

## Phosphorus Mitigation during Springtime Runoff by Amendments Applied to Grassed Soil

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Permanent grass vegetation on sloping soils is an option to protect fields from erosion, but decaying grass may liberate considerable amounts of dissolved reactive P (DRP) in springtime runoff. We studied the effects of freezing and thawing of grassed soil on surface runoff P concentrations by indoor rainfall simulations and tested whether the peak P concentrations could be reduced by amending the soil with P-binding materials containing Ca or Fe. Forty grass-vegetated soil blocks (surface area 0.045 m<sup>2</sup>, depth 0.07 m) were retrieved from two permanent buffer zones on a clay and loam soil in southwest Finland. Four replicates were amended with either: (i) gypsum from phosphoric acid processing (CaSO<sub>4</sub> × 2H<sub>2</sub>O, 6 t ha<sup>-1</sup>), (ii) chalk powder (CaCO<sub>3</sub>, 3.3 t ha<sup>-1</sup>), (iii) Fe-gypsum (6 t ha<sup>-1</sup>) from TiO<sub>2</sub> processing, or (iv) granulated ferric sulfate (Fe<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub>, 0.7 t ha<sup>-1</sup>), with four replicates serving as untreated controls. Rainfall (3.3 h × 5 mm h<sup>-1</sup>) was applied on presaturated samples set at a slope of 5% and the surface runoff was analyzed for DRP, total dissolved P (TDP), total P (TP), and suspended solids. Rainfall simulation was repeated twice after the samples were frozen. Freezing and thawing of the samples increased the surface runoff DRP concentration of the control treatment from 0.19 to 0.46 mg L<sup>-1</sup>, up to 2.6–3.7 mg L<sup>-1</sup>, with DRP being the main P form in surface runoff. Compared with the controls, surface runoff from soils amended with Fe compounds had 57 to 80% and 47 to 72% lower concentrations of DRP and TP, respectively, but the gypsum and chalk powder did not affect the P concentrations. Thus, amendments containing Fe might be an option to improve DRP retention in, e.g., buffer zones.

GRASSED BUFFER ZONES (BZs) are widely used between annually tilled croplands and watercourses to decrease off-site transport of soil matter and nutrients. As a result of the Agri-Environmental Support Scheme (EEC 1992), the area of 3-m buffer strips (obligatory) or 15-m BZs (voluntary) along Finnish streams and rivers, and around lakes has been expanding since 1995. Currently, narrow buffer strips and wider BZs are estimated to cover, in total, about 11,000 ha.

Although grass vegetation filters soil particles and particulate P (PP) from surface runoff, permanently vegetated field areas appear to be ineffective in reducing losses of dissolved reactive P (DRP) (Dillaha et al., 1989; Magette et al., 1989; Uusi-Kämpä et al., 2000; Dorioz et al., 2006; Hoffmann et al., 2009; Stutter et al., 2009). On the contrary, DRP losses often increase when fields or field margins are left uncultivated. This has been addressed to convert settled PP into soluble form in permanently vegetated soil (Dillaha et al., 1989) and to liberate DRP from decaying or frost-injured vegetation (Timmons et al., 1970; Sharpley, 1981; Sturite et al., 2007). For example, in the Lintupaju BZ experiments during 1992 to 2001, springtime runoff delivered 64 to 79% of the annual DRP transport (Uusi-Kämpä and Jauhiainen, 2010). In Nordic conditions, both runoff volume and DRP concentration typically peak during snowmelt (Turtola and Paajanen, 1995; Øygarden, 2000; Uusi-Kämpä, 2005; Turtola et al., 2007).

The part of DRP loss that originates from above-ground biomass may be substantial after freezing and thawing (Ulén, 1984; Uusi-Kämpä and Jauhiainen, 2010). As an example, Bechmann et al. (2005) measured DRP concentrations of 9.7 mg L<sup>-1</sup> in runoff after repeated freezing and thawing of annual ryegrass used as a cover crop. This concentration was almost two orders of magnitude higher than the concentrations in runoff from bare soil (at 0.14 mg L<sup>-1</sup>). Based on laboratory measurements, Uusi-Kämpä (2007) estimated that the vegetation of a grassed BZ could contribute up to 1.6 kg ha<sup>-1</sup> P loss, with most of the P being in soluble form.

With BZs in the margins of conventionally tilled fields, mowing and removing the swath from the BZ is a way to decrease DRP losses in springtime surface runoff (Uusi-Kämpä and Jauhiainen, 2010). However, when the surface runoff entering the field margins originates from a permanently

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**Abbreviations:** BZ, buffer zone; DRP, dissolved reactive P; DUP, dissolved unreactive P; PP, particulate phosphorus; SS, suspended solids; TDP, total dissolved P; TP, total P; WTR, water treatment residuals.

vegetated area, such as a pasture or no-till field, and contains high concentrations of DRP, mowing vegetation from the field margins is not effective in catching P and other methods are needed for DRP mitigation.

