

Client Report

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**Assessment of a novel technique to
remove phosphorus from streamflow**

R. W. McDowell and M. F. Hawke

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1. Executive Summary

Decreasing the concentration of phosphorus in streamflow entering P-limited lakes is central to the prevention of eutrophication. We trialled a novel technique that aimed to remove P from streamflow by sorbing P onto a heavy-weight steel slag encased in a mesh: termed a P-sock. This technology allows P-socks and entrained P to be removed on demand, and prevents P-rich material from washing into the lake in storm events. One-hundred and eighty P-socks were installed on a 200 m reach of streambed in a herringbone fashion allowing fish passage and good mixing of stream water and P socks. Water samples were taken at various positions down the reach and suspended sediment, pH and P fractions such as dissolved reactive P (DRP) and total P (TP) determined. Socks and bed sediment were also sub-sampled, which indicated that after 6 months only 20% capacity (P sorption maximum 4.5 g kg^{-1}) was left. Overall, concentrations of DRP and TP decreased on average 35 and 21% after the P-socks. However, this was flow dependant with no P removal occurring above a flow rate of 22 L s^{-1} for DRP and 18 L s^{-1} for TP, which occurred 33 and 45% of the time for DRP and TP, respectively. Consequently, the current setup is restricted to small streams unless P sorption efficiency of the encased material is improved or flow rates decreased.

2. Introduction

Lake Rerewhakaaitu is a mesotrophic lake and one of 15 among the Rotorua lakes formed up to 140,000 years ago via volcanic eruptions in the Bay of Plenty and Waikato regions of the North Island of New Zealand (1). While Rerewhakaaitu currently enjoys reasonable water quality, other lakes in the area have become eutrophic due to the inputs of nutrients from domestic and rural sources. During the 1980's supply from domestic sources were cleaned-up and many of the lakes including Rerewhakaaitu enjoyed a period of improved water quality (2). However, since then water in the lake has seen a steady increase in nitrogen concentrations. This could be due to the delayed transmission of water to the lake, which takes about 1-10 years from shallow groundwater (2). This contrasts with other lakes in the region which have delays of up to 100 years, but also means that changes in management within the catchment can affect the lake sooner. However, while primary production in many of the Rotorua lakes may be limited by nitrogen (3), Rerewhakaaitu is currently thought to be strongly phosphorus limited (2, 4, 5).

Much like the delay in N inputs via groundwater a decrease in P concentrations can take a long period. For instance, Rutherford et al. (6) estimated that due to sewage inputs, the bottom sediments of Lake Rotorua may negatively impact water quality for up

to 200 years. Historically, major inputs of P to Rerewhakaaitu are due not to domestic but agricultural inputs, specifically pastoral farming. Although, the proportion of the catchment in pasture has decreased from 100% in 1978 to 77% in 1996, in that time there has been an increase in the use of fertilisers (especially nitrogen) and a change from low intensity sheep and beef farming to dairying (2). The increased use of nitrogen in intensive farming is likely to mean that P will remain the limiting nutrient in the near future and thus a greater focus on P than past lake management strategies have taken should restrict primary productivity better than focusing on N and P or just N.

Inputs of P to the lake have been estimated at $0.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and are not high when compared to other New Zealand catchments in intensive agriculture (range $0.3 - 1.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$; 7). As such, land-based best management practices may have limited effect in decreasing this further. However, management practices to prevent P loss once in stream flow are limited. Furthermore, soils in the region are derived from Taupo ash and Kaharoa ash and are naturally prone to erosion. The loss of dissolved P is also inevitable due to the weathering of primary minerals such as apatite. These losses are difficult to prevent and many techniques such as dosing the stream with alum or altered bentonite clays to sorb P also rely on the P attached to the adjuvant remaining on the stream bed or for the material to cap the bed and block P dissolution from sediment below (8, 9). This is unlikely to occur as materials can be lost during flood events unless the material is very heavy. Furthermore, the input and deposition of new P-rich sediment decreases the cap's effectiveness.

