indicate that two principal P removal mechanisms predominate:

- sorption processes, whereby dissolved P is retained within the bed by the medium, which has a strong affinity for P, and which binds it on the surface and within pores in the matrix, and
- physical filtration (which may include sorption as well), where particulate material containing P is retained in or on the filter bed.

The selection of available P-sorbent materials is also quite varied, and includes naturally sorbent soil materials, limestone, dolomite, shells, various slag materials, mine drainage residuals, and modified clays and minerals (Penn et al. 2017). Ballantine and Tanner (2010) reviewed materials that may be incorporated in constructed wetlands to enhance P retention. Olsen et al. (2013) evaluated two materials with potential for use in New Zealand farming systems and conditions. In a series of articles, Hamilton and Landman (2011) describe use of one of these agents (Aqual P) for controlling DRP input and availability in the Rotorua Lakes. More recently Gibbs and Hickey (2018) reviewed use of several products and materials that have been used in New Zealand lake systems to remove P. These included Aqual-P.

NIWA was engaged by DairyNZ to investigate the usefulness of one aspect of P mitigation – use of Aqual P as a P sorbent in a flow-through trapping filter in a field trial. Preliminary work was undertaken in two phases: 1) Identification of candidate sites for field trials, and 2) design of a modular P removal system. The results of this work were reported previously (McKergow et al. 2016). The identification of candidate sites was supported by earlier work (Tanner et al. 2014).

The field trial was originally conceived to be undertaken as a two-year project, but difficulties in identifying a suitable site in the Waituna Lagoon catchment, Southland delayed the start of the project. The first period of trial data (May 2016 – March 2017) were reported in 2017 (Hudson et al. 2017). A second trial period was commissioned, and the results of both assessment periods are combined in this report. DairyNZ and project partners wished to understand the performance of this technology in terms of DRP removal efficacy, and to understand the extent to which the bed material was saturated with DRP and an assessment of the P sorption potential at the start and end of the trial.

To overcome the limitations of the initial trial, the contract for the second trial indentified several specific requirements:

- **Assessing the site infrastructure, and making minor modification (specifically the pump inlet), if required.**
- **Adjusting the pump to increase the hydraulic loading rate on the filter bed.**

2 Materials and methods

The materials and methods were previously described (McKergow et al. 2016; Hudson et al. 2018), and similar processes were used throughout the project. The design, dimensions and equipment installed in the P filter were described previously (McKergow et al. 2016), and limited information derived from initial reports is included below to facilitate use of this report.

2.1 Location of the P filter

Initially a site for the P filter was identified on the Pirie Farm, on the upper Waituna Creek, Southland. However, subsequent investigations revealed that major P losses in the Waituna Lagoon catchment occurred from soils with low anion storage capacity (ASC). Several suitable sites identified on a farm where discharge drains into Currans Creek and into the Waituna Lagoon (FI 1-4, Figure 2-1). The drain with the highest DRP concentration and flow was selected as a trial site (FI 2). The location of this site within the Waituna catchment is shown in Figure 2-2.



Figure 2-1: Annotated aerial photograph of P-filter location (FI2), drains (blue lines) and 2 m contours (orange lines; generated from LIDAR data by Andrew Hughes, NIWA).

Extensive redesign of the experimental equipment and setup originally envisaged was required – initially the trial had been conceived as a passive drainage system, with P-laden drainage water entering the filter under gravity (i.e., without any requirement for a pump). All four of the candidate sites on the property finally selected to trial the filter required a pumped system, with P-laden water delivered to the filter via a pump.

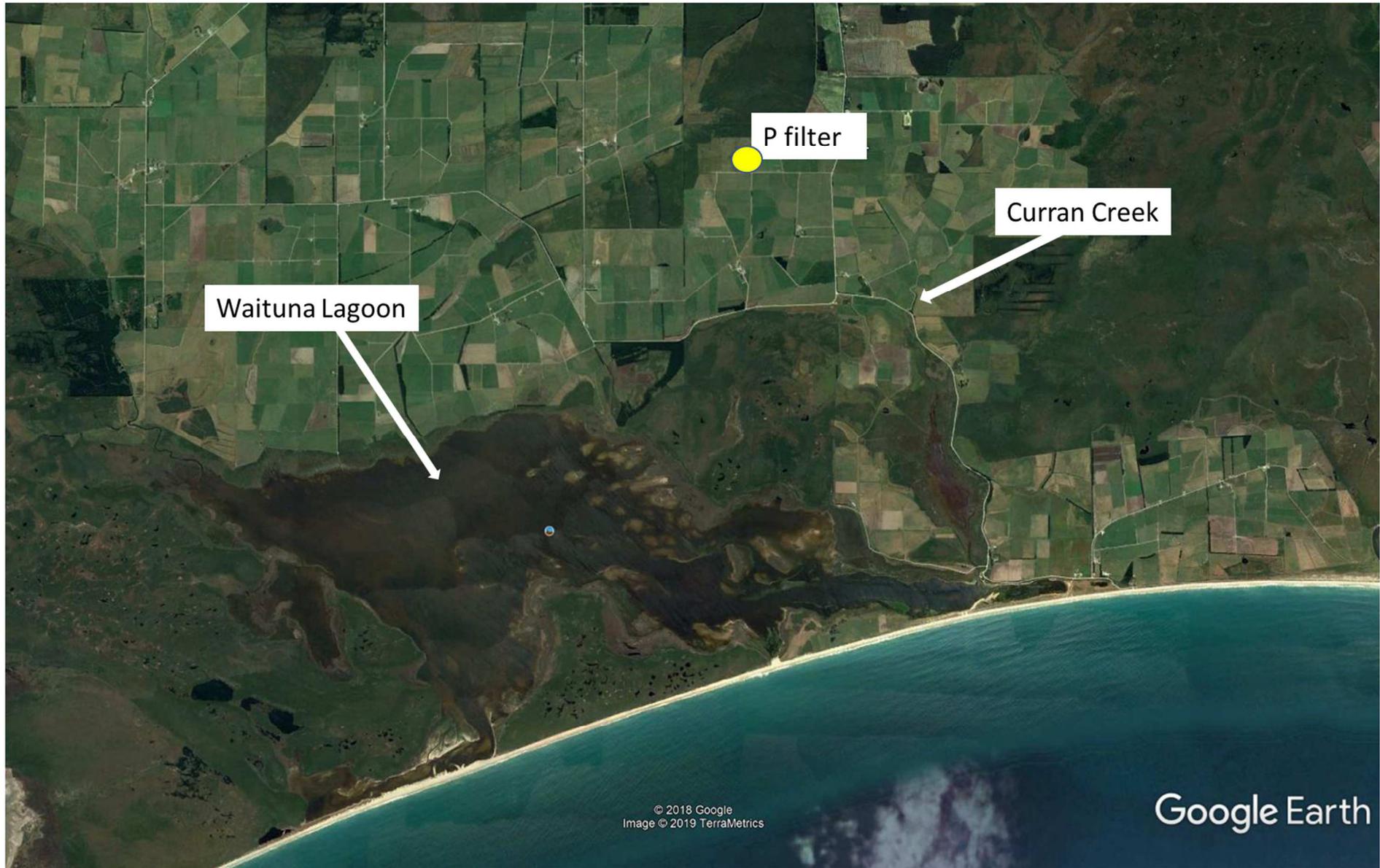


Figure 2-2: Location of the P filter in Curran Creek catchment, Southland.

