

Treatment of Drainage Water with Industrial By-Products to Prevent Phosphorus Loss from Tile-Drained Land

R. W. McDowell* AgResearch

A. N. Sharpley University of Arkansas

W. Bourke SteelServ

Tile drained land with phosphorus (P)-rich topsoil is prone to P loss, which can impair surface water quality via eutrophication. We used by-products from steel and energy industries to mitigate P loss from tile drains. For each by-product, P sorption maximum (P_{\max}) and strength (k) were determined, while a fluvium trial assessed P uptake with flow rate. Although two ash materials (fly ash and bottom ash) had high P_{\max} and k values, heavy metal concentrations negated their use in the field. The fluvium experiment determined that P uptake with by-products was best at low flow, but decreased at higher flow in proportion to k . A mixture of melter slag (<10 mm) and basic slag (high P_{\max} , 7250 mg kg⁻¹; and k , 0.508 L mg P⁻¹) was installed as backfill in eight drains on a dairy farm. Four drains with greywacke as backfill were constructed for controls. The site (10 ha) had P-rich topsoil (Olsen P of 64 mg kg⁻¹) and yielded a mean dissolved reactive P (DRP) and total P (TP) concentration from greywacke backfilled drains of 0.33 and 1.20 mg L⁻¹, respectively. In contrast, slag backfilled drains had DRP and TP concentrations of 0.09 and 0.36 mg L⁻¹, respectively. Loads of DRP and TP in greywacke drains (0.45 and 1.92, respectively) were significantly greater ($P < 0.05$) than those from slag drains (0.18 and 0.85, respectively). Data from a farm where melter slag was used as a backfill suggested that slag would have a life expectancy of about 25 yr. Thus, backfilling tile drains with melter slag and a small proportion of basic slag is recommended as an effective means of decreasing P loss from high P soils.

THE loss of phosphorus (P) from soils to surface waters is recognized as a key factor in eutrophication, causing poor water quality. Mitigation strategies have centered on management to decrease the likelihood of P loss, such as balancing the inputs and outputs of P from the farm or maintaining soil Olsen P concentrations at the agronomic optimum (McDowell et al., 2004). However, P loss from some areas, such as wet soils, areas abutting streams, soils with a limited capacity to retain P, or tile-drained land is inevitable. Over the past two decades, by-product materials rich in P-sorptive Ca, Al, and Fe have been identified as decreasing P solubility and loss from soils with varied success (Vlahos et al., 1989; O'Reilly and Sims, 1995; Hausteine et al., 2000; Stout et al., 2000). These include, but are not limited to, zeolites, aluminium sulfate, water treatment residuals, and fluidized bed bottom-ash and fly ash from coal-fired power plants (e.g., Reichert and Norton, 1994; Sakadevan and Bavor, 1998; Moreno et al., 2001; Callahan et al., 2002).

When considering each by-product for use, three criteria must be considered: (i) cost of the material (does it need to be mined or is there a readily available and cheap source?), (ii) toxicity to the environment, and (iii) efficacy of P sequestering. In terms of cost, most by-products are cheap, readily available, and their use more economically viable than mining and transporting naturally occurring P-sorptive materials such as dolomite. However, a major drawback can be environmental toxicity. For instance, many steel slags can contain concentrations of heavy metals, such as As, Cd, and Hg, well in excess of that permitted for disposal on land. For New Zealand soils, limits for concentrations of As, Cd, and Hg are 10, 3, and 1 mg kg⁻¹, respectively (Whitehouse et al., 2000). In addition, when applied to grazed pastures some by-products can impair stock health, and as such have traditionally been seen as hazardous. In a well documented case, cattle that grazed paddocks to which basic slag or fly ash (both pH > 12) was recently applied had increased rumen pH, stopping fermentation and causing death in most cattle (Dewes et al., 1995). Thus, a lag period between by-product application and grazing must be observed. When given a lag period, the broadcast application of fly ash can

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Published in J. Environ. Qual. 37:1575–1582 (2008).

doi:10.2134/jeq2007.0454

Received 24 Aug. 2007.

*Corresponding author (richard.mcdowell@agresearch.co.nz).

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677 S. Segoe Rd., Madison, WI 53711 USA

R.W. McDowell, AgResearch, Invermay Agricultural Centre, Private Bag 50034, Mosgiel, New Zealand; A.N. Sharpley, Dep. of Crop, Soil, and Environmental Sciences, 115 Plant Sciences Bldg., Univ. of Arkansas, Fayetteville, AR 72701, USA; W. Bourke, SteelServ, Glenbrook, South Auckland, New Zealand.

Abbreviations: DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; PP, particulate phosphorus; SS, suspended sediment; TDP, total dissolved reactive phosphorus; TP, total phosphorus.

significantly decrease the potential for P loss in overland flow from soils with an initial pH > 6.5 (McDowell, 2005).