One solution may be to entrap P in a material in a casing which prevents it washing away during a flood but enables the material and P to be periodically removed. Following a survey of possible alternative P sorbing materials, McDowell (10) settled on a slag produced as a by-product from a steel manufacturing plant. This material met criteria for good P sorption capacity and low toxicity. The material was tested as a backfill for tile drains and showed good effectiveness in removing P from drainage (11). We therefore propose to test a mixture of slag in a casing as a novel technique to remove P from streamflow. In order to make sure the P flows freely around the slag, is entrapped and removable we have encased the slag mixture in a highly porous mesh – subsequently called a P sock. It is envisaged that this would allow the P sock to be removed when sorption capacity is nearly exhausted and new socks can be put on the stream bed. Given the P sensitivity of Lake Rerewhakaaitu, our objective was to test an arrangement of P socks for P uptake from the Mangakino stream which feeds the lake.

3. Materials and methods

Site

The Mangakino Stream is spring fed and nominally drains an area of approximately 688 ha (Figure 1). However, due to very porous geology much flow may be lost to deep groundwater and the actual area contributing to streamflow is much less than this (12). Quarterly measurements taken by the regional council (Environment B.O.P.) as part of a regular monitoring programme from 1995 to the present day established a mean discharge of 23 L s^{-1} and range of flows from 3 to 172 L s^{-1} . In addition, a larger historical data set for the Mangakino stream (1972 to 1976) was combined with recent data and correlated against a permanently gauged site in an adjacent stream. This yielded a coefficient of determination of $R^2 = 0.76$ ($P < 0.001$ level of significance) and was used to estimate the distribution of flows (Table 1). This yielded a similar (17 L s^{-1}) mean flow rate to the Mangakino stream.

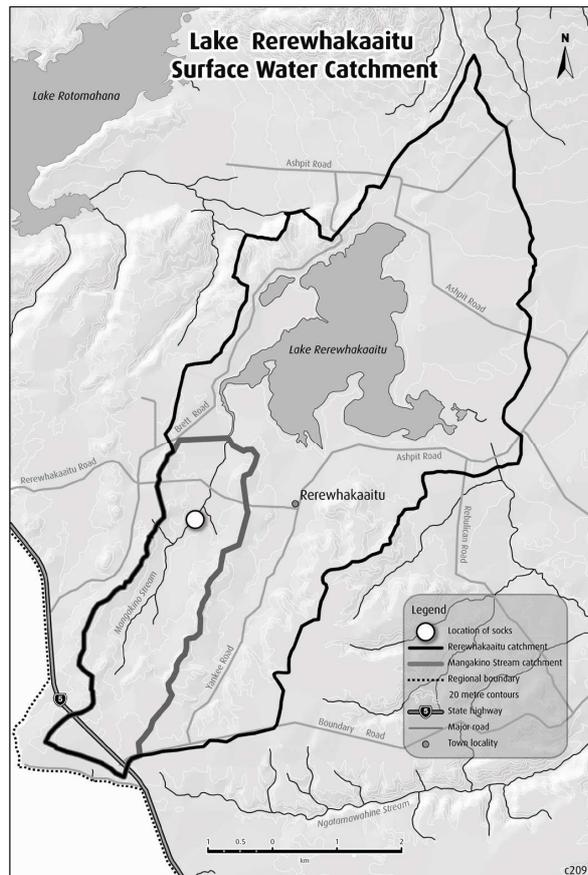


Figure 1. Map showing the location of the P-socks in the Mangakino stream, its' catchment area and Lake Rerewhakaaitu.