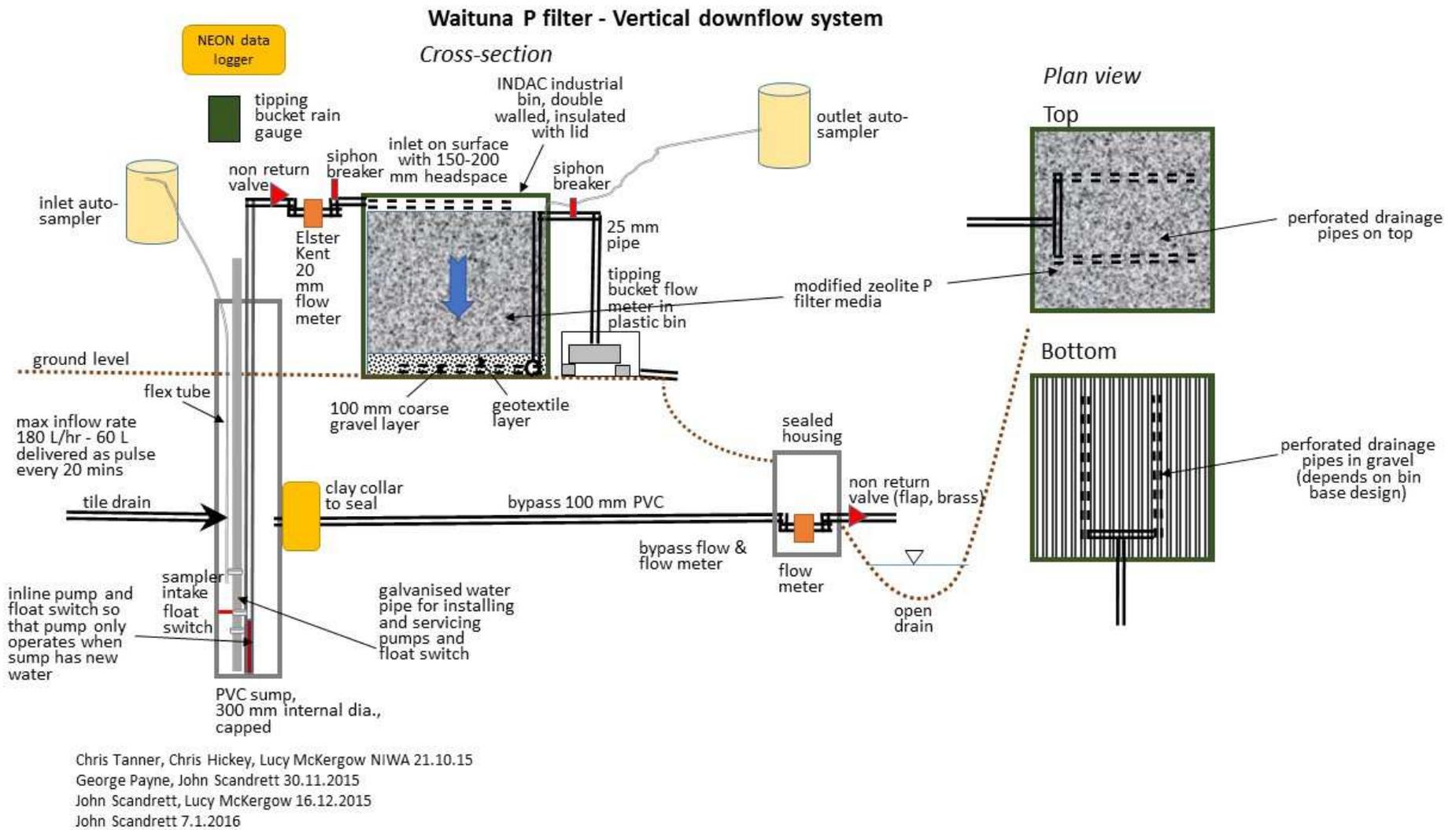


Figure 2-3: Schematic of P filter showing dimensions and key components of the as-built filter.

2.2 Description of the P filter

P filters are typically compact units filled with P sorbing material. For surface flows, small shallow (20 cm deep x 2 m long) boxes downstream of a weir have been used (Penn et al. 2012). This design is less suitable for tile drains on flat land where limited hydraulic head is available. Where at least 500 mm of head is available between the tile drain outfall and the surface drain a passive, gravity fed system is feasible. When the head difference is <500 mm, a pumped system is required.

The following description is largely derived from the original report (McKergow et al. 2016):

The P-filter installed in Waituna catchment was designed so that the Aqual-P could be removed and replaced. Water is pumped into the unit which was designed for a 3 hour retention time, and receives 180 L/hr in three pulses. The P-filter has a vertical downflow design, to ensure adequate contact time between the water and reactive material. The configuration relies on good dispersion of flow across the top of the filter bed – this is achieved using perforated pipes.

The P filter is a (nominal) 1 m³ plastic box with lid. The box is a twin walled insulated storage bin, with dimensions of 1160L x 1160W x 1100H (INDAC Limited, Blenheim). The bin is made for grape harvesting and is made from food grade polyethylene. The inside walls and base of the box are smooth (channels may encourage short-circuiting flows). The box has four-way forklift access. To reduce temperature fluctuations the bin has a lid (secured by latches), is insulated and green in colour. The box sits on the ground surface and the weight of box (~80 kg) and the material inside provides sufficient mass to overcome buoyancy.

The tile drain is intercepted by a 300 mm diameter PVC pipe sump. The sump provides a place for sedimentation to occur and has a 100 mm bypass to the open drain. The water is pumped from the sump when a float switch is in the 'on' position. The pump cannot operate when float switch is 'off' and there is insufficient water in the sump. The pump is a small inline bilge pump (RULE 280, 17 l/min, 12 V) powered by a battery bank with solar panel.

Water flows into the filter and is distributed across the surface of the filter by a U-shaped pipe (25 mm black polyethylene pipe with 5 mm holes at 100 mm centres). The outflow structure helps to retain water in the P-filter. Water enters the outlet through a U-shaped collector pipe (25 mm black polyethylene pipe with 5 mm holes at 200 mm centres). The collector pipe was covered with a layer of shade cloth to reduce the chance of gravel blocking the pipe holes and then covered with a 100 mm layer of coarse gravel. The structure outlet is a vertical standpipe (25 mm polyethylene) and water leaves the pipe and enters Currans Creek via a surface drain.

Key features of the P filter described above are shown in the schematic in Figure 2-3 and the photos in Figure 2-4. A schematic showing the monitoring and data transfer equipment deployed on site is included in Appendix A (Figure A-1).



A



B

Figure 2-4: Photographs of P filter showing key components of the monitoring equipment at the as-built filter.

The P-filter was designed and equipped to measure inflowing and outflowing DRP concentrations and loads or flux. DRP flux or loads are calculated directly as the product of flow rate and concentration.

Performance of the system was assessed as the difference between inflow and outflow load, which was estimated using Equation 2-1:

$$\text{Removal efficacy (\%)} = \frac{\text{inlet load} - \text{outlet load}}{\text{inlet load}} \times 100 \quad \text{Equation 2-1}$$

Removal efficacy expressed according to Equation 2-1 is the reduction of DRP load as a proportion of the influent load. Removal performance in terms of “efficacy” is further defined in the glossary, where the relationship to similar terms is clarified.

2.3 Sample analysis

2.3.1 Liquid samples

Dissolved reactive phosphate (*ortho*-phosphate, PO_4^{3-} , DRP) and total phosphorus (TP) concentrations were measured in discrete samples collected from the inflow and outflow of the P-filter using ISCO automatic samplers. The system was designed so that a sample was collected after passage of a given flow volume. Measurement of the sample volume was undertaken by the NEON logger, which triggered the sampler. The hydraulic load to the P filter was fixed, but the concentration of phosphorus species in the inflow could vary in response to rainfall events, seasonal influences and farm management practices.

Median spacing between samples was approximately 6.5 days. Samples were collected from the autosamplers once the carousel of 24 bottles was filled. To minimise biological alteration of the samples during storage in the field, sample bottles were preserved using a solution of mercuric chloride (0.5 mL), which was dispensed into the automatic sampler bottles in the Hamilton water quality laboratory prior to despatch to the field. Samples were submitted to the laboratory for analysis of DRP and TP using the molybdenum blue colorimetric method on a flow injection analyser in the NIWA Water Quality Laboratory. TP was determined after acid digestion. The detection limit for both variables was 1 $\mu\text{g/L}$.

2.3.2 Bed matrix samples

At the conclusion of the trial period, replicate samples of bed material were collected from three horizons: a “Top” layer (0-200 mm depth), a “Middle” layer (350-450 mm depth), and a “Bottom” layer (~800 mm depth). A sample of unused Aqual-P was also provided for comparison. The visual appearance of the filter material is indicated in a photo included as Figure B-1. There is sign of progressive staining of the matrix material from bottom to surface. This staining is probably from humic substances and/or iron derived from the peaty anoxic soils discharging into the tile drain. Samples of the original Aqual-P material and each layer were briefly rinsed, oven dried and ground to < 500 μm . These were submitted for analysis of Total P by ICP-MS to determine where P is absorbed in the system.