Loss of P from tile drains is an important mechanism for the enrichment of lowland streams worldwide (Sims et al., 1998). Losses up to 1 kg P ha⁻¹ are common, but this can increase to >2 kg P ha⁻¹ where the soil has limited capacity to sorb P (Sims et al., 1998). This commonly occurs in organic matter-rich soils, which can block P sorbing sites, soils with little Al- or Fe-hydrous oxides (e.g., well leached), or soils with a history of continued P applications in excess of crop removal rates, which load up P sorbing sites limiting the sorption of subsequently added P (Miller, 1979; Culley et al., 1983). Several studies have shown that soils rich in P have elevated P concentrations in drainage water (e.g., Sharpley et al., 1994). Furthermore if a soil has a large number of macropores then these can act as a direct conduit for P loss to tile drains and drainage water. This is thought to be a major mechanism behind the direct loss in drainage of dairy shed effluent irrigated onto pastures, and can be especially problematic when the soil is already wet and the likelihood of the soil matrix retaining added water and thereby P is extremely limited (Monaghan et al., 2002). However, in some shrinking and swelling soils large cracks appear when soil dries, which act as macropores. Consequently, some P loss in tile-drained land is inevitable and means that a cheap and effective method of mopping up P in drainage water is desirable.

In New Zealand, two industries could potentially provide large quantities of by-products rich in P-sorbing Al, Fe, and Ca that are presently considered of low value or are a waste to be disposed of. These are slags from iron and steel manufacturing (280,000 Mg yr⁻¹) and ash from coal-fired power plants (100,000 Mg yr⁻¹). Our objectives were to (i) test the efficacy of these slags and ash materials in sorbing P in a batch equilibration experiment and continuous flowing stream of P-rich solution simulating drain flow and (ii) to test a mixture of by-products as a drainage medium to mitigate P loss from tile-drained land with P-rich topsoil (Olsen *P* > 50 mg kg⁻¹ at 0–7.5 cm depth) in South Auckland and Waikato, New Zealand.

Materials and Methods

Initial By-Product Assessment

Ash materials were obtained from the coal-fired power station at Huntly, Waikato, New Zealand in 2002. The first was fly ash (0–1 mm), scrubbed from the exhaust of each furnace, and the second was a sample of bottom ash, or clinker, left behind after burning and sampled from the outwash en-route to the ash pond for disposal. Bottom ash was separated into particle size fractions 0 to 2 and 2 to 4 mm which represent about 20 and 5% of bottom ash by weight, respectively. Four samples of steel industry slags were obtained from SteelServ, based at the Glenbrook Steel Mill, South Auckland, New Zealand. Two were melter slags (0–5 and 0–10 mm), another was basic slag (0–10 mm), and the last was an electric arc furnace slag (0–5 mm). Melter slag is an iron making slag based on iron sand as the main iron ore source. Basic slag comes from a basic oxygen steel furnace and electric arc furnace slag is a by-product of a steel-making process normally using scrap steel or a combination of directly reduced iron and scrap steel.

To determine the efficacy of P sorption by each by-product, samples (1 g) of each were mixed with 20 mL of 0.003 mol L⁻¹ CaCl₂ solutions (simulating the ionic strength of drainage water; Schofield, 1955) containing graduated concentrations (0, 1, 2.5, 5, 10, 20, 50, and 150 mg P L⁻¹) of P as KH₂PO₄, and shaken for 16 h. Samples were filtered (Whatman no. 42) and soluble P determined after adjusting pH using the colorimetric method of Watanabe and Olsen (1965). The Langmuir isotherm equation was used to obtain estimates of P sorption maxima (*P*_{max}, mg kg⁻¹) and P sorption affinity constants or sorption strength (*k*, mg P L⁻¹).

To determine the effect of flow rate on P sorption in a flowing stream of P-rich solution, experiments were conducted in a fluvium (see McDowell and Sharpley, 2003). Attached to each downslope end of four 10-m long by 20-cm wide by 20-cm deep troughs (slope angle variable from 0 to 15%) was a reservoir with a total capacity of 300 L. Plumbing and a pump for each trough and reservoir allowed solution to re-circulate through a pipe installed downstream of the flumes at flow rates varying from 1 to 20 L s⁻¹. Attached to each of the reservoirs was a back-flow system, which siphoned off a small proportion of flow moving through pipes back into the reservoir to agitate and keep the reservoir solution continually mixed.

For each run of the fluvium, by-product (0.5 kg) was placed within a tube (8-cm diameter) of nylon mesh material (pore size 1 mm) and closed off at either end making a sock, which was then placed into a drainage pipe housed at the outlet of each flume. The four troughs within the fluvium were set at an angle of 5% and each reservoir filled with 200 L of 2 mg P L⁻¹ solution. Flow within each flume was then set at 0.05, 0.1, 0.3, or 0.6 L s⁻¹, representing storm flows commonly found in tile drains of New Zealand pastures (Hudson et al., 1962). Samples of flow were taken over time, initially every 10 min for 2 h and then every 1 h for 24 h once it had passed through the by-product-filled sock. These were filtered (<0.45 μm) and P determined by colorimetry using the method of Watanabe and Olsen (1965). This is termed dissolved reactive P (DRP). Additional subsamples (detection limits in parentheses) were also analyzed for As (0.001 mg L⁻¹), B (0.005 mg L⁻¹), Cd (0.00005 mg L⁻¹), Cr (0.0005 mg L⁻¹), Ni (0.005 mg L⁻¹), and Pb (0.0001 mg L⁻¹) by ICP-MAS. Water flowed easily around and through the by-product-filled socks and did not restrict flow in the fluvium.