Landuse within the catchment is representative of the entire Lake Rerewhakaaitu catchment with a dominance of pastoral agriculture (70% dairy, 7% sheep and beef, and 15% forestry; 13). Immediately adjacent the sites selected for stream sampling was a dairy farming operation with 300 head of cattle; one of 27 dairy farms in the catchment. Soils within the catchment are Tarawera gravely sand, Rotomahana silt loam derived from the 1886 eruption, Kaharoa sand derived from an eruption about 7-800 years ago and Taupo silty sand derived from an eruption 1800 years ago (13). According to the New Zealand soil classification (14) these are classified as Buried-Pumice Tephric Recent, Typic Tephric Recent, Podzolic Orthic Pumice, and Immature Orthic Pumice soils, respectively. Regular applications of fertilisers to increase and maintain fertility occur with mean annual application rates of 168 kg N and 42 kg P per hectare on dairy farms (2).

In June of 2005, 180, 1 m by 9 cm diameter socks were made using a woven geotextile (polyester) cloth with a 2 mm mesh. This was filled with a combination of melter slag (85%), electric arc furnace slag (10%) and basic slag (5%), sourced from a steel mill in South Auckland, New Zealand (15). Each slag had a minimum mean particle size of 2 mm and maximum mean particle size of 5 mm. The slag mixture had a P sorption maximum (Langmuir isotherm) of about 4,500 mg P kg⁻¹, a pH of about 7.8 and each sock weighed about 10 kg. Socks were laid on the stream bed about 0.3 m apart in a herringbone alignment to allow fish to pass (*pers. comm.* Rob Pitkethely, Fish and Game New Zealand) while yielding maximum opportunity for interaction with stream flow. At the upstream and downstream ends a 20 cm deep and wide V-channel was cut into the bed to allow for the determination of stream flow at low flow. After laying the socks down it was noticed a small (on average, < 3 L s⁻¹) stream entered about two-thirds down the socked channel. A V-channel was cut in the side-stream 3 m upstream of the confluence to allow for flow measurements.

Sampling and flow rate determinations

At each channel and before and after the confluence on the main stem samples were taken (1 L) and flow velocity determined three times per sampling using a Marsh-McBirney, Inc. Flow-Mate 2000 portable water flow meter. Samples were taken one day before sock installation, on the day of installation, and after installation every two days for ten days then every fortnight for five months and then monthly for an additional three months (a total of 20 samplings) Flow rate was generated from the average velocity

multiplied by the cross-sectional area of flow. In instances where a V-channel had not been cut, flow area could be approximated by a rectangle.

Usually at the confluence of two streams the difference between the sum of the measured flow rates of the two incoming tributaries and the measured flow rate of the outlet was < 20%. However, because of the potential errors in streamflow measurements, flow balances were corrected using the chemical mass balance equation:

$$q_1C_1 + q_2C_2 = q_tC_t \quad [Eq. 1]$$

where q_1 and q_2 are flow rates of the two incoming streams, C_1 and C_2 are their chemical constituent concentrations, q_t is the flow rate of the outflow stream equal to the sum of q_1 and q_2 , and C_t is concentration of the chemical constituent in q_t . This equation can be applied to any dissolved conservative species. In this study it was used to verify or correct flow measurements at the confluence by setting $q_t = 1$ and using three replicate measurements of Cl and Br at each site. When a mass balance showed flows were different (greater than 1 standard deviation from the mean) from those measured, values of q_1 and q_2 were discarded and the remaining values used to calculate the relative flow ratios and to produce a “perfect” flow balance at a resolution of 1 L s^{-1} .

These flow rates were assumed to be representative of the daily flow (adjusted to L day^{-1}) and then multiplied by the concentration of dissolved reactive P (DRP) and total P (TP) in the samples and used to establish the days’ load of DRP and TP taken up by the socks before and after the confluence. Dissolved reactive P was determined via colorimetry on a filtered (< $0.45 \mu\text{m}$ cellulose acetate syringe filter) subsample and TP determined colorimetrically after an unfiltered subsample had been digested using persulphate (16). Total dissolved P (TDP) was measured on filtered samples after persulphate digestion and used to gain dissolved unreactive (largely organic) P by difference of TDP-DRP and particulate P by difference of TP-TDP. Additional measurements of dissolved organic P and Suspended sediment (SS) was determined on the remaining sample volume by filtration through a GF/A glass fibre filter paper and weighting the oven-dried (105°C) residue.