2.4 Freundlich isotherm analyses

For each sample of Aqual-P material (original, bottom, middle and top of filter) 50, 100, 200, 400, 600 and 900 mg of dried material was treated with 50 mL of USEPA soft water dosed with ca. 11 mg/L DRP. The tubes were mixed at 12 rpm for 24 hr and centrifuged. The supernatant was filtered through 0.45 μm filters and the filtrate samples were analysed for DRP. The data was then used to calculate mass loadings and plot isotherm graphs to estimate the DRP adsorption capacities of the materials. The plots are reproduced in Appendix E.

3 Results

3.1 Concentration and flux values

Summary statistics for sample concentration data for the two variables are summarised in Table 3-1, and flux (instantaneous load) values are listed in Table 3-2. These data are summarised graphically in Figure 3-1.

Table 3-1: Summary statistics for inflow and outflow DRP and TP concentrations. LCL = lower confidence level of arithmetic mean, UCL = upper confidence level of arithmetic mean.

Statistic (Entire assessment period)	Dissolved reactive phosphate concentration (µg/L)		Total phosphorus concentration (µg/L)	
	Inflow	Outflow	Inflow	Outflow
N of samples	61	57	61	56
Minimum	19	0.5	83	12
Maximum	1240	25	1770	126
Median	86	1	180	29.5
Mean	117.9	2.3	265.6	38.9
Standard Error of Mean	21.6	0.5	35.8	3.4
95.0% LCL of Mean	74.6	1.3	193.9	32.0
95.0% UCL of Mean	161.1	3.4	337.2	45.8
Standard Deviation	168.8	3.8	279.7	25.8
Variance	28490.5	14.5	78225.0	664.5
Cleveland percentiles				
0.01	20.0	0.5	83.1	12.1
0.05	33.6	0.5	86.7	13.3
0.1	39.0	0.5	91.6	17.1
0.2	44.8	0.5	122.0	20.0
0.25	54.0	0.5	136.5	21.0
0.3	62.6	0.5	145.4	22.6
0.4	73.9	0.5	162.8	25.0
0.5	86.0	1.0	180.0	29.5
0.6	88.0	1.0	188.0	37.1
0.7	92.0	2.0	218.6	42.7
0.75	95.8	3.0	234.3	45.0
0.8	108.9	4.0	301.6	54.5
0.9	206.6	6.0	584.8	69.6
0.95	359.3	7.7	868.1	101.0
0.99	1159.6	24.0	1676.1	125.2

Table 3-2: Summary statistics for inflow and outflow DRP and TP flux values. LCL = lower confidence level of arithmetic mean, UCL = upper confidence level of arithmetic mean.

Statistic (Entire assessment period)	Dissolved reactive phosphate flux (µg/s)		Total phosphorus flux (µg/s)	
	Inflow	Outflow	Inflow	Outflow
N of Cases	34	35	34	35
Minimum	0.002	0	0.007	0.001
Maximum	1.593	0.122	3.15	0.977
Median	0.51	0.005	0.783	0.079
Arithmetic Mean	0.513	0.013	1.074	0.225
Standard Error of Mean	0.088	0.005	0.177	0.044
95.0% LCL of Mean	0.335	0.004	0.713	0.136
95.0% UCL of Mean	0.691	0.023	1.435	0.314
Standard Deviation	0.51	0.027	1.033	0.259
Variance	0.261	0.001	1.068	0.067
Cleveland percentiles				
0.01	0.002	0	0.007	0.001
0.05	0.003	0	0.01	0.002
0.1	0.004	0	0.014	0.002
0.2	0.013	0	0.029	0.005
0.25	0.016	0.001	0.042	0.007
0.3	0.024	0.002	0.076	0.011
0.4	0.122	0.004	0.233	0.029
0.5	0.51	0.005	0.783	0.079
0.6	0.58	0.006	1.696	0.236
0.7	0.778	0.007	1.892	0.354
0.75	0.985	0.007	1.91	0.41
0.8	1.032	0.009	2.11	0.462
0.9	1.304	0.029	2.489	0.594
0.95	1.405	0.09	2.58	0.659
0.99	1.593	0.122	3.15	0.977

It should be noted that different number of paired samples are available for calculating summary statistics for concentration or flux values. As we noted in the previous report, the pump delivery system was subject to clogging which influenced the ability of the system to measure the discharge continuously. It was not possible to estimate the flux for all the samples for which concentration exist.

The technical reasons underlying these measurement difficulties are discussed in Section 5.

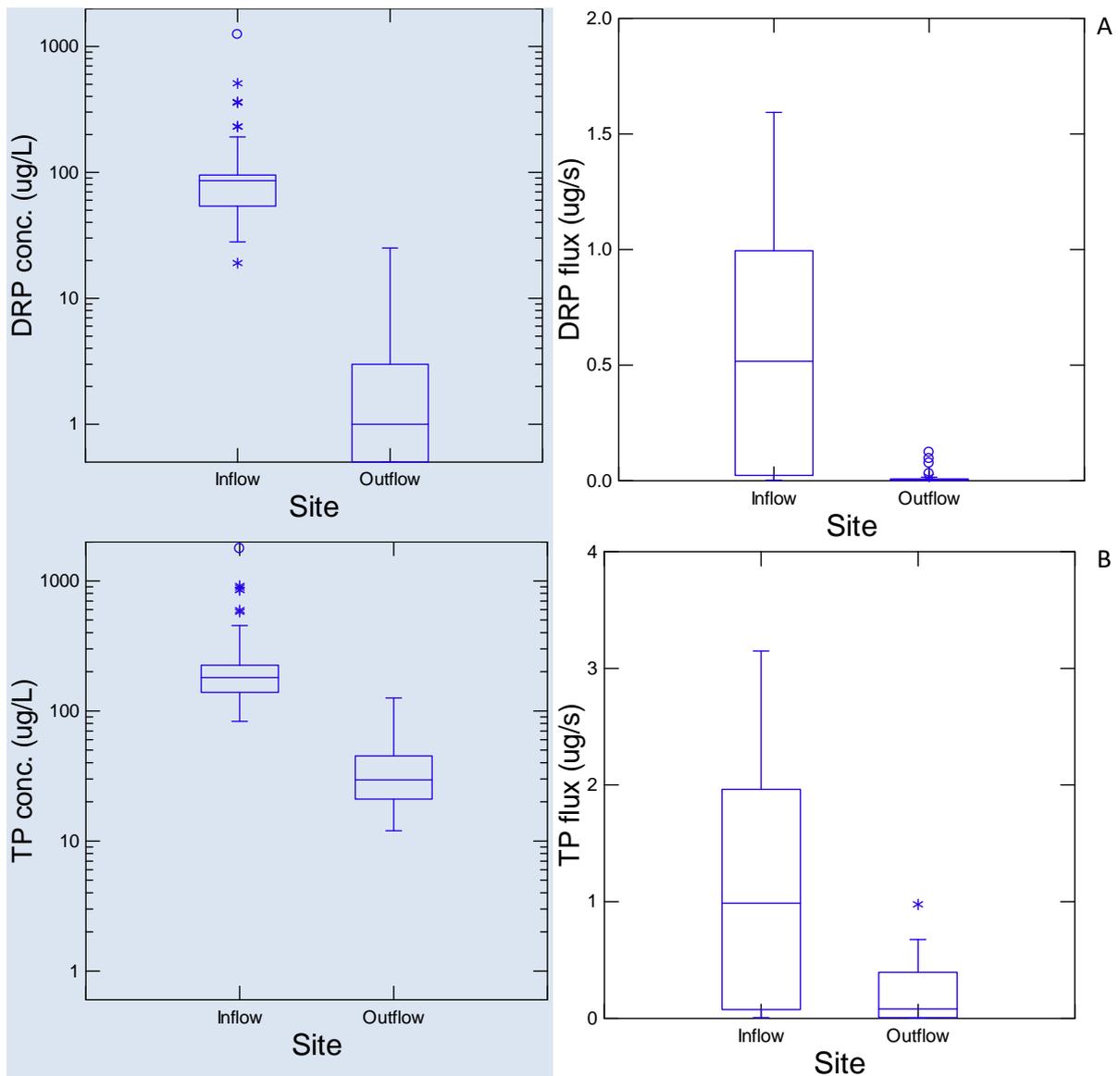


Figure 3-1: Comparison of DRP concentration and flux (A), and TP concentration and flux (B).