Field Trials

Karaka

A field trial ran from July 2004 to July 2006 on an imperfectly drained Allophanic soil (New Zealand soil classification, Karaka silt loam; Motled Orthic Allophanic; USDA Taxonomy, Udand) near Karaka, South Auckland, New Zealand. The 10-ha site was a paddock that had received effluent from a 300-head dairy via a traveling irrigator for >15 yr but not for the last 3 yr. Twelve tile drains were installed at 70-cm depth. Four of the drains contained commonly available greywacke (control) backfilled on top to 20 cm below the soil surface while the eight others had a combination of melter slag (90% 0–10 mm) and a small quantity (as not to elevate pH) of basic slag (10%, 0–50 mm). This mixture was washed be-

Table 1. Major constituents of each by-product. Data for ash and slag by-products courtesy of Genesis Power Ltd and SteelServ, respectively.

Constituent	Fly ash	Bottom ash	Bottom ash	0–5 mm Melter slag	0–10 mm Melter slag	Basic slag	Electric arc furnace slag
Particle size (mm)	<1	0–2	2–4	0–5	0–10	0–50	0–10
pH (in water)	>12	10	9.5	7.0	7.0	>12	7.5
SiO ₂ (g kg ⁻¹)	340	430	490	146	141	140	290
CaO (g kg ⁻¹)	250	180	170	145	146	522	248
Al ₂ O ₃ (g kg ⁻¹)	200	200	160	190	179	140	63
Fe ₂ O ₃ (g kg ⁻¹)	100	80	80	29	24	nd†	290
MgO (g kg ⁻¹)	26	22	20	135	131	53	74
P ₂ O ₅ (g kg ⁻¹)	8	6	5	3	3	7	2
As (mg kg ⁻¹)	37	21	18	<0.001	<0.001	0.008	<0.02
B (mg kg ⁻¹)	6500	3700	2900	1.0	0.9	1.0	0.3
Cd (mg kg ⁻¹)	0.1	0.1	0.08	<0.005	<0.005	1.0	0.02
Se (mg kg ⁻¹)	3.0	4.9	4.3	nd	nd	<0.3	nd
Pb (mg kg ⁻¹)	46	30	23	0.07	0.06	8.0	<0.1
P _{max} (mg kg ⁻¹)	6650	3440	2400	2580	2450	50,000	6560
k (L mg P ⁻¹)	0.588	0.121	0.026	0.150	0.248	1.246	0.028

† Not known.

fore installation. Four of the slag drains each had two additional “P socks” inserted in the outlet, which contained *c.* 10 kg of the same slag mix but was housed inside an 80 mm diameter nylon mesh, crimped at either end. This subset of the slag drains are referred to as “sock” drains from here on.

Flow events from each drain were measured via a tipping bucket and a composite subsample taken for analysis. Within 24 h the flow samples were analyzed for DRP and pH. Total dissolved reactive P (TDP) was determined via persulphate digestion (Eisenreich et al., 1975) of a filtered (<0.45 μm) sample within 48 h of collection. An unfiltered sample was also digested and total P (TP) measured within 7 d. Fractions defined as dissolved unreactive (largely organic) P (DURP) and particulate P (PP) were determined as the difference between TDP and DRP, and TP less TDP, respectively. Subsamples were also analyzed for As, Cd, Cr, Ni, and Pb by ICP-MAS. All P analyses used the colorimetric technique of Watanabe and Olsen (1965). Suspended sediment (SS) was determined by weighing the residue left after filtration through a Whatman GF/F glass fiber filter paper of a shaken 250-mL subsample. Soil samples from the field trial were taken at 0- to 7.5- and 7.5- to 15-cm depth before drains were installed and analyzed for Olsen P (Olsen et al., 1954) and P sorption isotherms as per the by-products.

Data for the mean-flow-weighted concentrations in flow and loads from each of the three treatments were compared using an analysis of variance and the least significant difference for $P < 0.05$ presented. Data is only presented for the entire trial period as variation between years, determined as 1 yr from installation (June to July), was not significant.

Te Kauwhata

As the field trial at Karaka could not be run indefinitely to determine the lifetime of melter slag as a backfill, water samples were also taken from a dairy farm of similar size (320 cows) to that at Karaka, but around 100 km south near Te Kauwhata, Waikato. Here, the farmer had used melter slag (0–10 mm) at various stages as a backfill fill for tile drains since 1994. This gave us the opportunity to sample drains of different ages (2 mo, and 1, 5, 7, 8, 11, 12, and 13 yr old) and therefore estimate the longevity of drains with melter slag as a backfill to retain P compared

to greywacke chip. Unfortunately, the soil type was different to the Karaka silt loam, being a poorly drained Ultic soil (New Zealand soil classification, Maramarua silty clay loam; Mottled Yellow Ultic; USDA Taxonomy, Ultisol). However, mean soil Olsen P concentrations (0–7.5 cm depth) from the drained paddocks were similar at 64 mg kg⁻¹ with a 95% confidence interval of ± 7 mg kg⁻¹. Water samples were taken at baseflow on two occasions (no rain previous 5 d), once in spring and once in summer 2006–2007 and analyzed for DRP, TDP, TP, and SS.