After one month and at the end of the trial, three socks were removed from the upstream and downstream sites and the solid material (slag plus entrained sediment) removed. Sediment was separated from slag by passing the material through a 2 mm sieve. Total P was determined via Kjeldahl digestion (17) on the sediment and slag to determine how much P had been retained. To determine P sorption parameters, whole

wet sediments (equivalent of 1 g dry weight) were mixed with 20 ml of solutions containing graduated (0, 1, 2, 4, 10, 20, and 50 mg P ml⁻¹) solutions of P (as KH₂PO₄) in 0.003M CaCl₂ (equivalent to the ionic strength of stream water, 18) and shaken for 16 h. Samples were then filtered and P determined colorimetrically. The Langmuir equation was used to obtain estimates of the P sorption maximum (P_{max} ; mg kg⁻¹) and the P affinity parameter (binding strength, k ; mg P l⁻¹). The initial slope of a graph of P sorption against P in solution was used to estimate equilibrium P concentration (EPC₀) as the concentration at which no net sorption or desorption occurs and which represents the likely P concentration in streamflow if influenced only by sediment - assuming good mixing with the water column.

4. Results

During the study period stream gaugings taken at the time of sampling, and by the Regional authority during a regular monitoring period, were regressed against historical data for an adjacent permanently gauged stream. This analysis yielded a highly significant coefficient of determination ($R^2 = 0.73$, $P < 0.001$) and was used to estimate the flow regime and range of flows within the Mangakino stream during the study period (Table 1, Figure 2). Despite being a headwater with a large catchment area (668 ha), flow within the Mangakino stream was characterised by a relatively steady baseflow at about 20-25 L s⁻¹ with only 30-40% of flow exceeding this rate (Table 1). Of the 20 samplings, about half were taken when flow was > 20 L s⁻¹.

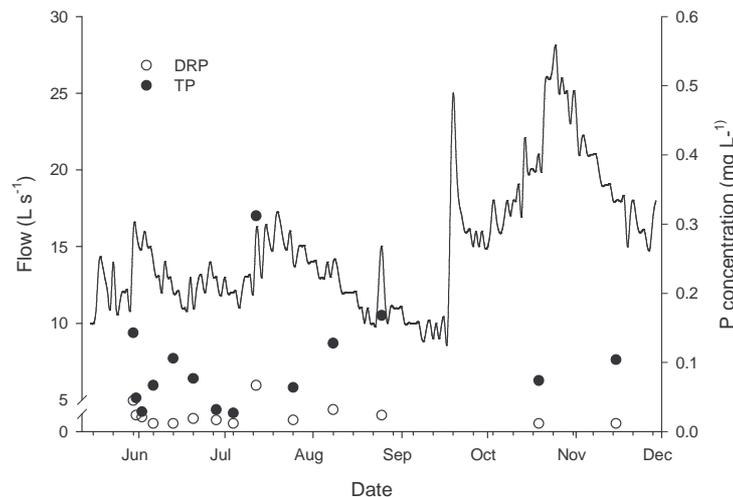


Figure 2. Estimated daily mean flow and the concentrations of dissolved reactive P (DRP) and total P (TP) in streamflow for the Mangakino Stream during the study period (beginning May 2005).

Table 1. Distribution of flows estimated within the Mangakino Stream.

