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The Use of Alum to Decrease Phosphorus Losses in Runoff from Grassland Soils

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Abstract

Phosphorus (P) loss from land can impair surface water quality. Aluminum sulfate (alum)-treated, compared with untreated, manure or slurry decreases P loss when applied to land; our hypothesis was that alum may also decrease P loss when directly applied to grassland grazed by dairy cows. A rainfall simulation showed that alum decreased mean concentrations of filterable reactive P (FRP) by 25 to 70% and total P (TP) by 20 to 40%, depending on soil P, Al, and Fe concentration and alum application rate. Using these factors, we predicted that FRP losses would be significantly less from alum-treated grasslands than from untreated grasslands for 70 to 96 d. A 14-mo field trial compared runoff P losses from plots that received 0, 25, and 50 kg Al ha^{-1} applied within a week of grazing by dairy cattle in spring. Runoff-weighted concentrations (and loads) of FRP and TP decreased in alum-treated plots by 47 to 52% and 25 to 34%, respectively. At US\$157 to US\$944 kg^{-1} P mitigated, cost-effectiveness was estimated as medium to low compared with existing strategies for mitigating P loss in dairy farms but could be improved if applied to critical source areas of P loss. However, additional work, such as determining the need for repeat applications, is required before alum can be recommended to decrease P losses from grazed grassland.

Increasing soil test P concentration (e.g., Mehlich-III or Olsen P) may increase the risk of P losses in surface runoff (hereafter termed runoff) and subsurface flow, which can impair the quality of receiving surface waterways via algal growth and eutrophication (McDowell et al., 2004). Of the forms of P lost in runoff, dissolved (otherwise known as "filterable") reactive P (FRP) is immediately algal available. In New Zealand, FRP loss in runoff can be estimated by the quotient of Olsen P and P retention; P retention, otherwise known as "anion storage capacity," is a measure of a soil's Al and Fe concentrations involved in P sorption (McDowell and Condron, 2004). Consequently, to decrease the potential for FRP losses, either Olsen P should decrease or P retention increase. The current recommendation to minimize P loss (filterable and particulate) is that soils should be fertilized with P to no more than their agronomic optimum. However, in soils with low P retention, an agronomically optimum Olsen P concentration could still result in excessive FRP losses (McDowell and Condron, 2004).

One strategy to increase soil P retention is through the application of compounds rich in P-sorptive Al, Fe, and, to a lesser extent, Ca. A variety of compounds, ranging from industrial by-products (e.g., fly ash, water treatment residuals) to naturally occurring materials (e.g., volcanic tephra) have been shown to be effective at decreasing P solubility and increasing P retention of soils (Ryden and Syers, 1975; Stout et al., 2000; Callahan et al., 2002). The application of some industrial by-products may, however, be limited by hazardous concentrations of heavy metals such as As, Cd, and Hg. Furthermore, products that increase soil pH above 6.0 may, due to their effect on P solubility, increase FRP loss (McDowell, 2005). Hence, when considering a compound for use, the following criteria must be considered: (i) compounds should be inexpensive and in ample supply, (ii) compounds should not be toxic to the environment, (iii) compounds should be efficient at decreasing P losses, and (iv) compounds should be suitable for use within a particular farm system or land use.

Aluminum sulfate (alum) is an effective, inexpensive, and readily available compound that has been widely shown to flocculate P in water columns for potable water supply and to

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Abbreviations: CSA, critical source area; FRP, filterable reactive phosphorus; FURP, filterable unreactive phosphorus; PP, particulate phosphorus; TFP, total filterable phosphorus; TP, total phosphorus; WSP, water-soluble phosphorus.

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mitigate algal growths in lakes and reservoirs (Paul et al., 2008). When examining the effect on P losses from land, work has shown that the application of alum-treated poultry litter at 10 to 40 kg Al ha^{-1} does not detrimentally affect forage growth (Warren et al., 2006a) or animal performance if ingested via forage (Mora et al., 2006; Moore and Edwards, 2007). However, most studies have examined incorporation with cattle or poultry manure and dairy or pig slurries before surface application (e.g., Smith et al., 2001; Brennan et al., 2011; O'Flynn et al., 2013) or incorporation with cropping soils (Warren et al., 2006b). Few studies have examined if alum would decrease P loss from ungrazed grassland soils (e.g., Novak and Watts, 2005), and fewer still have examined the effect on losses from grazed grassland. For intensive grassland, such as on a dairy farm, unless used during cultivation to re-grass parts of the farm every 8 to 15 yr, alum would have to be surface applied. Only one study thus far has examined the efficacy of a surface application of alum (40 kg Al ha^{-1}) to grazed dairy pasture. This study showed that in a high-rainfall environment (>4500 mm yr^{-1}), alum sprayed onto pastures as a liquid did not decrease P losses (McDowell, 2010). It was hypothesized that alum had been washed off the soil surface in frequent runoff events before it could interact with the soil. However, the vast majority of grazed grasslands receive much less rainfall. In another study, alum at 40 kg Al ha^{-1} was shown to decrease P losses from grazed and irrigated (annual precipitation, 1100 mm) forage crops by about 30% (McDowell and Houlbrooke, 2009).