Prior to formal statistical testing, DRP and TP concentration data were tested for normality, and application of a non-parametric test appeared most appropriate. Results for a Wilcoxon Signed-Rank Test indicate that inflow DRP concentrations are statistically different (larger) than outflow concentration data ($p < 0.0005$). The same result was obtained for TP ($p < 0.0005$).

3.2 Removal efficacy

Using the same data used to calculate the DRP and TP flux estimates summarised in Table 3-2, removal efficacy was calculated using Equation 2-1. Performance is expressed as the difference between inflow and outflow flux, expressed as the proportion of influent contaminant flux. These data are summarised graphically in Figure 3-2 and summary statistics are provided in Table 3-3.

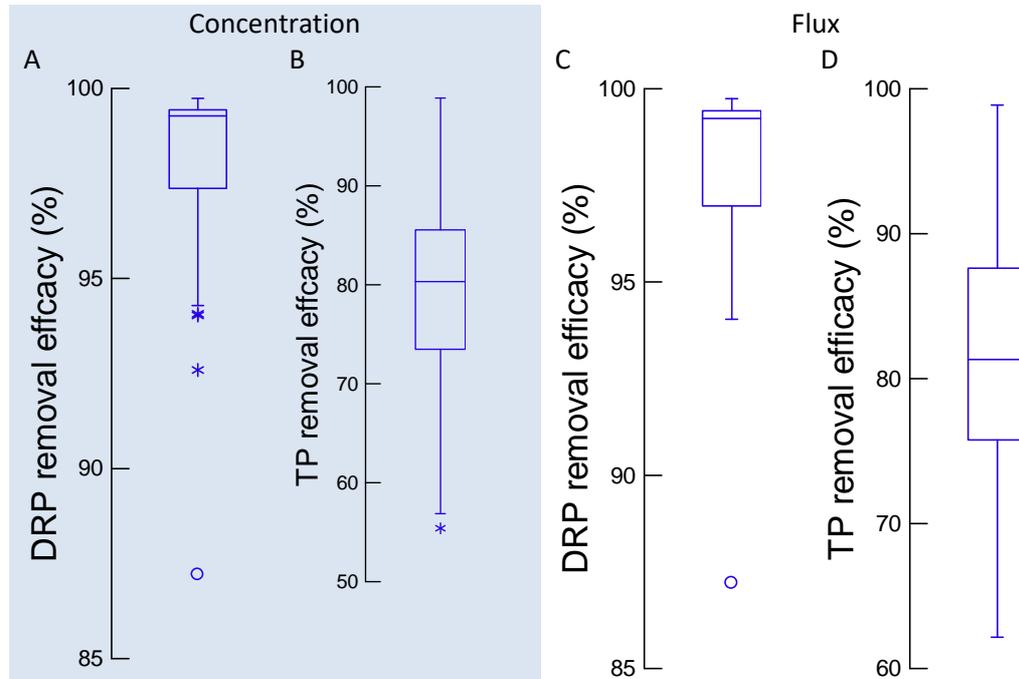


Figure 3-2: Comparison of DRP removal efficacy (A), and TP removal efficacy (B). Efficacy is expressed as the proportion of influent DRP or TP removed as indicated in Equation 2-1. Note the y-axes for the two figures are different.

Table 3-3: Summary statistics for DRP and TP removal efficacy. Efficacy is expressed as the proportion of influent DRP or TP removed as indicated in Equation 2-1. Results are expressed in terms of inflow an outflow concentration, or inflow and outflow flux.

Statistic	Concentration		Flux	
	DRP removal efficacy (%)	TP removal efficacy (%)	DRP removal efficacy (%)	TP removal efficacy (%)
N of Cases	46	45	28	28
Minimum	87.2	55.4	87.2	62.2
Maximum	99.7	98.9	99.7	98.9
Median	99.3	80.3	99.2	81.3
Arithmetic Mean	98.1	79.2	97.8	81.5
Standard Error of Arithmetic Mean	0.4	1.6	0.5	1.8
95.0% LCL of Arithmetic Mean	97.4	75.9	96.8	77.8
95.0% UCL of Arithmetic Mean	98.8	82.5	98.9	85.2
Standard Deviation	2.4	11.0	2.7	9.6
Coefficient of Variation	0.0	0.1	0.0	0.1
Method = CLEVELAND				
1.00%	87.2	55.4	87.2	62.2
5.00%	93.7	59.9	93.3	65.8
10.00%	94.4	62.8	94.1	67.5
20.00%	97.1	70.0	96.7	74.6
25.00%	97.4	73.3	97.0	75.8
30.00%	97.6	74.6	97.4	77.5
40.00%	99.2	78.0	99.1	79.0
50.00%	99.3	80.3	99.2	81.3
60.00%	99.3	82.2	99.3	82.8
70.00%	99.4	85.4	99.4	86.3
75.00%	99.4	85.7	99.4	87.6
80.00%	99.4	87.6	99.4	88.4
90.00%	99.5	94.1	99.5	95.9
95.00%	99.7	97.0	99.7	97.8
99.00%	99.7	98.9	99.7	98.9

4 Laboratory assessment of bed matrix materials

4.1 Pore water

The concentrations of DRP in replicate samples of pore water recovered from the bed of the P-filter are summarised in Figure 4-1. With regard to the pore water (Figure 4-1 A):

- The surface sample or top sample contained approximately five times the amount of recoverable DRP relative to either the middle or bottom samples collected from within the filter bed, and the difference between the surface and middle samples is statistically significant ($p = 0.008$).¹
- There is no significant difference between the amount of recoverable DRP in the samples collected from deeper within the bed ($p = 0.07$).¹

With regard to the TP recovered from the bed matrix material (Figure 4-1 B):

- Although the differences in analytical results between the sample analyses cannot be tested formally because the analyses were not replicated
 - the surface or top sample results are markedly higher than any of the other samples
 - there is little difference in the TP that was recovered from the other three samples, suggesting that the middle and bottom material in the bed was not exposed to phosphorus.
- The absence of difference between the original material and the middle and bottom bed material suggests that there was little breakthrough of DRP from the surface layer, i.e., the P retention capacity of the surface layer has not been exceeded.

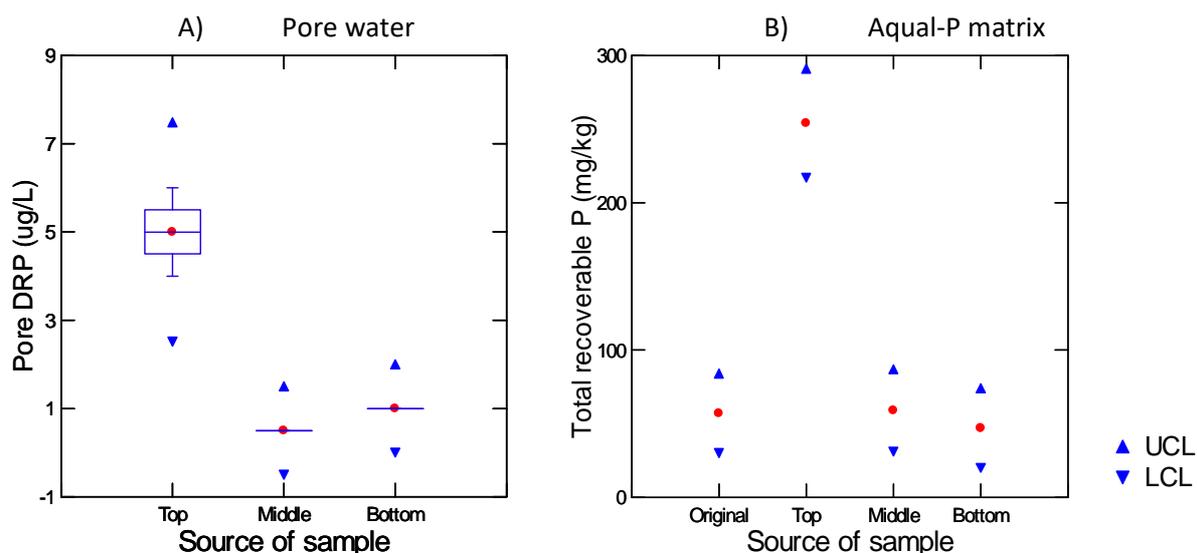


Figure 4-1: Comparison of DRP in pore water following equilibration with bed material (left) and TP recovered from dried bed material (right). Red dots indicate the mean concentration and blue triangles are the upper and lower confidence intervals. Note the y-axes for the two figures are different.