Percentage of flow exceeding	Flow (l/s)
0	1800 (estimated)
10	38
20	30
30	24
40	19
50	16
60	13
70	11
80	8
90	6
100	1
Mean	20

Mean concentrations of P fractions and SS and pH are given in Table 2 at sites before and after water flowed over the P-socks and in the side stream. Mean concentrations of DRP and TP were in excess of the ANZECC (19) guidelines for good surface water quality in lowland streams (0.01 mg DRP L⁻¹; 0.033 mg TP L⁻¹). Mean SS concentrations of 40 mg/L which relates to a turbidity value of about 20 NTU (SS = 2NTU for New Zealand rivers; 20), was also in excess of the recommended guideline for lowland water quality of 5.58 NTU (19), and the limit for aesthetic value and contact recreation (4 mg L⁻¹; 21).

Listed in Table 2 are the results of a mass balance (Eq. 1) for each parameter showing the projected concentration at the after site based on the assumptions that no loss of the parameter or water occurred and that there was good mixing of the side-stream tributary with the main reach: it was assumed that the side stream contributed on average 20% of the flow (and entrained chemical constituents) and would proportionately alter the concentration at the after site. For example, for DRP the projected concentration at the after site was 0.1 mg DRP L⁻¹. However, the actual concentration was 35% less (0.065 mg DRP L⁻¹). This decrease could be due to either uptake by stream sediment or by the socks. However, given that the sediment had a

poor P sorption maximum (Figure 3: 373 mg kg⁻¹) an order of magnitude less than the socks and a poor affinity constant (2.4 mg P L⁻¹) it was likely that most of the uptake was due to the socks. This was supported by the sub-sampling of socks along the reach after 1 month and again after 6 months, which showed that about 2000 and 3500 mg P kg⁻¹ of slag had been sorbed, respectively: the concentration of total P in sediment during did not change between samplings (~ 400 mg kg⁻¹).

Table 2. The mean concentration of P fractions and suspended sediment and pH and flow for samples taken before and after water had flowed over the P-socks and from the tributary (side) which entered about half-way down the sock laden reach. A projected value for steam water at the after site is determined from the relative contribution of flow of each stem. The effect of this is given as percentage difference of the projected from the real (after) value.

Site	DRP (mg L ⁻¹)	DOP (mg L ⁻¹)	TDP (mg L ⁻¹)	PP (mg L ⁻¹)	TP (mg L ⁻¹)	SS (mg L ⁻¹)	pH	Flow (L s ⁻¹)
Before	0.024	0.016	0.040	0.057	0.097	40.4	7.2	19.6
After	0.065	0.020	0.085	0.060	0.145	41.9	7.2	24.5
Side	0.400	0.029	0.429	0.106	0.534	45.6	7.1	4.9
Projected [†]	0.100	0.019	0.118	0.067	0.184	41.5	7.2	
Effect [‡]	-35	+5	-28	-10	-21	-1	-	

[†] The projected value assumes effective mixing.

[‡] A negative difference indicates an uptake while a positive value indicates a release.

By assuming that the P sorption maximum of 4500 mg P kg⁻¹ slag will be reached eventually then a potential of 8.1 kg of P can be sequestered and retained by the P socks (180 socks, each with 10 kg of slag). This represented about 3% of P lost, assuming a load of 0.5 kg TP ha⁻¹ for the 668 ha catchment (2). This did not include sediment associated PP that may be retained within pores of the slag mixture: about 30% of each sock's mass but only 10% of sock TP. However, of total P measured during the study, DRP constituted 25% (before site, Table 2). Data from 1995 to 2003 indicated that DRP contributes about half of TP (EBOP, unpublished data) suggesting that overall DRP uptake may be less efficient or that DRP now comprises less to total P.