Outside of high rainfall environments, these studies suggest that there is potential to incorporate alum application to grassland as a strategy to mitigate P loss. However, knowledge gaps in determining the efficacy of alum application as a strategy to mitigate P losses include (i) the effect of different soil P concentrations (e.g., Olsen P) or soil P retention and (ii) the likelihood that alum would decrease annual P losses from grazed grassland where P losses also occur from dung deposits. Hence, the aims of this paper are (i) to model soil factors influencing the efficacy and longevity of different rates of alum applied to the soil surface in mitigating P losses in runoff produced under simulated rainfall and grazing (removing forage by hand pulling and comparing turf plots with and without dung application) from different grassland soils and (ii) to determine the potential to mitigate P losses in runoff under field conditions from a grassland soil intensively grazed by dairy cattle.

Material and Methods

Rainfall Simulation

Soils for this study were chosen from established (>10-yr-old) dairy farms (stocking rates, 3.0–3.3 cows ha^{-1}) and 3- to 4-yr-old grassland that contrast a range of New Zealand soil types and climate. Soils used were a Horotiu, Warepa, Wharekohe, and Woodlands silt loams and a Taupo silty sand. These were classified under the New Zealand soil classification as Typic Orthic Allophanic, Mottled Fragic Pallic, Perched-gleyed Densipan Ultic, Typic Firm Brown, and Immature Orthic Pumice soils, respectively, which correlate to Cryand, Fragiudalf, Aquult, Dystrochrept, and Vitrand in USDA Taxonomy (Hewitt, 1998). Soils from each site were sampled (12 cores per site) to 7.5 cm depth, air-dried, crushed, and sieved (<2 mm) for later analysis.

Over a period of 3 d in summer 2010, 48 intact turf plots of each soil type were taken by inserting a 1-m (length) by 20-cm (width) metal cutting blade horizontally into the soil to 10 cm depth. Forage (mixed ryegrass [*Lolium perenne* sp.]–white clover [*Trifolium repens* sp.]) covered approximately 95% of the ground at each site. Turf samples were placed in boxes (length: 1 m; width: 20 cm; height: 10 cm), with six holes drilled in the bottom to allow drainage (≤3 mm h^{-1}). Immediately after that, all turf plots were saturated from beneath using capillary action and left to drain for 2 d before grazing was simulated by hand pulling forage plants until a cover of about 1300 kg dry matter ha^{-1} was reached (determined by rising plate meter). This simulated grazing was repeated on a monthly basis and has been shown not to increase particulate P loss (McDowell et al., 2007). Simulated grazing always occurred at least 7 d before a rainfall simulation to avoid the potential for P loss from plants confounding the data (McDowell et al., 2007).

Seven days after the first grazing, half of the 48 turf plots of each soil type were treated with a 0.5 kg fresh dung pat (moisture content, ∼88%). The dung pat (∼20 cm diameter) was at the upslope end of each box. Dung (40 kg; total P concentration of 2.48 g kg^{-1} dry weight) was collected from fresh dung patches on a grazed paddock of a dairy farm 10 km from the lab and thoroughly mixed before application. The application rate (delivering ∼62 kg P ha^{-1}) was equivalent to twice that deposited for a typical 24-h grazing period to 0.2 m^2 at a farm stocked at 2.5 to 3.0 cows ha^{-1} but comparable to that expected for a more intensive 48-h grazing period (Haynes and Williams, 1993). Sufficient aluminum sulfate (solid form, Analar grade) was dissolved in 500 mL of deionized water and sprayed onto turf plots to deliver 0, 20, 40, or 80 kg Al ha^{-1}. There were six replicates of each soil by alum by dung treatment combination. Turf samples were watered with 10 mm of deionized water the day before rainfall simulation or weekly if no simulation was scheduled within 7 d and allowed to drain overnight to minimize any difference in hydrologic response between soil types.

Runoff was generated by applying artificial rainfall (tap water, P less than detection limit of 0.005 mg P L^{-1}) at 20 to 25 mm h^{-1} to each turf, inclined at 5% slope. The rainfall simulator uses one TeeJet 1/4HH-SS14WSQ nozzle (Spraying Systems Co.) approximately 250 cm above the soil surface to allow raindrops to gain terminal velocity. The nozzle, plumbing, in-line filter, and pressure gauge were fitted onto a 305 × 305 × 305 cm aluminum frame with tarpaulins on each side to provide a wind screen. The simulated rainfall had drop-size, velocity, and impact energies approximating natural rainfall (Shelton et al., 1985). The return intervals for a 30-min event at 20 mm h^{-1} are 25 d for the Wharekohe soil, 47 d for the Horotiu soil, 175 d for the Taupo soil, and 2.7 and 3.6 yr for the Woodlands and Warepa soils, respectively (National Institute of Water and Atmospheric Research, 2010). Runoff was initiated within 10 min of the start of the rainfall event and collected for a further 30 min, after which a subsample was taken for analysis. Simulations occurred at an indoor rainfall facility 2, 4, 7, 14, 38, and 118 d after imposing treatments. Turfs were left to drain at a 5% slope in a glasshouse maintained at 20°C until the next simulation.

The rainfall simulation was designed to mimic saturation-excess conditions (Srinivasan et al., 2007). Despite textural differences (Table 1), a consistent depth and volume of boxed turf plots resulted in similar volumes of runoff across soil types, meaning that P losses reflect the availability of P to runoff.

Field Trial

The field trial was located on a dairy farm at Tussock Creek, located 20 km northeast of Invercargill, Southland, New Zealand, and was situated on a Pukemutu silt loam (mottled fragic Pallic soil in New Zealand soil classification and a Fragiudalf in U.S. Taxonomy) (Hewitt, 1998) with an annual rainfall of between 850 and 1000 mm and a slope of about 2%. The farm was representative of intensively grazed dairy properties in the area, stocked at 3.2 cow ha^{-1} and producing on average (last 5 yr) 1037 kg milksolids ha^{-1}.