¹ Quade nonparametric test, $p_{crit} = 0.02$

4.2 Freundlich adsorption isotherm analyses

The Freundlich adsorption isotherm analyses are summarised in four figures in Appendix E. These figures show the results of a model fitted to the data derived from samples of Aqual-P spikes with varying amounts of DRP. This provides a relationship between a solution with a specific DRP concentration and the equilibrium DRP mass loading. These values are summarised for a 0.2 mg/L solution in Table 4-1.

Table 4-1: Adsorption capacity of Aqual-P samples for a 0.2 mg/L DRP solution.

Sample	Adsorption capacity (mg/g)	Remaining capacity relative to original material (%)
Top	0.11	26
Middle	0.12	28
Bottom	0.18	43
Unused original material	0.42	-

For this study, these values can be used to indicate the relative capacity of DRP (mg/g) of the various Aqual-P samples, if they were to be exposed to a nominal DRP concentration of 0.2 mg/L. The upper half to two-thirds of the filter bed has potential to retain less than 30% of the DRP that the original material could retain, whereas the bottom third of the bed has the potential to adsorb approximately 60% of the DRP that the original material could retain.

5 Discussion

As indicated in Section 1, successful conduct of the trial required an increase to the hydraulic loading rate. The pump was refurbished at the start of the trial, and the flow rate was adjusted at that time. We failed to maintain the flow rate at the required level, which did not allow the performance of the filter bed to be assessed as required in terms of the contract conditions. The consequences of failure to achieve the required conditions are discussed below.

5.1 Removal efficacy

From Section 3, we saw that DRP and TP concentration in the inflow varied over a wide concentration range, and that approximately 50% of the influent TP was DRP (DRP 86 µg/L and TP 180 µg/L respectively). Outflow DRP and TP concentrations were much smaller (median concentrations 1 µg/L and 29.5 µg/L for DRP and TP respectively). DRP concentrations in the inflow were almost invariant over the project life, and the median concentration in the outflow was equal to the detection limit of the analytical method.

The flux of P entering the filter bed was relatively small (for reasons discussed below), but was approximately 100 times larger than that leaving the filter, indicating a two-log reduction performance. This performance should be regarded as conservative, because as the concentration data in Table 3-1 indicate, 50% of the DRP concentration data in the outflow are less than the analytical detection limit. In the case of TP, all results for inflow and outflow exceeded the analytical limit of detection. Smaller efficacy was indicated by these data (approximately one-log reduction, using median TP values).

When expressed in terms of load or flux removed, the filter consistently provided greater than 95% efficacy for DRP removal (median >99%), and greater than 80% removal (median) for TP. These results indicate that a fraction of the P entering the filter system is in a form that is not amenable to adsorption to Aqual-P. The peaty nature of soils in the catchment suggests that this P is an organic form, where ligands² binding to the P probably reduce the electrical charge on the P and/or increase the size of the P-containing molecule so that it is unable to bind to P absorption sites within the bed matrix. Further investigation would be required to confirm this inference. We conclude, however, that this organic P is not measured in the DRP analysis, but is included in the TP results. In situations where the drainage water is anoxic and enriched with iron-containing minerals, aeration is likely to cause precipitation of iron-containing materials on the filter bed. This may reduce the load of DRP to the bed (because some of the DRP may bind to the iron once it oxidises), but may also reduce the P-binding capacity of the bed material. These effects are also pH dependent, so it would be useful to obtain additional information regarding the drainage water chemistry as part of the design process.

5.2 Mass load removal

Earlier trials had established that Aqual-P had a sorption capacity of approximately 1.7 g P/kg (tested at DRP concentrations <0.1 mg/L). A 500 kg filter bed with material of this sorption capacity therefore had a theoretical P retention capacity of approximately 850 g P at an influent concentration of approximately 0.1 mg/L (Gibbs and Hickey 2018).

P sorption capacity of the original material used in this trial was approximately 0.42 mg/kg at an influent concentration of approximately 0.2 mg/L (Appendix E, Figure E-1). For a bed containing 500

² Compounds that bind with or are bound by the *ortho*-phosphate molecule by weak intermolecular forces, or almost irreversible covalent bonding.

kg of material, the theoretical sorption capacity was 210 g. At the end of the trial period, the remaining capacity of the filter material was approximately 18 g, 20 g and 30 g for the top, middle and bottom third of the bed. The bed had a theoretical remaining capacity of approximately 68 g, or approximately 1/3 of the original capacity.

Estimation of the mass of DRP or TP removed by the filter material requires a continuous flow record. This does not exist. For the period when flows through the bed were recorded (5,400 hours of the approximately 15,400 hours of the trial), the inflow P load was approximately 13 g (as DRP), but this under-represents the actual P load.

Based on this analysis we conclude that the bed was underloaded in terms of DRP, and that the adsorption isotherm data indicate a capacity to retain DRP remains, particularly in the lower third of the bed. Despite this limitation imposed primarily by equipment performance, we have demonstrated that the filter has consistently removed the bulk of the influent P load.

5.3 P saturation of the sorbent

In section 4 we characterised the extent to which DRP saturated the matrix material, and the extent to which DRP could be expected to remobilise from the matrix after binding. These results indicate that the system still has capacity to remove phosphorus from inflow water and that at least 50% of the bed volume (middle to bottom) has a substantial capacity for P-binding. Data derived from analysis of DRP in pore water samples and the phosphorus content of bed material is consistent with the isotherm data – all these data indicate that substantial P sorption in surface layers, and a decreasing P content through the lower bed. These data suggest that the bed was probably subject to a higher but unknown volumetric and mass loading rate.

5.4 Performance

The results above confirm that the filter material has high efficacy in terms of DRP and TP removal. The mass loading rate to which it was subject could be increased to further test the efficacy of the material. Three key reasons contributed to the lower than anticipated mass loading rates:

1. Particulate material in the inflow. Summary statistics for continuously measured turbidity values are included in Appendix D – these indicate that for approximately 70% of the assessment period, turbidity exceeded 3 NTU, suggesting a persistent supply of particulate material from the drainage system.
2. The basic design of the system required a pump to dose P-containing water to the filter bed. Drainage water collected in a sump, from where it was pumped onto the filter bed. This was necessary because drainage volume had to exceed a pre-set volume (determined by a level switch) before the pump would actuate. Particulate material tended to collect in this sump, which caused the pump to be subject to clogging. This led to deterioration in performance (the delivery rate decreased over time), and on occasions caused complete occlusion of the intake. It was necessary to service the pump several times during the project life to maintain some level of performance. This alteration in performance did however reduce the P loading rate between inspection and service intervals.
3. Seasonal variability in the supply of drainage water, causing the tile drain to be dry (or the flow in the tile drain to be below the sensitivity of measurement equipment). There was no- to low bypass flow for several weeks during each summer when flows were small and likely to test the measurement capability of the management system.

As a consequence of the lower than anticipated flows and reduced number of measurements of flow in the system, fewer results were obtained to estimate the flux of material than the total number of concentration results – for much of the trial period, the drainage water applied to the filter bed was unmetered. We cannot determine whether this was because the flow rates were too small to measure, or whether the meter malfunctioned. From the P-sorption capacity trials, we conclude the flows were generally low. For the system design, however, it is justifiable to compare inflow and outflow concentrations – the outflow was derived solely from the inflow, which means that the flow was identical for either inflow or outflow for each sample pair. In this circumstance, the inflow and outflow concentrations are surrogates for the inflow and outflow flux. They cannot be interchanged however because flow data are not available for all concentration results. The efficacy in terms of reduction in the concentration of either DRP or TP is similar to what was observed for flux. These results are summarised together in Table 5-1.