In recent years, research has increasingly focused on amendments that decrease the solubility of P in soils (e.g., Stout et al., 1998; Agyin-Birikorang et al., 2007) and animal wastes (Dao et al., 2001; Dou et al., 2003), or on ways to retain dissolved P from runoff water (Penn and Bryant, 2006; Wagner et al., 2008; Watts and Torbert, 2009). A wide selection of different materials have been studied for P retention properties (see, e.g., O'Connor et al., 2005; Cucarella and Renman, 2009), but those containing soluble Ca or common metals (Al and Fe) in soluble or solid oxide forms have received the keenest interest. The mechanisms of P retention may be either precipitation or sorption, depending on the chemical and physical forms of the amendments. As for the amendments that contain soluble Ca, the most important mechanism is precipitation as Ca phosphates that effectively remove P from the solution in the basic side of the pH scale and at high concentrations of soluble Ca (see, e.g., Berné and Richard, 1991). Amendments containing Al or Fe oxides may result in precipitation (or coprecipitation) of P when added as soluble salts that hydrate and flocculate in water or in soil. In addition, hydrated metal oxides are the principal natural P sorption components in soils and sediments (e.g., Hsu, 1964; Richardson, 1985). Metal (hydr)oxides applied in solid form to soil also retain P.

The purpose of this work was to study the changes in P concentration in surface runoff when a grass-covered soil freezes and thaws. The freezing treatment served as a simulation of the conditions during the springtime P runoff peak (mostly DRP) observed in earlier field studies. At the same time, we applied four different amendments containing Ca or Fe on the soil surface to find out what kind of amendments would be effective in mitigating the spring DRP peak from permanently vegetated fields. The amendment materials were (i) gypsum ( $\text{CaSO}_4 \times 2\text{H}_2\text{O}$ ) obtained from a phosphoric acid plant, (ii) chalk powder ( $\text{CaCO}_3$ ), (iii) Fe-rich gypsum residue from  $\text{TiO}_2$  pigment production, and (iv) granulated ferric sulfate ( $\text{Fe}_2[\text{SO}_4]_3$ )—trade name Ferix-3, which is used as a water treatment chemical. The study was done in a laboratory, using a stationary rainfall simulator. The samples consisted of undisturbed soil blocks retrieved from two BZs with different levels of soil test P. The rainfall simulations were first done for unfrozen soil blocks and repeated twice after subjecting the soil blocks to freeze–thaw cycles.

## Materials and Methods

### Soil Blocks and Amendments

Altogether, 40 undisturbed surface soil samples were taken in November 2008 from two BZ sites located on clay soil (Vertic Cambisol, according to the FAO 2006 classification) at Jokioinen and on loam (Eutric Regosol) at Pöytyä, southwest Finland. The Jokioinen site was a 17-yr-old grass BZ in the Lintupaju field (Uusi-Kämpä and Jauhiainen, 2010) and the Pöytyä site was a 13-yr-old grass BZ. In both BZs, the grass had been mowed annually and the swath removed.

The soil test P concentrations of the uppermost soil surface (0–2 cm), expressed as ammonium acetate-extractable P (pH 4.65, Vuorinen and Mäkitie, 1955), were “fair” ( $6.4 \text{ mg L}^{-1}$ ) and “excessive” ( $47 \text{ mg L}^{-1}$ ) in the Jokioinen and Pöytyä samples, respectively (Table 1). The water-extractable P ( $P_w$ , 1:60 soil-to-water ratio) was determined after 21 h of shaking and filtration through  $0.2 \mu\text{m}$  Nuclepore polycarbonate discs (Hartikainen, 1982). In both methods, determination was done using molybdate blue colorimetry. Concentrations of total N and C in the soil were determined using a LECO CN-2000 analyzer (LECO Corp, St. Joseph, MI). The particle size composition of the mineral material in the soils was determined by a pipette method (Elonen, 1971).

Soil sampling for rainfall simulations was done with a spade to 7-cm depth, with care being taken not to break the soil's natural structure. The sampled soil blocks were carefully cut to fit inside 24-cm-diam. metal bowls and stored in plastic bags in the dark at  $6^\circ\text{C}$  for 2 to 4 wk before applying the amendments.

The Ca amendments were gypsum and chalk powder. The gypsum was a byproduct from the processing of apatite from Siilinjärvi in eastern Finland (Yara Suomi Oy, Helsinki, Finland), an apatite source that is uniquely free from harmful elements. The chalk powder ( $\text{CaCO}_3$ ) was filter cake from chalk processing (used, e.g., in the paper industry) that was obtained through the Helsinki Office of Omya AG (Oftringen, Switzerland) and originated from Omya's Rügen Island plant in northern Germany. The Fe amendments were Fe-rich (about 8% Fe) gypsum residue from  $\text{TiO}_2$  production at the Pori (western Finland) plant of Sachtleben Pigments Oy, and ferric sulfate (trade name Ferix-3) from Kemira Oyj (Helsinki, Finland), which is used as a chemical precipitant in water and wastewater treatment plants.