Sixteen runoff plots were installed on the site in November 2011 on slopes between 1 and 2%. Plots at Tussock creek were bounded by wooden boards (4 m long by 2 m wide) dug 25 cm deep into the soil, leaving 5 cm above the surface. At the downslope end, the wooden board was replaced by a metal frame (140° v-shaped) of the same width and depth. At the center of the v-shape, an outlet directed any runoff into a 2.5-cm-diameter pipe (protected by a 5-cm steel cover) connected to a 100-L container.

As part of the farm's normal grazing rotation, 260 dairy cattle were allowed to graze the 5-ha paddock containing the trial (and plots themselves) for 24 to 36 h every 25 to 35 d depending on forage production. Grazing occurred year round except during June and July when no grazing occurred. Phosphorus fertilizer was applied in September 2011 at a rate of 30 kg P ha^{-1} across all plots. Treatments consisted of eight control replicates and two alum treatments replicated four times. Aluminum was applied at rates of 25 and 50 kg Al ha^{-1} by dissolving solid aluminum sulfate in 5 L of water and applying evenly to the respective plots. Application occurred in late August 2012, 1 wk after grazing, to allow alum to interact with the soil and to avoid ingestion by cattle. Herbage samples were taken 2 wk after treatment to test for total Al after a nitric-perchloric digestion (Jones and Case, 1990). Six soil samples (0–7.5 cm depth) were taken from each plot in late April 2012, bulked within a plot, air-dried, ground, and sieved (<2 mm) for later analysis. Rainfall was measured with a tipping bucket (Campbell Scientific TE 525).

Measurements

Runoff samples were collected after each rainfall simulation and runoff event at Tussock Creek. Volumes were measured, and the samples were analyzed for P fractions. All analyses were measured in duplicate, and P determinations were made colorimetrically using the method of Watanabe and Olsen (1965), with a limit of detection of 0.001 mg L^{-1}. Runoff samples were immediately filtered (<0.45 μm) and analyzed for FRP within 24 h and total filterable P (TFP) after acidified persulfate digestion within 48 h (Eisenreich et al., 1975). An unfiltered sample was also digested and total P (TP) measured within 7 d. Fractions defined as filterable unreactive (FURP) (largely organic P) and particulate P (PP) were determined as TFP minus FRP and TP minus TFP, respectively.

Soil samples collected from turf plots and field site were analyzed for water-soluble P (WSP) using the method of McDowell and Condron (2004), bicarbonate-extractable P (Olsen P) using the method of Olsen et al. (1954), and P retention using the method of Saunders (1965) and by a commercial laboratory for bulk density; pH (1:2 soil to water ratio); organic carbon; total nitrogen, carbon and P; and Mehlich-3–extractable P, Al, and Fe (Hill Laboratories).

Statistical Analyses

For the rainfall simulation, mean concentrations of P fractions for each runoff event and for the whole sampling period were analyzed by ANOVA, fitting terms for the factorial interaction of soil type, alum application, dung treatment, and days after application. For the field trial, runoff-weighted means for an event were used for comparison between treatments. Loads were not used due to the potential for a different hydrologic response among plots that would bias P loads toward plots exhibiting the largest runoff volumes. Before analysis by ANOVA, all data were tested for normality and $\log_{10}$ transformed if necessary. To compare between means, ANOVA outputs are presented as least significant differences at the $P < 0.05$ level of significance.

Additional analysis for the rainfall simulation involved fitting either a simple linear regression or a power function to the change in concentration with time since alum application. The time at which FRP concentrations reached 90% of the mean control FRP concentration, termed FRP$_{90}$, was the last point

Table 1. General soil parameters of soils studied.

Chemical parameter	Soil					
	Allophanic	Brown	Pallic†		Podzol	Pumice
			Rainfall simulation	Field trial		
pH	5.6	5.9	5.7	5.8	5.6	5.6
Olsen P, mg kg^{-1}	48	28	35	45	32	124
Bulk density, g cm^{-3}	0.91	0.95	1.01	1.01	1.11	0.70
P retention, %	78	56	26	28	7	46
Total P, mg kg^{-1}	1990	1140	540	860	728	3300
Total C, g kg^{-1}	75	58	40	42	36	95
Total N, g kg^{-1}	7.3	5.2	3.3	3.8	3.3	9.9
Organic matter, g kg^{-1}	127	100	70	75	62	170
Mehlich-3 P, mg kg^{-1}	44	48	88	124	112	530
Mehlich-3 Al, mg kg^{-1}	1910	1450	770	840	400	2360
Mehlich-3 Fe, mg kg^{-1}	110	290	280	290	230	160

† The Pallic soil used for the rainfall simulation and field trial was of the same type but was taken from different locations.

at which FRP concentrations were likely, according to the standard errors, to no longer be significantly less than the control soils. Previous analysis of rainfall simulations (e.g., McDowell, 2006) indicated that these functions gave the best compromise between fit to the data and the fewest number of parameters possible. For the power function ($y = \alpha t^{\beta}$), the parameters α and β were fitted coefficients relating to the initial value of y (P fraction) and the decrease in y as a function of time, t, respectively. Line fits were generated by least-squares regression, with data weighted according to standard errors. Only significant fits (at the $P < 0.05$ level) with $r^2 > 0.7$ are presented.

Results and Discussion

Rainfall Simulation

Analysis of variance indicated that there were significant effects of ($P < 0.05$) soil type, alum and dung applications, and time on the mean concentration of all P fractions (Table 2). There were also significant interactions between soil type and alum or dung application for all P fractions except FURP, and also with time. The most notable effects are discussed below.