Table 5-1: Summary of phosphorus removal performance.

Water quality variable	Removal efficacy (removal as proportion of inflow, %)	
	Concentration	Flux
DRP	99.3	99.2
TP	80.3	81.3

Correlation between either DRP in the inflow and outflow, or TP in the inflow and the outflow was weak, and there was little indication that removal performance deteriorated as the concentration of either DRP or TP increased.

Varying DRP yields have been measured in tile drainage water in Southland. Monaghan et al. (2000) measured DRP yields from 100 g/ha/y to 250 g/ha/y during 1998. P losses in mole and tile drainage from sandy loam soils in east Southland (near Edendale) were 48±16 g/ha/y (DRP), 59±19 g/ha/y (TDP)³ and 152±76 g/ha/y (TP), and the average DRP concentration was 23 µg/L (range 5-121 µg/L) (Monaghan et al. 2002). The concentrations measured in tile drainage in the current study fall in this range (mean 118±21 µg/L as DRP). From the available bypass flow data (approximately 10,000 hours with average flow of 0.21 L/s, and a median DRP concentration of 86 µg/L), the DRP flux is 1.5 g/d, and the yield is approximately 570 g/ha/y, which is relatively high with respect to other Southland data, reflecting the leaky nature of these peaty soils with low anion storage capacity with regard to DRP.⁴ The theoretical P-sorption capacity was earlier estimated to be approximately 210 g P. Theoretically the as-built filter bed has the capacity to treat the entire mass of P in the drainage water for approximately 134 days. High levels of P removal over that period of time is unlikely however, because the hydraulic loading rate would be excessive, reducing the contact time between the DRP and the bed material.

Although these results do not indicate the cumulative mass of P that was or ultimately may be retained in the filter bed, they confirm that sorbent materials may be deployed on-farm to reduce the mass load of material to receiving waters. The challenge is to design a system that will operate in a consistent manner for the specific situation where mitigation is required. Guidance is available from the literature. For example, Penn and Bowen (2018) recently published a textbook that describes P removal structures, and provides detailed information to guide the design, operation and

³ TDP = total dissolved phosphorus

⁴ From Figure 2 1, the area drained by the tile drain was likely to be smaller than 100 m x 100 m (1 ha).

implementation of these structures. It also introduces and describes use of the PHROG software, which may be used to identify which removal devices are suitable for the specific situation where P-removal is required; this software can also assist with design optimisation. This information was derived from review of recent technical publications, and practical experience with design and operation of these devices in various environments (including broadacre cropping, large-scale animal production systems and urban drainage).

One of the recommendations of Penn and Bowen (2018) is development of “P-removal design curves”, which summarise the performance of flow-through sorption experiments. It is possible to tailor these to mimic real-world conditions such as persistent or intermittent hydraulic load, variable P load, and varying contact times. A design curve may be established from one or more flow-through experiments or estimated using a model. Either approach offers advantages over the more traditional batch isotherm approach, which cannot account for these time varying factors. The PHROG model (Penn et al. 2016) may be used to predict P-removal for any sorbent material as a function of retention time and influent P load. Trials similar to those recommended by Penn and Bowen (2018) were undertaken as part of the design process for the current P filter (Olsen et al. 2013).

Success of a mitigation tool is determined by several factors. The mass of contaminant removed is important, but equally important is the concentration (and mass load) of P in water discharged from the removal system. The current trial has demonstrated that achieving below detection limit concentrations is possible over an extended trial period. Unfortunately, problems with the measurement system have made it impossible to estimate the total mass load applied to the filter bed, and the total P-sorption capacity that may be achievable.

6 Conclusions

A field trial of Aqual-P as a P-removal filter medium was undertaken between May 2016 and August 2018. Although seasonal effects combined with sample characteristics and operational difficulties made it difficult to estimate flow consistently through the trial, it was possible to demonstrate consistent reduction in the concentration of DRP and TP:

- Expressed as a reduction in the influent concentration, the median efficacy was 99.3 % for DRP and 80.3% for TP.
- Expressed as a reduction in the influent flux, the median efficacy was 99.2 % for DRP and 81.3% for TP.

The laboratory assessment of the Aqual-P recovered from the filter bed suggests that approximately 32% of the sorption capacity remains, based on a P concentration of 0.2 mg/L, with greater capacity in the lower third of the bed than the upper material.

NIWA and the Project Manager acknowledge that failure to ensure that the hydraulic loading rate was maintained at the required level did not meet the contract conditions, which in turn did not allow the performance of the filter material to be assessed as required. It will be necessary to repeat the trial to quantify the P removal efficacy of AqualP.

Suggestions for improvement

The removal efficacy of Aqual-P has been characterised in several trials. The current trial demonstrated consistent performance over a 27-month period. Review of the literature revealed several tools that may prove useful for designing and optimising P removal structures using Aqual-P. This will include optimising the dimensions of the removal structure to achieve optimal porosity and residence time within the filter bed.

One recommendation that comes out of this study is that gravity-fed systems should be utilised wherever possible. The persistent load of fine particulate material in the tile drainage was one factor that limited the value of this trial because of the deleterious effect on pump performance, causing complete failure on several occasions. Where hydraulic head greater than approximately 500 mm is achievable, gravity fed systems may be feasible (Penn and Bowen 2018). The nature of tile drain systems is likely to make this difficult to achieve, which means that use of pumps and power supplies are almost mandatory. Systems that use air-lift pumps or other pumps less prone to clogging are desirable. Systems that incorporate air-lift pumps and header tanks offer other benefits, including aeration of the drainage water (which will encourage flocculation, binding of DRP with iron containing minerals and settlement in the header tank. This will also reduce the particulate load on the filter bed. As was noted in a parallel assessment of a woodchip denitrification filter (Hudson et al. 2019), the design of a mitigation tool should consider the water quality improvement targets for the receiving environment. This will ensure that the system may be designed to provide adequate nutrient removal at the time of year when it is most required.

7 Glossary of abbreviations and terms

Effectiveness	To be effective is when results accomplish their purposes, thus giving an effective outcome.
Efficacy	<p>The power or capacity to produce a desired effect.</p> <p>To be efficacious involves possession of a quality that gives the produced results the potential to lead to an effective outcome.</p> <p>Efficacy has to do with the ability or capacity to do something, but not about how something is done.</p> <p>Efficacy may be expressed as the difference between inflow and outflow mass load, or flux.</p> <p>Efficacy may also be expressed in terms of mass removed/volume of treatment material/unit of time, e.g., “g P/m³/day”.</p>
Efficiency	<p>Efficiency is the quality or property of being efficient.</p> <p>To be efficient is to produce an output in a competent and qualified way.</p> <p>Efficient means acting or producing with a minimum or waste, expense, or unnecessary effort.</p>
Flux	<p>This is the product of concentration and discharge or flow. It is reported as mass/unit of time, and may be expressed as g/s, g/d or any other suitable equivalent unit.</p> <p>These units are interchangeable (with unit conversion).</p>
Load	<p>This is the product of concentration and discharge or flow integrated over a period of interest. It has units of mass, but the period of time over which the flux is integrated must be specified. For example, if the flux is integrated over a day, the load is reported as g/d or similar.</p>

8 Acknowledgements

We acknowledge the field assistance provided by DairyGreen, and contribution of Blue Pacific Minerals, suppliers of AqualP.