Results and Discussion

Initial By-Product Assessment

For each by-product, P_{max} and k were calculated by Langmuir isotherm equations using the data for variation in P sorbed from solutions with gradually increasing P concentration. The P_{max} values ranged from 2400 mg P kg⁻¹ in the bottom ash 2- to 4-mm sample to 50,000 mg P kg⁻¹ in the basic slag (Table 1). The extremely high P_{max} calculated for the basic slag (50,000 mg P kg⁻¹), should be considered an estimate due to likely Ca-P precipitation via free CaO (52%). Values of k ranged from 0.026 L mg⁻¹ in the bottom ash 2- to 4-mm sample to 1.246 L mg⁻¹ for basic slag (Table 1).

It is well known that P sorption data from batch isotherm experiments only give an indication of performance as they negate the action of continuous flow (Sparks, 2003). Hence, four by-products (bottom ash 2–4 mm, electric arc furnace slag, and two melter slags) and greywacke chip as a non-P-sorbing control were chosen to test their uptake of P in relation to flow in a fluvarium. In addition to basic slag, which was unavailable at the time of testing, these by-products would allow for good flow of drainage water if used as a backfill in drains or as a polishing unit to remove P in drainage (e.g., in a sock). In general, the concentration of P in the fluvarium decreased with time from 2 mg L⁻¹ to a low of about 1.2 mg L⁻¹ after 24 h recirculation through a sock of electric arc furnace slag. An example of this behavior is given in Fig. 1 for the bottom ash 2- to 4-mm by-product. Uptake of P from solution was characterized by a rapid phase which lasted 1 h when most uptake occurred, followed by a gradual decline. The exception to this rule was the greywacke chip, which sorbed neg-

Bottom Ash (2-4mm)

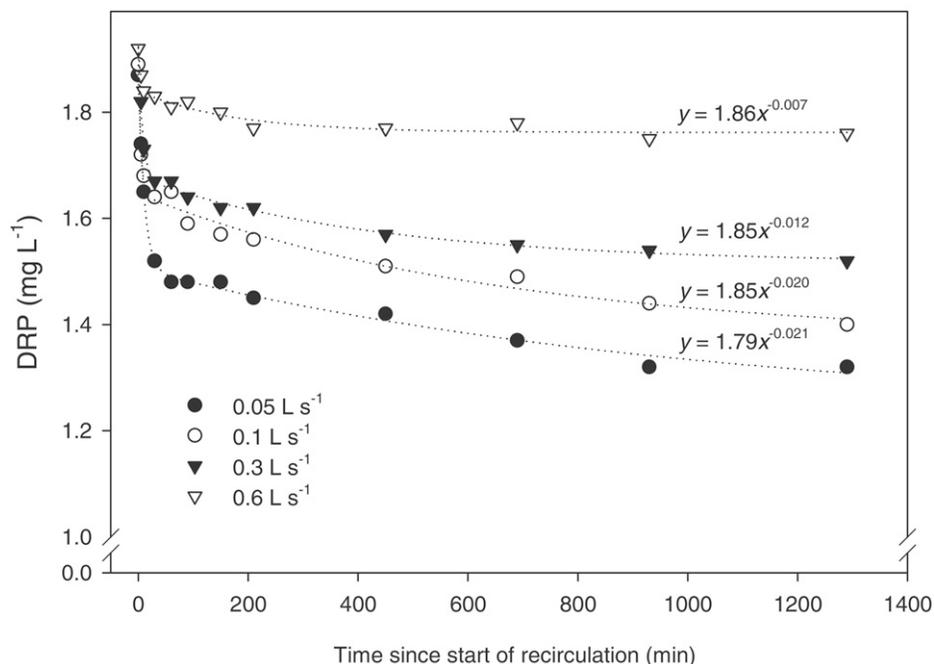


Fig. 1. DRP concentration (mg L^{-1}) with time since the start of fluvarium recirculation for the bottom ash (2–4 mm) sample. All line fits are significant at $P < 0.05$ level.

ligible P; DRP concentrations of flume water after 24 h recirculation was 1.89 mg L^{-1} at the slowest flow rate (0.05 L s^{-1}).

Data for each by-product and flow rate was fitted to an exponential decay function, which yielded an estimate of the decline in P concentration with time (β). All fits were significant ($P < 0.05$) and demonstrated that β increased with flow rate, meaning the rate of P uptake was less at higher flow rates (Fig. 1, Table 2). A correlation analysis of β values to P_{max} and k gave significant relationships between β and P_{max} at the lowest flow rate ($r = 0.92$, $P < 0.05$), while k was correlated at the highest flow rate ($r = 0.92$, $P < 0.05$). No significant relationships occurred between β and P_{max} or k at the other flow rates. This data suggested an increasing dependence on sorption strength with flow, and little influence by sorption capacity unless at slow flow. As the flow rates tested were representative of storm flow rates, it is likely that retention of P by the by-products at lower flow rates commensurate with slow percolating water during drainage events may be better. It is also important to realize that the configuration used here was only to determine potential performance with flow and utilized a highly P-enriched solution and very little by-product. As a consequence the P retained by 0.5 kg of material, at the lowest flow rate (0.06 L s^{-1}),

represented only 5 to 13% of that added (400 mg). In reality by-products such as melter slag are used in much greater quantities.