Mean concentrations of P fractions in runoff decreased in the order of Pumice > Podzol > Pallic > Brown > Allophanic (Fig. 1). Although the soils exhibited a wide range of Olsen P concentration (28–124 mg kg^{-1}) (Table 1), this could not explain the variation in P losses. For example, although the Olsen P concentration in the Podzol soil was less than a quarter that of the Pumice soil (Table 1), the concentration of FRP in runoff without dung was only 20% less (0.1 mg L^{-1}) (Fig. 1). This is likely due to the lower P retention capacity of the Podzol compared with Pumice soil. McDowell and Condron (2004) demonstrated that FRP in runoff was best related, among a variety of predictors, to the quotient of Olsen P and P retention.

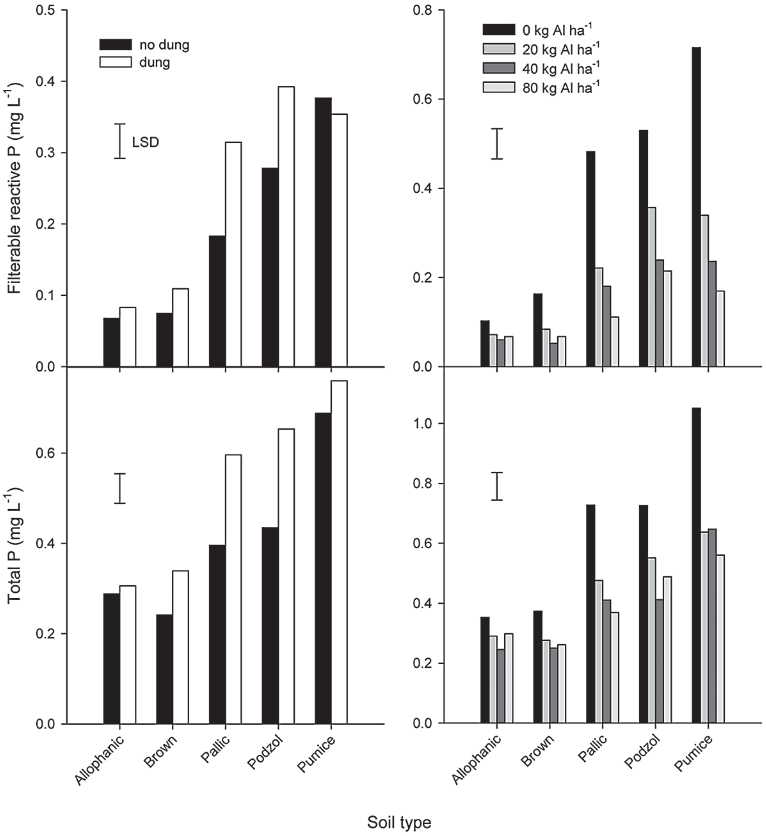

Fig. 1. Mean concentrations of filterable reactive P and total P in runoff after rainfall simulation for each soil type either with or without dung (graphs on the left) or alum (graphs on the right) applied at different rates to all turfs. The LSD is the least significant difference at the $P < 0.05$ level for the comparison of means between soils with or without dung applied or for soils with different rates of alum applied.

When dung was added to soils, concentrations of FRP, FURP, and TP increased in both the Pallic and Podzol soils (Fig. 1; Table 2). It is likely that sorption mitigated the effect of dung on P losses in the remaining soils. For example, P retention was greatest in the Allophanic soil, followed by the Brown soil, whereas the Pumice soil had a low bulk density that would

Table 2. Results (*F* probabilities) of the analysis of variance for the effect of soil type, alum application rate, dung application, time since application, and their interactions on the mean concentrations of filterable reactive phosphorus, filterable unreactive phosphorus, particulate phosphorus, and total phosphorus in runoff during the rainfall simulation.

Treatment	FRP†	FURP	PP	TP
Soil type	<0.001	0.035	<0.001	<0.001
Alum	<0.001	<0.001	0.003	<0.001
Dung	<0.001	<0.001	0.001	<0.001
Time	<0.001	<0.001	<0.001	<0.001
Soil type × alum	<0.001	0.092	<0.001	<0.001
Soil type × dung	<0.001	0.071	0.006	<0.001
Alum × dung	0.242	0.379	<0.001	0.005
Soil type × time	0.051	0.191	0.071	0.064
Alum × time	<0.001	<0.001	<0.001	0.402
Dung × time	<0.001	<0.001	0.004	0.084
Soil type × alum × dung	0.686	0.688	0.002	0.015
Soil type × alum × time	0.002	<0.001	<0.001	0.117
Soil type × dung × time	0.004	<0.001	0.530	0.125
Alum × dung × time	0.064	0.314	<0.001	0.271
Soil type × alum × dung × time	0.878	0.209	0.071	0.580

† FRP, filterable reactive phosphorus; FURP, filterable unreactive phosphorus; PP, particulate phosphorus; TFP, total filterable phosphorus; TP, total phosphorus.

maximize P sorption via a greater soil surface area and interaction with untreated soil to depth. In general, concentrations of all P fractions in runoff decreased with time after dung application (Table 2). Presumably this was due to a combination of surface crusting, preventing interaction between runoff and underlying dung and infiltration, leading to subsequent sorption and uptake of P by the soil matrix (Smith et al., 2001; McDowell, 2006).