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Appendix A Flow measurement and sampling equipment

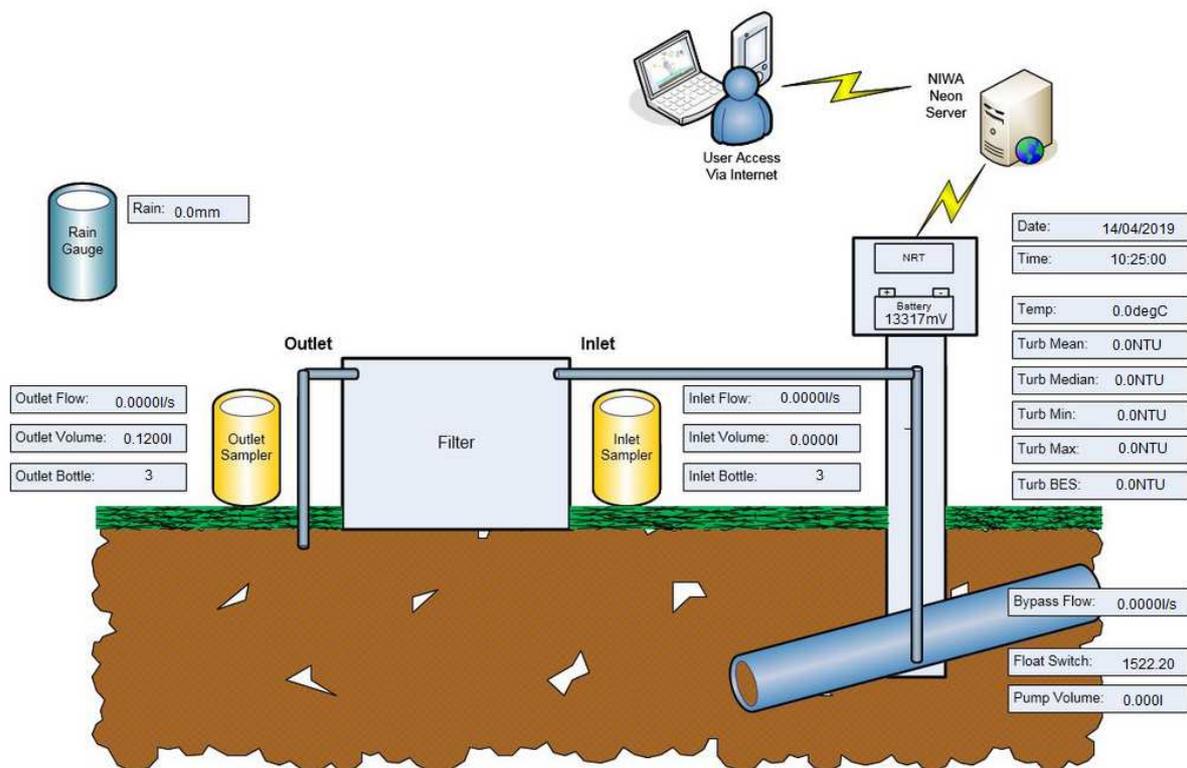


Figure A-1: Flow measurement and sampling equipment deployed at Waituna P-filter.

Appendix B Bed matrix material



Figure B-1: Filter bed material recovered from the Waituna P filter along with a sample of unused material. Photo courtesy of Greg Olsen, NIWA Hamilton.

Appendix C Statistical analysis

DRP concentration data

Data were tested for normality, and application of a non-parametric test appeared most appropriate. Results for a Wilcoxon Signed-Rank Test follow. Inflow DRP concentrations are statistically different (larger) than outflow concentration data ($p < 0.0005$).

Wilcoxon Signed-Rank Test Results

Counts of Differences (row variable greater than column)

	IN_DRP_MGM3	OUT_DRP_MGM3
IN_DRP_MGM3	0.000	46.000
OUT_DRP_MGM3	0.000	0.000

$Z = (\text{Sum of signed ranks}) / \text{Square root (sum of squared ranks)}$

	IN_DRP_MGM3	OUT_DRP_MGM3
IN_DRP_MGM3	0.000	
OUT_DRP_MGM3	-5.906	0.000

Two-Sided Probabilities using Normal Approximation

	IN_DRP_MGM3	OUT_DRP_MGM3
IN_DRP_MGM3	1.000	
OUT_DRP_MGM3	0.000	1.000

TP concentration data

Data were tested for normality, and application of a non-parametric test appeared most appropriate. Results for a Wilcoxon Signed-Rank Test follow. Inflow TP concentrations are statistically different (larger) than outflow concentration data ($p < 0.0005$).

Wilcoxon Signed-Rank Test Results

Counts of Differences (row variable greater than column)

	IN_TP_MGM3	OUT_TP_MGM3
IN_TP_MGM3	0.000	45.000
OUT_TP_MGM3	0.000	0.000

$Z = (\text{Sum of signed ranks}) / \text{Square root (sum of squared ranks)}$

	IN_TP_MGM3	OUT_TP_MGM3
IN_TP_MGM3	0.000	
OUT_TP_MGM3	-5.842	0.000

Two-Sided Probabilities using Normal Approximation

	IN_TP_MGM3	OUT_TP_MGM3
IN_TP_MGM3	1.000	
OUT_TP_MGM3	0.000	1.000

Appendix D Measured turbidity

Statistic	Hourly average turbidity (NTU)
N of Cases	22329
Minimum	0
Maximum	419.4
Median	5.2
Arithmetic Mean	6.5
Standard Deviation	7.1
Cleveland percentiles	
0.01	0.0
0.05	0.0
0.1	0.0
0.2	1.4
0.25	2.4
0.3	2.9
0.4	3.8
0.5	5.2
0.6	6.7
0.7	8.8
0.75	9.8
0.8	11.0
0.9	13.1
0.95	16.9
0.99	28.3

Appendix E Adsorption isotherms

Graphs (log/log) of mass P loading versus equilibrium [P] for Aqual-P filter materials.

In each case the blue line represents the Reference Isotherm for highly absorptive material, the burgundy line represents the Freundlich model line extrapolated from the data (blue diamonds). The vertical red line (at a typical in-situ concentration of 0.2 mg/L P) intersects with Model line and indicates the adsorption capacity of the Aqual-P material at that concentration.

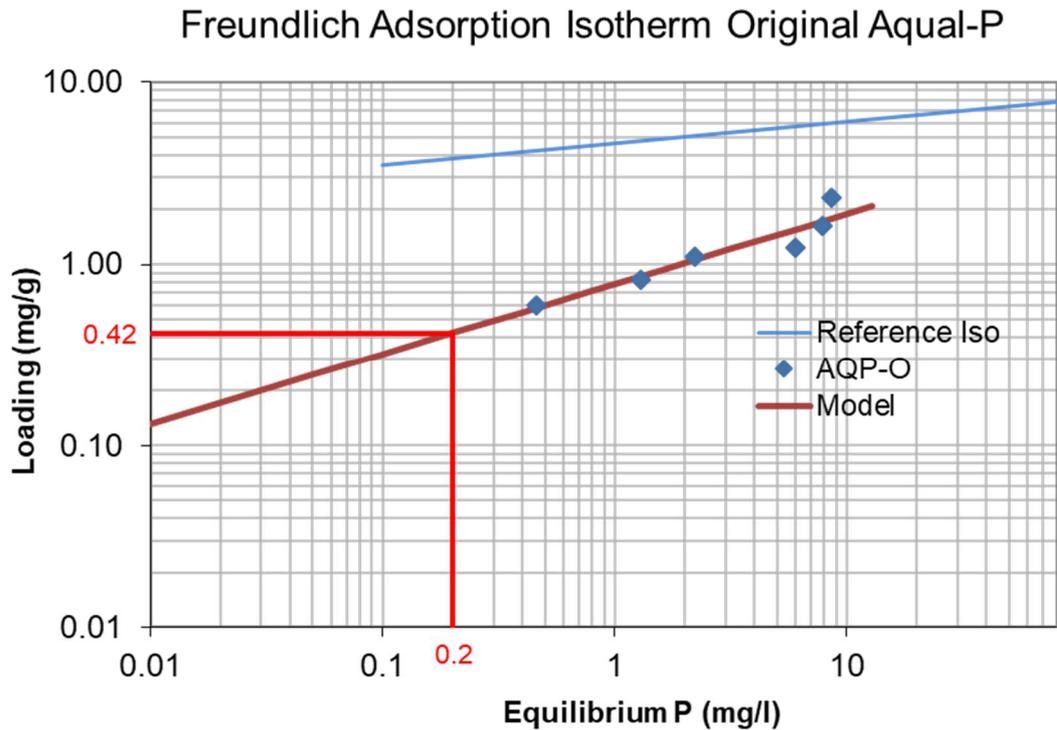


Figure E-1: Adsorption isotherm for original (unused) filter bed material used in the Waituna P filter (burgundy), along with isotherm for reference material (blue). The red line indicates the sorption capacity (y-axis) for a nominal 0.2 mg/L influent concentration.