As an example, by-products have been extensively used for wetlands where flow rates are similar, but several tons of material are commonly needed to make use of increased surface areas and likelihood of sorption to maximize the by-products P_{max} and decrease P before outflow (Coale et al., 1994; Wright et al., 1998). For instance, Sakadevan and Bavor (1998) calculated 300 m^3 of steel furnace slag in a constructed wetland would retain 99% of P from a 1200 L d^{-1} domestic sewage plant (mean P concentration of 1 mg L^{-1}), and would do so until saturated with P after >20 yr. Our data suggest that these materials may efficiently retain P at flow rates of up to $1.2 \text{ L s}^{-1} \text{ kg}^{-1}$ and a large quantity used in drains may significantly decrease P loss.

Additional data from the fluvarium study indicated that concentrations of heavy metals in solution after 24 h recirculation through each by-product were less than the detection limit of ICP-MAS ($0.001 \text{ mg As L}^{-1}$, $0.00005 \text{ mg Cd L}^{-1}$, $0.0005 \text{ mg Cr L}^{-1}$, $0.005 \text{ mg Ni L}^{-1}$, and $0.0001 \text{ mg Pb L}^{-1}$). However, B concentrations (detection limit of 0.005 mg L^{-1}) were, on average, 0.16 and 0.08 mg L^{-1} in solutions that had recirculated through bottom ash and fly ash and therefore could cause chronic toxic effects in rainbow trout (acute effects occur at $0.75\text{--}18 \text{ mg B L}^{-1}$) if used in large quantities. As such, bottom ash and fly ash were discounted for use in the subsequent field trial. Additional data for the leaching of basic slag over 3 mo had also indicated that concentrations of heavy metals were similar to the two melter slag samples tested above. However, to improve the potential for P retention a mixture of 90% melter slag (0–10 mm) and basic slag (0–50 mm) was used. When tested using the same procedure as for all other by-products,

Table 2. Values for β , which describes the kinetic decrease in P concentration (y) with time (x) in $y = \alpha x^{-\beta}$ used to fit data for each by-product and flow rate. The parameter α estimates the initial P concentration and did not significantly vary from one another.

Flow rate (L s^{-1})	Bottom ash (2–4 mm)	Electric arc furnace slag	Melter slag (<10 mm)	Melter slag (<5 mm)
0.6	–0.007	–0.006	–0.005	–0.006
0.3	–0.012	–0.014	–0.007	–0.008
0.1	–0.020	–0.019	–0.011	–0.013
0.05	–0.021	–0.029	–0.015	–0.016

it yielded a P_{\max} of 7250 mg kg⁻¹ slag. After washing the pH of the new mixture was 7.5.

Field Trials

Data for P fractions, SS, and pH from the control (greywacke), slag, and sock drains are shown in Table 3. Soil Olsen P concentrations for the 0- to 7.5- and 7.5- to 15-cm depths were 64 and 20 mg kg⁻¹, respectively. The corresponding P_{\max} values were 1300 mg kg⁻¹ (0–7.5 cm) and 1500 mg kg⁻¹ (7.5–15 cm). Over the trial period, there were on average 12 drainage events. Unfortunately, due to equipment breakdown two events were missed, meaning that an accurate load for P loss could not be determined. Furthermore, as drains were not hydrologically isolated from one another a catchment area of about 8000 m² could not be guaranteed. However, an estimate of the load of P fractions and sediment lost in drainage is given assuming a mean concentration and flow rate according to a water balance for the two missed events. Mean drainage flow was also within 15% between each of the treatments and did not exhibit any differ-

Table 3. Mean concentrations of P fractions and suspended sediment and least significant difference ($P < 0.05$) between the control, slag, and slag plus sock (sock) drains for all drainage events 2004–2006. The least significant difference at ($P < 0.05$) is also given. DRP, dissolved reactive P; DOP, dissolved organic P; PP, particulate P; TP, total P; SS, suspended sediments.

Treatment	DRP	DOP	PP	TP	SS	pH
	mg L ⁻¹				g L ⁻¹	
Control†	0.332	0.037	0.831	1.200	1.345	7.2
Slag‡	0.089	0.040	0.462	0.591	0.240	7.3
Sock§	0.042	0.036	0.285	0.364	0.359	7.3
LSD _{0.05}	0.049	0.013	0.181	0.205	0.940	0.15

† Fill for control drains was greywacke aggregate.

‡ Slag mixture was a combination of 90% melter slag and 10% basic slag.

§ Socks consisted of 2, 10 kg parcels of a 90:10 mixture of melter and basic slag encased in a mesh and inserted up the outlet of the drains.

ence between years (mean drainage for control plots = 180 mm, and 170 and 200 mm yr⁻¹ for slag and sock drains, respectively; rainfall was 1200 and 1251 mm for the July to June 04/05 and 05/06 yr).