With the addition of alum to soils, concentrations of all P fractions in runoff decreased in proportion to the application rate (Fig. 1; Table 2). However, PP concentrations were less in soils with alum applied, presumably due to increased flocculation. The greatest decrease in FRP concentrations with alum application occurred in soils with the lowest P retention (i.e., the Pallic and Podzol soils) (Fig. 1). Across all turf plots with alum applied, the concentration of FRP ranged from 0.03 mg L^{-1} 1 d after application and gradually increased to 0.42 mg L^{-1} 118 d later as the effect of alum wore off (Fig. 2). The rate of increase in P concentrations among FRP and TP fractions was well described by a power function. However, it was noted that PP losses in the first event after application were much greater in the Pumice soil (evident as TP enrichment in Fig. 2) compared with remaining events and the other soils. This may reflect the greater erosion potential of this soil order relative to other New Zealand soil orders (Rodda et al., 2001).

Power functions were used to estimate the likely time at which FRP concentration was within 90% of the control soil (FRP_{90}), determined to be the point at which alum was no longer causing a significant decrease in FRP losses in runoff. This varied from about 70 to 96 d, depending on alum application rate and the potential for P loss in runoff as predicted by the quotient of Olsen P and P retention (Fig. 3). A multiple linear regression indicated that 88% of the variance in predicting FRP_{90} could be accounted for by the log of the quotient of Olsen P and P retention and that this increased to 98.5% when alum application rate was included. Because Olsen P and P retention are commonly measured soil tests in New Zealand, the resulting equation (Eq. [1]) could be used to identify where alum would be of most benefit but should not be used outside the experimental range studied. This is especially the case for low application rates of alum because the relationship to FRP_{90} has not been established.

$$FRP_{90} = 80.7 - 20.9\log_{10}(\text{Olsen P/P Retention}) + 0.21\text{Alum}$$
$$(R^2_{(adj)} = 98.8\%;\ P < 0.001) \qquad [1]$$

Field Trial

Past work on grazed dairy pastures in New Zealand shows that a large amount of annual P losses occur in runoff generated in spring when cows resume grazing pasture (e.g., McDowell and Wilcock, 2004). Alum was therefore applied to pastures after the first "spring" grazing in late August 2012. Using Eq. [1] and data for Olsen P and P retention before treatments were applied (Table 3), rates of 25 and 50 kg Al ha^{-1} were estimated to last 80 to 90 d before FRP concentrations were within 90% of the control (unamended soil).

Comparing soil test data showed that across all plots there was, on average, no change in exchangeable Al, P retention, pH, or Olsen P after treatments were applied, whereas WSP decreased (Table 3). Ten months after alum was applied, P retention, pH, and Olsen P showed no difference in alum-treated plots compared with the control. However, exchangeable Al increased at both Al application rates compared with the control, whereas WSP decreased at the 50 kg Al ha^{-1} application rate (Table 3).

Mean runoff-weighted P concentrations for each event during the field trial are given in Fig. 4. Runoff during the 14-mo trial

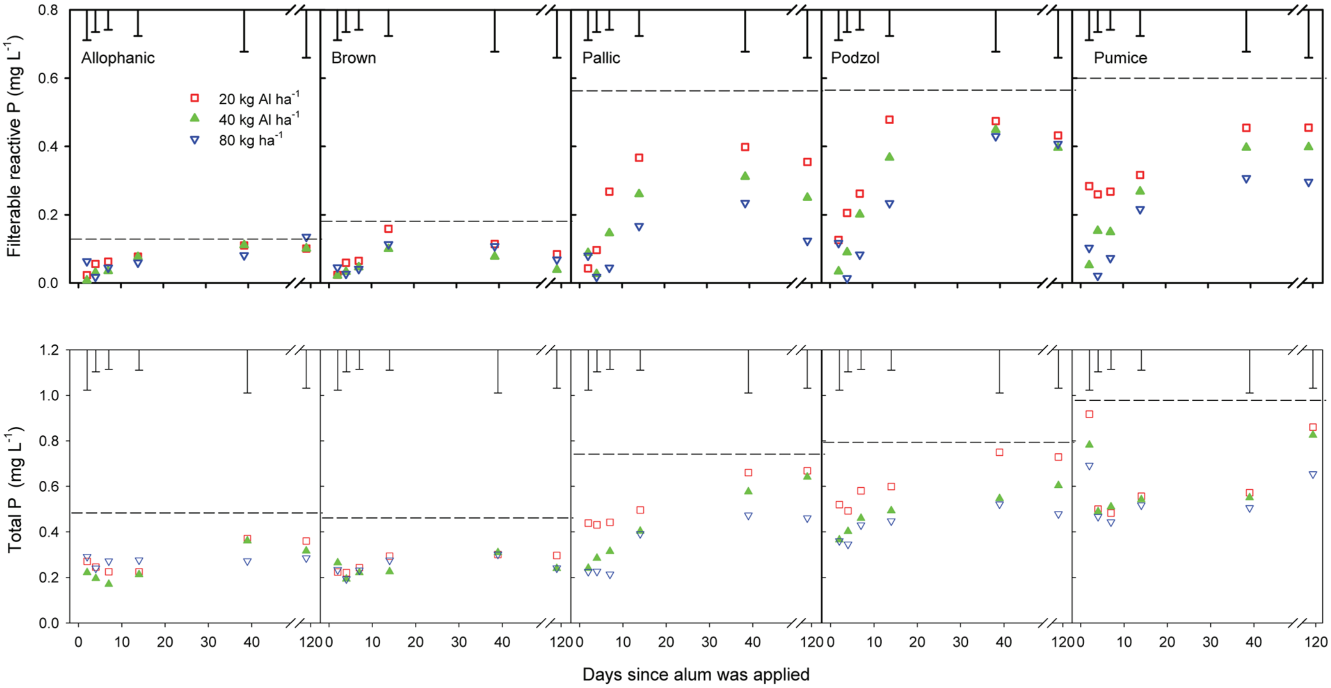

Fig. 2. Variation in mean filterable reactive and total P concentration in runoff after rainfall simulation with time since different rates of alum were applied to each soil type. Bars represent the least significant difference at the $P < 0.05$ level for the comparison of different rates of alum within the same soil type. Dashed lines represent the mean of soils not receiving alum. Individual lines showing the relationship between P concentration and time for different application rates have been removed for clarity.