Nevertheless, assuming DRP was only a quarter of TP during the study period then the capture of DRP flowing downstream by the socks can be adjusted to about 12% of DRP in stream flow. This uptake is significant since DRP comprises the main source of P instantly available to aquatic weeds and algae, which grow best at low flow when shear stress is low (22). In contrast, at higher flows the less available PP dominates P in streamflow and periphyton and macrophytes may be swept away. This raises an interesting point since it was evident from previous fluvium studies on the slag (11), and in this study, that the uptake of DRP was flow dependant. A plot of DRP uptake between sampling sites and the flow rate at sampling showed a significant negative relationship (Figure 4). The relationship was stronger for DRP than TP. The regression relationship indicated that at flow rates above 22 L s^{-1} DRP was not taken up. For TP, no uptake was likely at flow rates in excess of 18 L s^{-1} . Consequently, socks may at times serve as a source of P due to accumulated sediment. However, flow rates causing P loss were estimated to only be exceeded 31% of the time for DRP and 45% of the time for TP (Figure 4), and overall the mass balance in Table 2 showed a significant net uptake of DRP and TP, not loss.

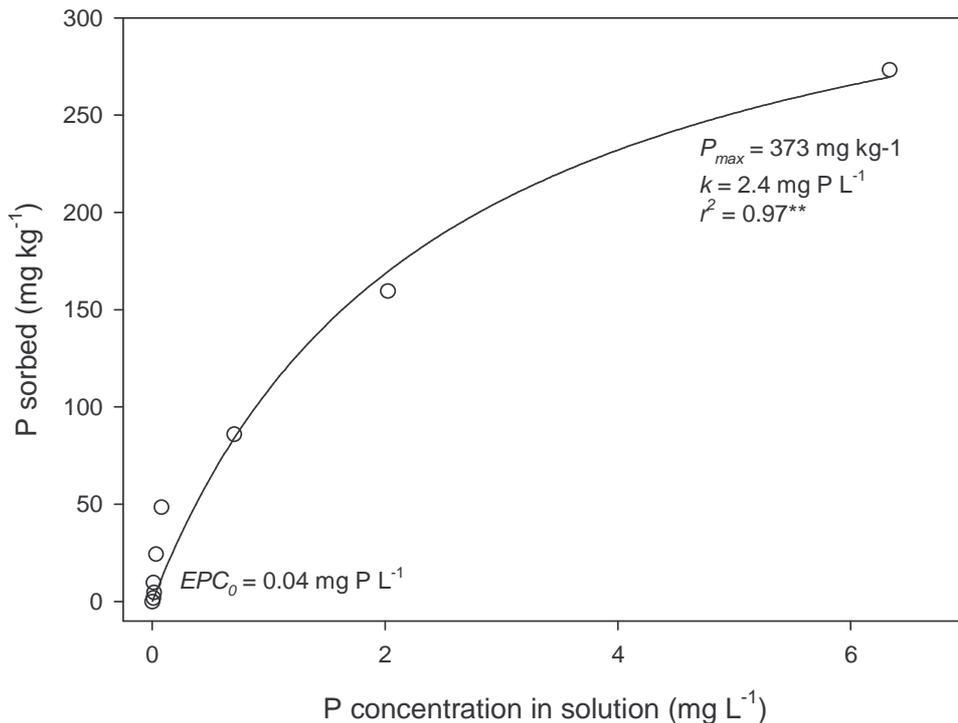


Figure 3. P sorption isotherm for stream bed sediment (0-2 cm depth) indicating the P sorption maximum, affinity constant and equilibrium P concentration at zero net sorption and desorption via a fitted Langmuir equation.