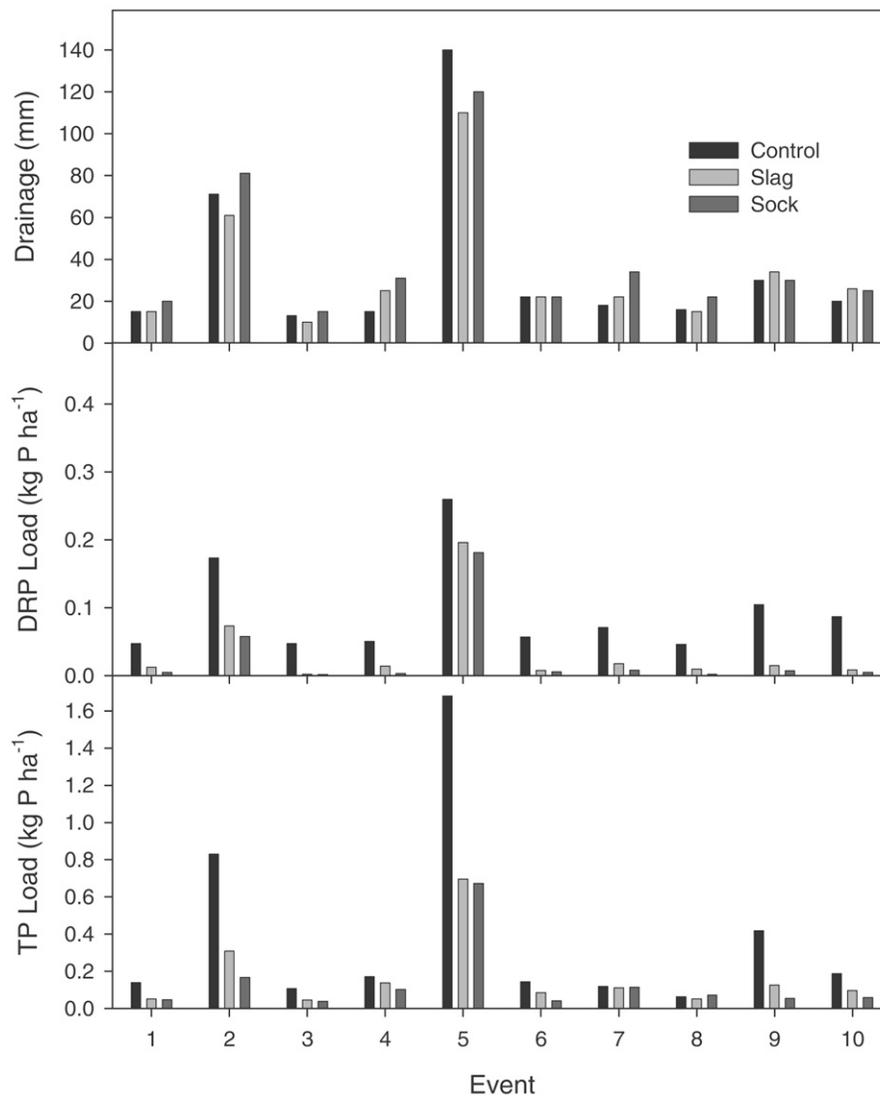


Fig. 2. Load of DRP and TP for each drainage volume measured. Note that due to equipment failure two additional storm events were missed.

Table 4. Estimated mean loads of P fractions and suspended sediment lost from the control, slag and slag plus sock (sock) drains. The least significant difference at ($P < 0.05$) is also given. DRP, dissolved reactive P; DOP, dissolved organic P; PP, particulate P; TP, total P; SS, suspended sediments.

Treatment	DRP	DOP	PP	TP	SS
	kg P ha ⁻¹				Mg ha ⁻¹
Control†	0.45	0.35	0.92	1.92	1.345
Slag‡	0.18	0.28	0.39	0.85	0.840
Sock§	0.14	0.32	0.18	0.64	0.559
LSD _{0.05}	0.06	0.12	0.16	0.20	0.940

† Fill for control drains was greywacke aggregate.

‡ Slag mixture was a combination of 90% melter slag and 10% basic slag.

§ Socks consisted of 2, 10 kg parcels of a 90:10 mixture of melter and basic slag encased in a mesh and inserted up the outlet of the drains.

The mean DRP concentration in drainage water from the slag and sock drains was significantly ($P < 0.05$) less than from the control drains (73 and 85% less, respectively) (Table 3). Loads showed a similar significant ($P < 0.05$) decrease: 60 and 69% for slag and sock drains, respectively. The mean TP concentrations in drainage from the slag and sock drains were also significantly ($P < 0.05$) less than the control: 51 and 70%, respectively. Loads for TP in the slag and sock drains were respectively 56 and 63% less than the control drains (Fig. 2, Table 4). The decrease was split roughly two-thirds due to less PP and SS, and one-third due to less DRP loss. There was no decrease in dissolved organic P (DOP) losses, which could be partly explained by the greater mobility of some DOP species in subsurface flow and decreased sorption compared to orthophosphate (e.g., Leytem et al., 2002). However, concentrations in slag and sock drains were still, on average, in excess of guidelines for lowland freshwater quality of slightly disturbed streams in New Zealand (0.01 mg DRP L⁻¹, 0.033 mg TP L⁻¹; ANZECC, 2000). This was probably due loss of P from topsoil that had been enriched with P for many years with dairy shed effluent. It is likely that past effluent applications will have decreased the sorption ca-

capacity of macropores. These macropores account for the majority of drainage but also provide a direct conduit for soil solution enriched with P from the topsoil to travel to tile drains (Ohnno and Crannell, 1996; Jensen et al., 2000). Thomas et al. (1997) proved this occurred for a range of tile-drained plots with different soil Olsen P concentrations.