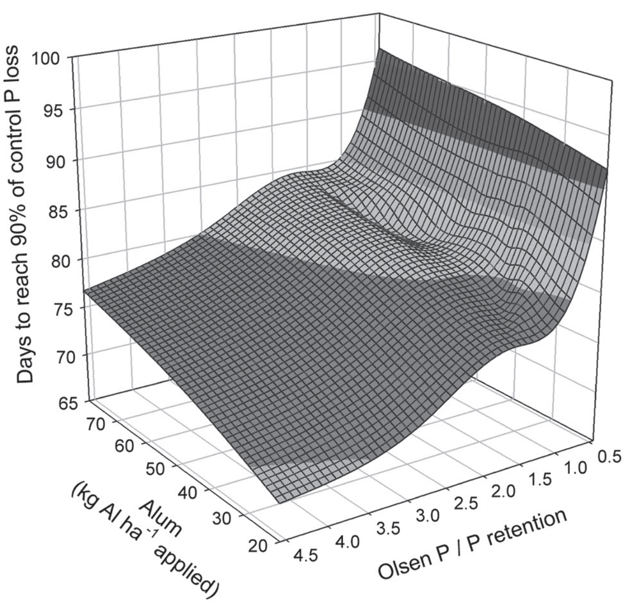

Fig. 3. Relationship between the time (days) taken to reach 90% of P lost in control (untreated) soils with the rate of alum applied and the quotient of Olsen P concentration and the percentage P retention.

varied between plots from a total of 48 to 147 mm, with a mean runoff of 96 mm from rainfall of 1096 mm. Rainfall was evenly spread among seasons. However, most runoff throughout the 14 mo of the field trial occurred due to saturated soil conditions in spring or late autumn, with only occasional runoff in summer in response to short (10–20 min), but intense (20–40 mm h^{-1}), rainfall events. The largest runoff events occurred in spring after the application of alum.

Concentrations of FRP from individual plots ranged from 0.036 to 2.896 mg L^{-1}, and TP varied from 0.076 to 3.906 mg L^{-1}. Deposition of dung was similar across all treatments, with an average of five dung pats being deposited per plot for the life of the trial. The application of P fertilizer, such as superphosphate, can enrich P (especially FRP) concentrations in runoff for events soon after application (Hart et al., 2004). However, P fertilizer was applied 9 mo before the trial began, and therefore a P contribution to runoff from fertilizer was likely to be very low (McDowell and Catto, 2005).

Mean runoff-weighted FRP concentrations were decreased by 80% in the first runoff event after application compared with the control treatment and remained <90% of the control for 112 d for the 25 kg Al ha^{-1} treatment and over 200 d for the 50 kg Al ha^{-1} treatment (Fig. 4). This is longer than that estimated using Eq. [1], possibly due to few runoff events in summer and autumn compared with a regular pattern under simulated rainfall; an irregular pattern of dung pats relative to the runoff plot outlet or the deposition rate used to generate Eq. [1] (equivalent to a 24-h grazing period across turfs with and without dung applied); a lower temperature in the field, which minimized the potential for mineralization and release of organic P; and a greater frequency of grazing, which possibly increased interaction of alum-treated soil with runoff. Over the 14-mo period of the field trial, runoff-weighted mean FRP concentrations from the 25 and 50 kg Al ha^{-1} treatments were on average 47 and 52% less than determined for the control treatment (Table 4). No significant differences were noted between treatments for FURP and PP. However, because FRP comprised about 50% of TP, there were significant decrease in TP concentrations by 25 and 34% for the 25 and 50 kg Al ha^{-1} treatments, respectively. Although there was some variation in runoff volumes between plots, mean loads of FRP were 32 and 44% less than the control treatment for the 25 and 50 kg Al ha^{-1} treatments, respectively. The comparative decreases for TP loads were 13 and 26%, respectively (Table 4).

Potential for Management

Past work has focused on adding alum directly to manure. This targets one of the main sources of P loss from confined and partially confined animal feeding operations and has generally been thought of as an efficient mitigation technology. For example, Moore and Edwards (2007) monitored two catchments since 1995 and found that, in one with poultry litter applied, much more P (1.5 kg P ha^{-1} yr^{-1}) was lost than from an adjacent catchment with applied poultry litter amended with alum (0.45 kg P ha^{-1} yr^{-1}). Recent research in Ireland has shown that mixing alum with dairy-soiled water (e.g., dairy shed effluent) or pig slurry can decrease concentrations and loads of FRP, TP,

Table 3. Mean concentrations in the field trial of soil-exchangeable Al, P retention, Olsen P, water-soluble P, and pH in each treatment 4 mo before and 10 mo after the treatment was applied in August 2012. The least significant difference at the 5% level is given for the comparison of all treatments before and after application and between alum treatments after alum had been applied.