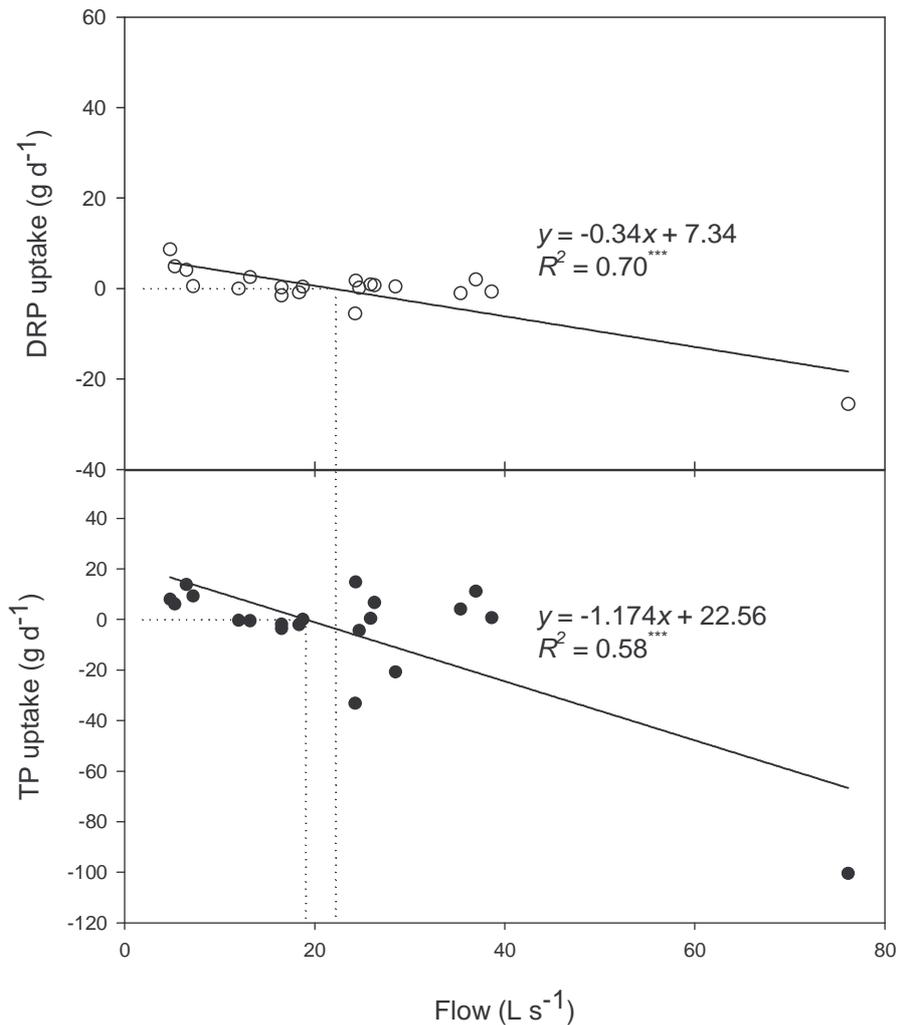


Figure 4. Relationship between the daily uptake or release of dissolved reactive P and total P calculated from grab samples and flow.

5. Discussion

Common for many strategies for lake management, the mitigation of P into Lake Rerewhakaaitu has focused on the elimination of point sources (principally domestic sewage and road runoff) and the gradual decrease of P from diffuse sources. With the decrease in point sources the importance of diffuse sources has increased, which has coincided with a change in land use from forest to pasture-based farming, especially dairying. Unfortunately, P losses from dairy farms tend to be greater than other pasture-based systems such as sheep and beef operations due to the more intensive use of fertilisers and grazing management. Using the nutrient budgeting software, Overseer[®]

nutrient budgets 2 (23) a dairy farm with a soil Olsen P of 35 mg kg^{-1} on flat ($< 7\%$ slope) land would lose about $1 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ in runoff whereas an extensive sheep operation would lose about 0.5 kg P ha^{-1} .

Although soils in the Lake Rerewhakaaitu catchment are erosion prone, the data indicated that on average 40% of the P measured in streamflow before flow over the socks was in dissolved form (DRP + DOP; Table 2). This figure was greater for the side stream ($\sim 80\%$ DRP). The increase could reflect sampling at low flow when sediment and particulate P transport is less, or the filtration of PP in overland flow by pasture or forest (24, 25), but is more likely caused by the input of DRP from dung washed-off a bridge on the side stream that sees dairy cattle crossing for 10 out of every 30 days. Of particulate P lost in stream flow, most was likely associated with erosion of the stream banks since bedrock was visible in areas of the stream bed and the stream banks were noticeably scoured.