Drainage pH was not significantly different between treatments. Mean concentrations of heavy metals in drainage were below detection limits (0.001 mg As L⁻¹, 0.00005 mg Cd L⁻¹, 0.0005 mg Cr L⁻¹, 0.005 mg Ni L⁻¹, and 0.0001 mg Pb L⁻¹). Boron concentrations for the first event were detectable (on average 0.01 mg L⁻¹), but soon dropped below detection limit (0.005 mg L⁻¹). This is not unexpected, as artificial wetlands stocked with melter slag as the treatment medium >12 yr ago at the Waiuku waste water treatment plant in South Auckland, New Zealand, as well as similar installations at Ngatea and Paeroa in Waikato, New Zealand, have maintained heavy metal concentrations in outflow less than inflow in recent samplings (Bourke et al., 2005).

Backfilling with slag decreases P in drainflow compared to traditional greywacke backfill. However, as noted in the fluvium trial this is likely to vary according to flow. The shrink-swell nature of the Karaka soil is likely to exacerbate this as cracks open in dry weather creating a direct conduit to by-pass the soil and travel quickly to the backfill medium. In time, these macropores can become P-rich and retain little P (Geohring et al., 2001). This will affect the ability of the backfill to retain P as P-rich solution gradually saturates the fill. Before installation the slag backfill had a P_{\max} of 7250 mg kg⁻¹ slag. Even if we assume an annual drainage of about 400 mm (twice that recorded over the last 2 yr), and a P concentration in flow of 1.5 mg P L⁻¹, the 12 drains installed in the field site (each with 6 Mg of slag) would take about 72.5 yr to saturate. This of course will not occur as fluvium results indicated that P retention was flow rate dependant. Furthermore, as slag

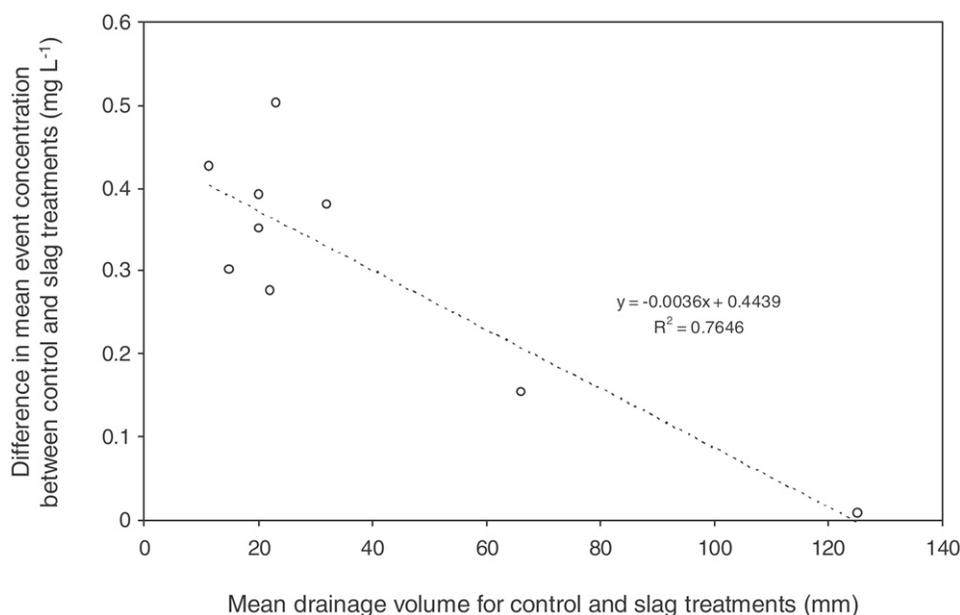


Fig. 3. Plot showing the decline in the difference between concentrations in drainage in the control and slag treatments with increasing event size. Line fit is significant at $P < 0.05$ level.