Sample/treatment	Exchangeable Al	P retention	Olsen P	Water-soluble P	pH
	cmol$_c$ kg^{-1}	%	mg kg^{-1}	mg L^{-1}	
Before					
Control	1.92	28.8	52	0.119	5.9
25 kg Al ha^{-1}	1.90	29.7	47	0.104	5.9
50 kg Al ha^{-1}	1.89	27.7	49	0.109	6.0
Mean before	1.90	28.7	49	0.111	5.9
After					
Control	1.42	28.8	48	0.112	5.9
25 kg Al ha^{-1}	2.05	29.8	45	0.091	5.9
50 kg Al ha^{-1}	2.29	30.2	41	0.083	5.8
Mean after	1.92	29.6	45	0.095	5.9
LSD					
Before vs. after	0.29	1.7	5	0.013	0.2
Treatments$_{\text{after}}$	0.49	4.2	11	0.026	0.2

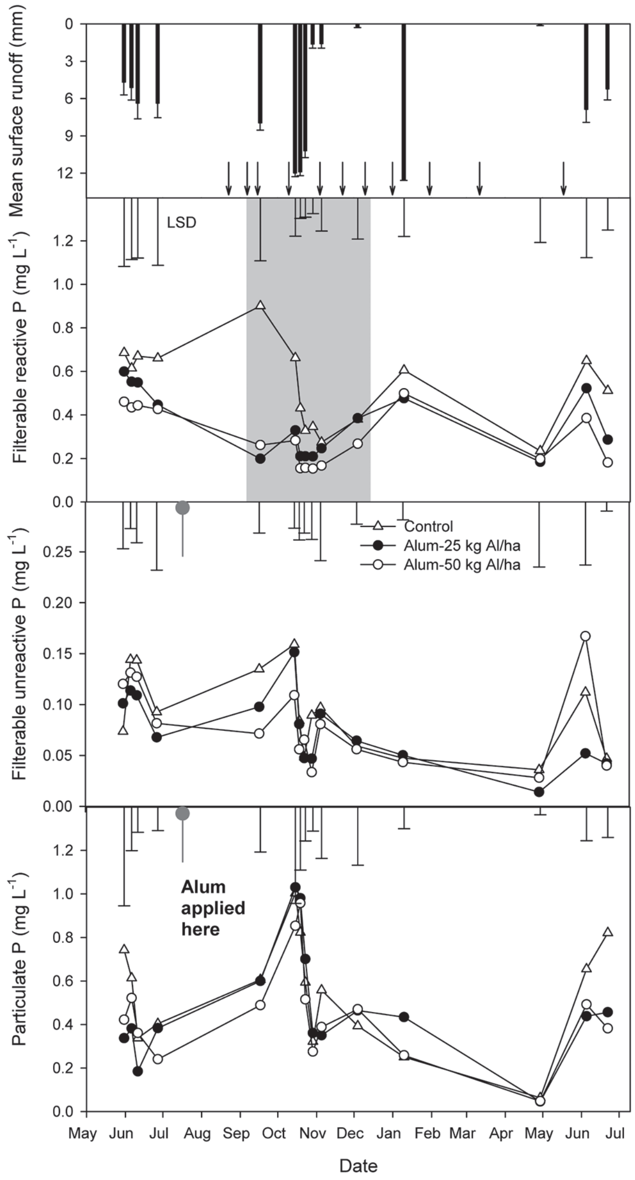

Fig. 4. Mean (± SEM) and flow-weighted concentrations of filterable reactive P, filterable unreactive P, and particulate P in runoff events from the field trial before and after alum was applied in August 2012. The grey box indicates where there was a significant effect due to alum application on mean filterable reactive P concentrations between treatments. Arrows indicate grazing events.

ammoniacal-nitrogen, and suspended solids in runoff generated by rainfall simulation onto ungrazed grassland (Brennan et al., 2011, 2012; Fenton et al., 2011; O'Flynn et al., 2012, 2013; Serrenho et al., 2012).

In most grasslands that are grazed most of the year, the application of dairy shed effluent occurs on 10 to 15% of the farm area, termed an "effluent block." Losses of P in runoff from the effluent block can be 50 or 100% greater than losses (on a per hectare basis) from the rest of the farm if bad practice occurs. For instance, Houlbrooke et al. (2004) found that applying effluent irrespective of soil moisture conditions resulted in a loss of 2 kg P ha^{-1} due to application when soils were near saturation. Adding alum to effluent is likely to decrease P losses from the effluent block but leaves the majority of the farm untreated. Furthermore, where cattle are rotationally grazed around farm paddocks, including on the effluent block, P losses come from multiple sources, notably dissolution of P from the soil or erosion of particulate-P, recently applied water soluble fertilizers, denuded plant material, and dung deposits (McDowell et al., 2007). Effluent can account for the majority of P loss from an effluent block, especially if applied when the soil is wet (Houlbrooke et al., 2006), but soil and dung deposits account for 70 to 80% of losses in the remainder of the farm. Losses from WSP fertilizer are likely to be low if applied during a period of low runoff potential (Hart et al., 2004). Furthermore, P losses in most dairy systems are dominated by the filterable fractions because slopes and erosion potential tend to be low (Nash and Murdoch, 1997). Filterable P is more available to algae than particulate P (Edwards and Withers, 2008). Hence, surface applying alum, which as our data show decreases the loss of FRP, is therefore a targeted option to minimize the potential impact of P losses from grassland grazed by dairy cows.