Management to decrease P losses from pasture-based farming focuses on best management plans (BMPs) which include optimisation of soil Olsen P concentrations at $20\text{-}30 \text{ mg kg}^{-1}$ for the average producing dairy farm, the spraying of farm dairy effluent at low intensities and on areas of land unlikely to contribute to stream flow (i.e. flat land away from stream edges), minimising treading damage to soil and thereby decreasing the likelihood of infiltration-excess overland flow, and not allowing cattle access to waterways (5, 26). Additional strategies include buffer strips, the planting of riparian areas and the creation of artificial wetlands (27). Each of these BMPs and strategies decrease P loss to different degrees. However, P loss inevitably occurs. For example, it can take many years for elevated soil P concentrations and thus P loss in overland or subsurface flow to decrease.

As a transmission route, streams such as the Mangakino represent the last opportunity to mitigate P loss before P enters the lake. Management strategies that prevent the deleterious effect of P once in the lake can be expensive or ineffective. Strategies considered for the Rotorua lakes include, engineering and re-routing incoming nutrient rich water, bubbling oxygen into the anoxic depth of a lake to oxidise Fe and thereby sorb P making it unavailable, or dosing the lake with P-sorbing amendments such as alum ($\text{Al}_2(\text{SO}_4)_3$) or Phoslock[®] (28). For Lake Rerewhakaaitu, engineering and oxygenation options are unrealistic or expensive. However, while amending the lake with P-sorbing materials may be effective, the effects are based on flocculation and there are questions over how long the benefit may last once new sediments settle on the lake bottom. This may require frequent treatment and make it too expensive. Amendments could be added to lake inflow and thereby settle out in the stream bed not the lake (e.g., 29, 8) but could be remobilised and transported to the lake

during a storm event. Consequently, there is a need for technologies such as the P sock which hold P in the stream bed in an unavailable form. If desired the P-rich sock could then be removed, dried and the slag used elsewhere such as in lane ways.

Financially, supply of the slag material, and construction and installation of 180 socks onto the stream bed equated to about \$4 USD per sock. If it is assumed that they are left on the stream bed until all P sorption capacity is used (4.5 g P kg^{-1} slag) then the cost per kg of P removed is about \$90 USD. This does not compare well with the potential precipitation of P from lake inflows by materials such as alum (about \$3 per kg of P). However, P sorbed via flocs with alum may be carried away in stream flow. Furthermore Pilgrim and Brezonik (30) showed that floc formation during treatment at 8 mg Al L^{-1} eliminated nearly all invertebrates. Consequently, use of an immobile P-sorbing material has potential in the removal of P from the water column at low flow rates and may become viable if P sorption capacity could be increased and the material regenerated.

6. Conclusions

Installation of 180 P-socks in the Mangakino stream caused a decrease in P concentration in streamflow and thus P entering Lake Rerewhakaaitu. For DRP the mean decrease was 35% whereas for TP this was 21%. With time and increasing flow the effectiveness of P retention by the socks decreased such that about 78% of capacity was reached after 6 months while on average it was estimated that flow rates were great enough that no uptake occurred about a third of the time for DRP and about 45% of the time for TP. However, assuming sorption capacity was reached and an historical average of DRP concentrations then about 12% of DRP load in the stream could be retained by the socks. While P socks have the advantage of being removable and potentially regenerated compared to materials based on flocculation, they are less economical compared to other P-sorbing materials on a \$USD per kg of P retained. As such, limitations due to flow rate and labour and manufacturing costs may restrict the wide spread use of the technology to small streams unless either flow rates can be moderated or the P-sorption potential of the material improved or an alternative material used.

7. Acknowledgements

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