Freundlich Adsorption Isotherm Top of Filter

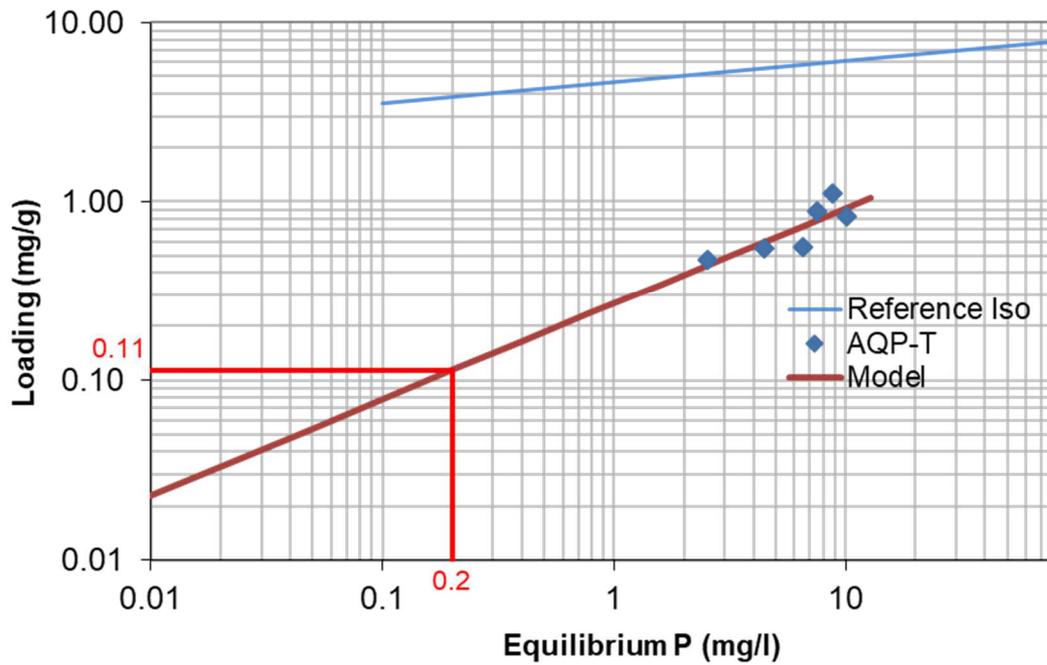


Figure E-2: Adsorption isotherm for filter bed material recovered from the top third of the Waituna P filter (burgundy), along with isotherm for reference material (blue). The red line indicates the sorption capacity (y-axis) for a nominal 0.2 mg/L influent concentration.

Freundlich Adsorption Isotherm Middle of Filter

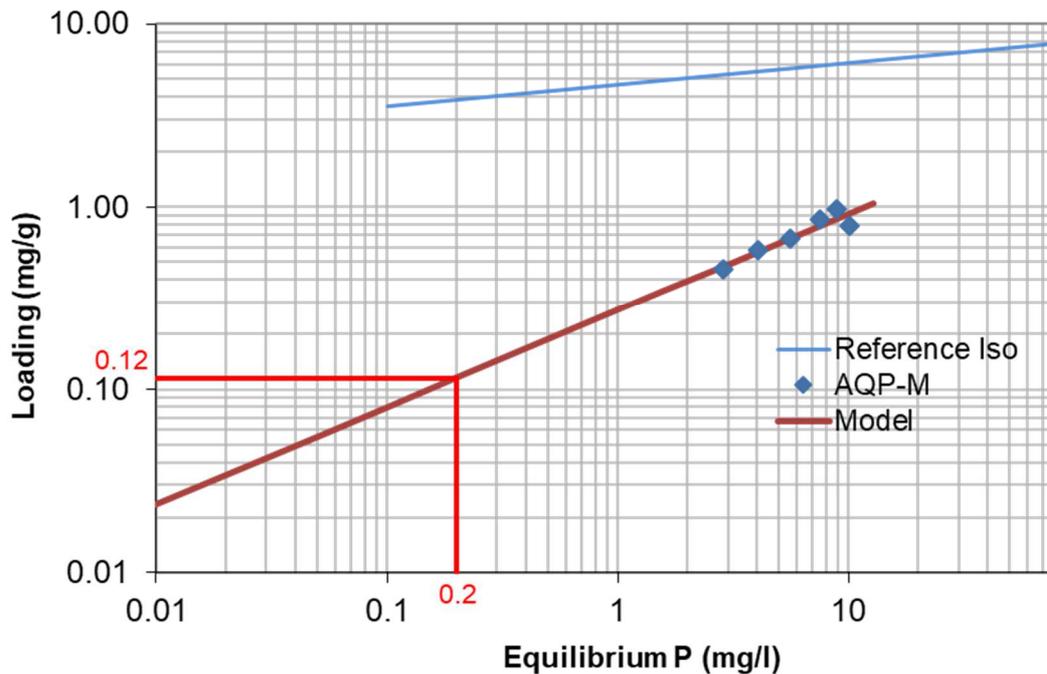


Figure E-3: Adsorption isotherm for filter bed material recovered from the middle third of the Waituna P filter (burgundy), along with isotherm for reference material (blue). The red line indicates the sorption capacity (y-axis) for a nominal 0.2 mg/L influent concentration.

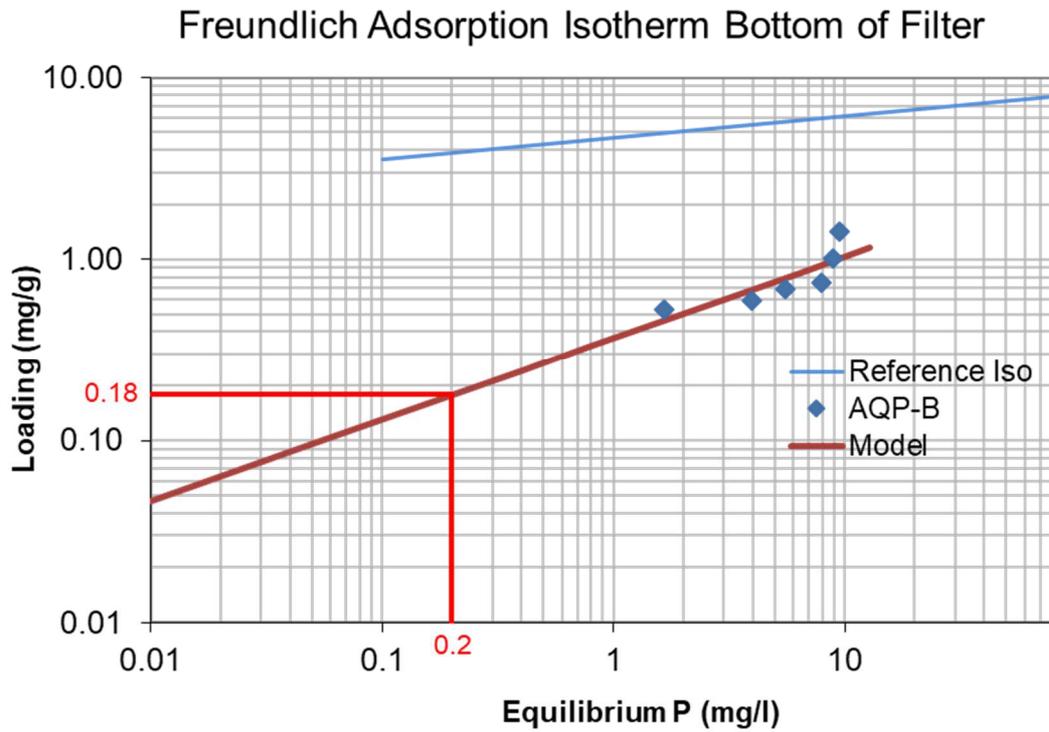


Figure E-4: Adsorption isotherm for filter bed material recovered from the bottom third of the Waituna P filter (burgundy), along with isotherm for reference material (blue). The red line indicates the sorption capacity (y-axis) for a nominal 0.2 mg/L influent concentration.