To further enhance the potential effect and cost-effectiveness of alum, surface applications should be targeted to areas that lose the most P to surface waterways and when most losses occur, especially of bioavailable FRP. These areas, often termed critical source areas (CSAs) (Gburek and Sharpley, 1998), vary spatially and temporally. For example, McDowell and Srinivasan (2009) found that although the majority of P loss in runoff from a grassland catchment grazed by cattle occurred from saturated zones in and around the stream during winter, P was also being lost in small storms from infiltration-excess areas like farm tracks and lanes. In our plots, most P loss occurred during spring (Fig. 4), commensurate with saturation-excess conditions similar to those around stream channels. Hence, application to these areas after the first spring grazing event would maximize interaction with deposited dung and the mitigation of P losses in runoff from entering a stream. To further mitigate P losses from a farm/catchment, alum could also be applied to tracks and lanes in summer and autumn. Although P losses from these areas are small on an annual basis compared with saturation-excess areas (McDowell and Srinivasan, 2009), they are dominated by FRP (McDowell et al., 2007; Monaghan and Smith, 2012) and occur year-round, including during summer and autumn when P entering a stream would be most likely to induce an algal response. At present, the only method to mitigate P loss from tracks and lanes is to re-route the runoff or to change their location (which can be expensive). Alum may be cheaper and could be used in addition to rerouting runoff, but work is required to establish an effective rate and the longevity of the effect before alum is washed off and needs to be reapplied. Models and software systems are becoming available that identify and isolate different CSAs, such as tracks and saturated areas, likely seasonal losses, and P form (e.g., Stafford and Peyroux, 2013). These models will enable the user to optimize the use of alum on a CSA that best protects water quality.

A full assessment of alum as a strategy to mitigate P losses requires us to assess the likely variability in response, any unintended consequences, and the use of alum compared with other strategies to mitigate P losses. Data suggest that alum will be effective at decreasing P losses, particularly as FRP, for 70 to 96 d depending on soil type, where soils with low P retention or high Olsen P benefit the most. Additional work has also shown that the application of P in sewage sludge and manure treated with

Table 4. Mean loads, runoff, and flow-weighted mean concentrations of filterable reactive P, filterable unreactive P, particulate P, and total P in runoff from each treatment (application of rate of alum in kg Al ha^{-1}) in the field trial (May 2012 to July 2013). The least significant difference at the $P < 0.05$ level is given for the comparison of mean concentrations between treatments.

Treatment	FRP	FURP	PP	TP	Runoff
	———	———	kg P ha^{-1}	———	mm
Loads					
0	0.505	0.080	0.514	1.099	91
25	0.341	0.081	0.512	0.934	107
50	0.284	0.073	0.449	0.807	97
Flow-weighted mean	———	———	mg P L^{-1}	———	
0	0.580	0.086	0.556	1.222	
25	0.311	0.075	0.529	0.916	
50	0.281	0.072	0.458	0.810	
LSD$_{\text{treatment}}$	0.199	0.023	0.191	0.181	

alum remains available to plants when applied to the soil surface (Huang et al., 2012; Warren et al., 2006a). This was supported in our study by the significant decrease in WSP but not in Olsen P. Furthermore, compared with alum dosing of streams and lakes, the loss of Al in runoff at the rates applied is unlikely to have a detrimental effect on aquatic biota (Pilgrim and Brezonik, 2005). However, data suggest that soil-exchangeable Al was increased after the application of alum, and sufficient lime must be applied to avoid decreasing the yield of forage species sensitive to Al (Moir and Moot, 2010; Wheeler et al., 1992). Finally, in a recent review, McDowell and Nash (2012) assessed the cost-effectiveness of alum alongside all other strategies to mitigate P loss that had been quantified. Alum application was ranked, using the data available, as having medium cost-effectiveness at US\$110 to >US\$400 kg^{-1} of P mitigated. This did not take into account the present data or targeting the strategy to CSAs for maximum effect. Using a cost of unrefined alum of US\$30 to US\$150 Mg^{-1} (18% w/w alum) (Anon, 2013), containing 16% Al, and decreases in runoff-weighted TP concentrations in Table 4, the cost-effectiveness of alum was US\$157 to US\$830 kg^{-1} P mitigated at the 25 kg Al ha^{-1} application rate and US\$172 to US\$944 kg^{-1} P mitigated at the 50 kg Al ha^{-1} application rate. This new estimate puts alum application in the medium to low range of cost-effectiveness for strategies available to mitigate P loss from grazed grassland (McDowell and Nash, 2012). However, the strategy may be more cost-effective in CSAs with greater P loss rates, such as tracks and lanes.

Conclusions

A rainfall simulation indicated that the mitigation effect of applying alum to grassland soils lasted for 70 to 96 d, depending on soil Olsen P and P retention and alum application rate. Applying 25 and 50 kg Al ha^{-1} to grassland after the first grazing by dairy cows in spring decreased annual runoff-weighted concentrations (and similar magnitudes for loads) of FRP by 47 and 52%, respectively. Because FRP was the greatest fraction of P lost in runoff, TP concentrations and loads also decreased (25 and 34%, respectively). Current assessments put the cost-effectiveness of alum as medium to low compared with other strategies. However, the spatial and temporal targeting of alum application to CSAs should improve its cost-effectiveness. Alum may be used in areas where few other strategies are suitable, such as on tracks and lanes. However, neither the need for additional applications of alum nor their potential implications have been explored. Such work needs to be conducted before alum could be recommended as a strategy to decrease P losses without trade-offs (e.g., if not sufficiently limed, soil-exchangeable Al could increase due to alum application, potentially impairing the growth of some forage species).

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