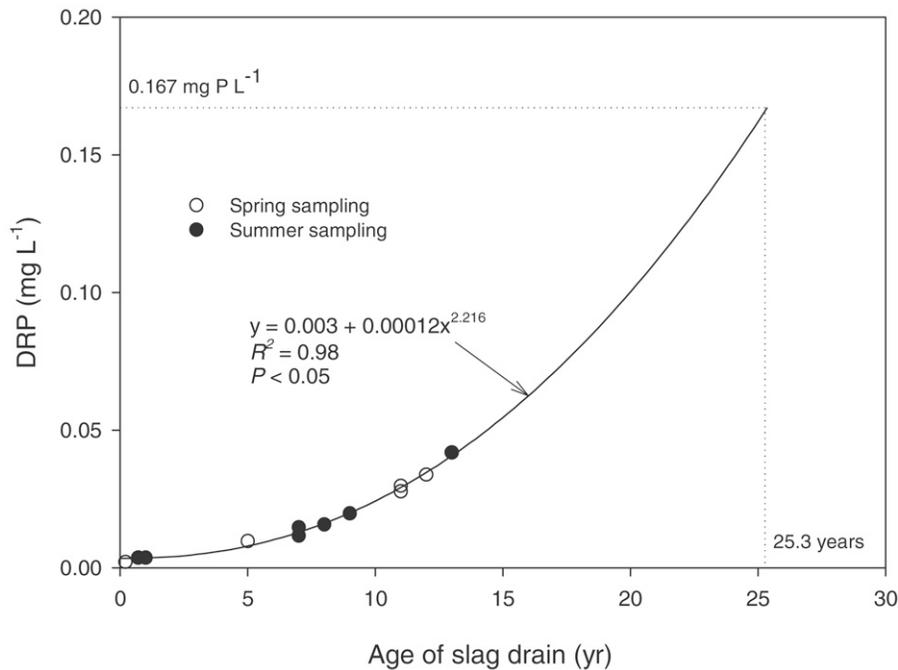


Fig. 4. The concentration of DRP in baseflow for two events sampled from drains at Te Kauwhata with slag installed as a backfill for < 1 y to 13 yr ago. The dashed line refers to the estimated concentration of P in drainage from a greywacke drain with topsoil of 64 mg kg⁻¹.

becomes saturated with P, retention will become less. If we assume mean uptake was representative of the P-retaining performance of slag drains during their lifetime, then 0.7 kg yr⁻¹ (80% of the per ha loss) was retained or 112 mg kg⁻¹ yr⁻¹, 1.5% of total sorption capacity. At this rate it would take about 60, not 72.5 yr for P retention to stop. The difference is due the changing performance of P-sorption with flow rate not accounted for by the batch sorption isotherm experiments used to determine P_{max} . This is further supported by the difference in concentrations between the control and slag drains with increasing event size (Fig. 3). Larger events resulted in less contact time with the slag and lesser uptake resulting in little difference in DRP concentration relative to the control drains. A similar picture is evident for loads (Fig. 2).

However, in the interim it is more likely that the system will have to be re-worked as most pipe drainage systems have a life span of 10 to 100 yr before they become clogged with silt and no longer drain (Bowler, 1980). To prevent this, tile drains could be installed in the middle of the backfill perhaps 10 cm from the bottom of the fill allowing particulate material to settle before excess water is drained.

The use of slag as a backfill in pipe drains and in constructed wetlands has occurred in the region for about 15 yr (Curtis, 1996; Tanner, 2003). One of the first was located at a farm near Te Kauwhata, which has been using melter slag (no basic slag) in a gradual process of rejuvenating old drains previously filled with greywacke. Samples of baseflow (i.e., 3–5 d after a storm event) were taken in spring and summer in 2006 from drains <1 to 13 yr old. The corresponding DRP data is plotted against the age of the drain in Fig. 4. The data was also fitted to a power equation ($P < 0.01$, $R^2 = 0.98$). Using the equation of McDowell and Condron (2004) the likely concentration of DRP in subsurface flow for a soil of Olsen P 64 mg kg⁻¹ was calculated at 0.167 mg P L⁻¹.

Unfortunately, only two older greywacke drains existed yielding a mean DRP concentration of 0.14 mg P L⁻¹ during the two events sampled. This estimate assumes no uptake of DRP by greywacke and transmission of flow from topsoil via macropores to drains (i.e., not piston displacement through subsoil). Extrapolating the plot to this line indicates that drains with melter slag will have an effective lifetime of just over 25 yr. Obviously, this time frame would change with silting up and flow rates. It is likely to be longer as flow rates at Te Kauwhata are generally greater than at Karaka due to good precipitation (about 1600 mm yr⁻¹) and low elevation (<50 msl) and slope (generally <1%).

Conclusions

Seven materials were chosen for study of P sorption in batch and continuous flow scenarios (i.e., a fluvium). While the three ash materials had greater P sorption compared to all other materials except basic slag, they were discounted due to limited supply, alkaline pH or dissolution of harmful constituents (e.g., B). Melter slag was considered suitable for field testing as it had both good flow properties and reasonable P uptake characteristics. Although alkaline (pH > 12), basic slag was also considered suitable for use as a backfill due to its high P sorption capacity and low concentration of toxic metals but, only if used in small enough quantities so that pH of drainage water was not significantly increased. A mix of 90% melter slag and 10% basic slag as backfill in pipe drains caused P losses to decrease by about two-thirds on a load basis. The further incorporation of the slag mix housed in a porous mesh (called a sock) and inserted in the outlet of some drains caused the decrease in DRP losses to be about 70% less than the control drains. Calculations using the P sorption capacity of the slag mixture indicated that it would take about 72 yr to become saturated

with P depending on flow rate. As the field trial could not be run indefinitely, water samples were collected from a farm with a history of slag used as a backfill in pipe drains indicated that it would take about 25 yr for drains with melter slag only to reach the DRP concentration of drains with greywacke backfill. Life expectancies (i.e., time taken for DRP concentrations to reach that lost from greywacke drains) of slag drains in other parts of the country are likely to be different according to soil type and climate. The life expectancy of tile drains is normally dictated by their drainage performance, which declines with siltation. Consequently, the use of a mixture of melter and a small proportion of basic slag is recommended as a backfill for pipe drains to retain P until the drain is reworked to improve water flow.

Acknowledgments

Funding for this work was supplied by the International Science and Technology Linkages Fund (contract no. 03-CSP-10-MCDO and ISATA07-40) and the Foundation for Research Science and Technology (contract no. C10X0320).

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