The moist Fe–gypsum sample was dried and ground to pass a 2-mm sieve before use, whereas larger crumbs of the gypsum from the phosphoric acid plant were crushed by hand. The chalk sample was fine powder and applied as such. The ferric sulfate (Ferix-3) was a granulated product with a median

**Table 1.** Soil characteristics at two sites (Jokioinen and Pöytyä), with a depth profile in surface soil layer.

Site	Depth cm	pH <sub>water</sub>	Total N — g 100 g <sup>-1</sup> —	Organic C mg kg <sup>-1</sup>	P <sub>water 1:60</sub> mg L <sup>-1</sup>	P <sub>Ac</sub> mg L <sup>-1</sup>	Particle size distribution†			
							<2 μm	2–20 μm	20–200 μm	>200 μm
Jokioinen	0–2	5.5	0.35	5.5	5.9	6.4	58	27	11	4
	2–5	5.5	0.16	2.6	2.8	3.5				
	5–10	5.6	0.16	2.6	3.5	4.1				
Pöytyä	0–2	6.1	0.26	3.4	25.7	47.5	21	19	55	5
	2–5	6.1	0.14	1.7	11.6	22.9				
	5–10	6.5	0.11	1.2	8.3	28.1				

† Sample from 0–10 cm depth.

granule size of 2 mm; the Ferix-3 granules are easily dissolved in water. The dry amendments were applied to the soil surface, followed by addition of 500 mL of water to moisten the amendment and soil surface. The soil blocks were then allowed to stand for 7 d at 6°C in darkness. Application rates were adjusted to supply an amount of 1.3 tn Ca ha<sup>-1</sup> of gypsum and chalk powder (Table 2). The Fe-gypsum amendment contained both Ca (0.88 tn ha<sup>-1</sup>) and Fe (0.71 tn ha<sup>-1</sup>), whereas the Ferix-3 amendment contained 0.13 tn Fe ha<sup>-1</sup> but no Ca.

## Rainfall Simulation and Surface Runoff Analyses

After the 7-d incubation with amendments, the soil blocks with bowls were put into larger containers (diam. = 0.27 m) from which surface runoff water could be collected via a tube into plastic bottles. The samples, set to 5% slope, were fully saturated with 300 to 700 mL of deionized water by applying 5 mm h<sup>-1</sup> intensity rain under a stationary drip-type rainfall simulator (see Uusitalo and Aura, 2005). The samples were kept in rain for 16 to 82 min and covered when surface runoff was just about to begin. Once completely saturated, the samples were left to stand for 0.5 to 1.0 h before the first runoff event.

The duration of each rain event (5 mm h<sup>-1</sup>) was 3.3 h, totaling 17 to 18 mm water, during which an approximately 1000-mL sample of surface runoff water was obtained as two separate 500-mL subsamples. The mass of the surface runoff water obtained was recorded. After the first rainfall simulation was completed, the samples were sealed in plastic bags and frozen (-18°C) for 7 wk. The concentrations of nutrients and suspended solids (SS) were estimated to be 21% higher in the surface runoff from blocks than in the sampled water due to dilution of the irrigation water from the space between the larger container and smaller bowl; final results were corrected for the dilution. The nutrient and solids concentrations of the deionized irrigation water were below the detection limit of the methods used.

Before the second rainfall simulation (after the first freezing), the samples were allowed to thaw in the dark (6°) for 20 h, during which about 5 mm of the soil surface thawed. The second rainfall simulation and runoff sampling proceeded as the first one. During the second simulation, 15 to 20 mm of the soil surface thawed and the temperature of the surface runoff water reached 15°C. After the second rainfall simulation cycle, the samples were again sealed in plastic bags and frozen once more for 10 wk. The third rainfall simulation (after the second freezing) was repeated with the same settings as the preceding ones.

The runoff subsamples were passed through Nuclepore (Whatman, Maidstone, UK) 0.2 µm polycarbonate membranes for DRP analysis on the day of collection. The use of 0.2-µm filter size instead of 0.4 µm (Nuclepore polycarbonate) or 0.45 µm (Sartorius PFN) filters probably had no or marginal effect on the results (Turtola, 1996), by excluding some small-sized particles and PP that would otherwise be included as a part of the

estimate of DRP. For the analyses of total P (TP) unfiltered and for total dissolved P (TDP) filtered (0.2 µm), subsamples were digested in an autoclave with peroxodisulfate and sulfuric acid (Turtola, 1996). Phosphorus concentrations were measured with a FIAstar autoanalyzer, according to the Finnish standards SFS 3025 (1986) and SFS 3026 (1986) that are based on molybdate blue colorimetry (Murphy and Riley, 1962). The concentration of PP was calculated as the difference between TP and TDP, and dissolved unreactive P (DUP) as the difference between TDP and DRP. These estimates were calculated to evaluate possible differences in P forms due to freezing cycles and amendments.

The concentration of SS was determined gravimetrically, according to the European Standard SFS-EN 872 (1996), weighing the residue retained on Nuclepore 0.4-µm polycarbonate filters.

## Statistical Analysis

The mean concentrations of the first and second 500-mL subsamples obtained during each simulation event were used in the statistical analyses. All response variables were analyzed using the following statistical model:

$$y_{ijk} = \mu + \text{replicate}_i + \text{treatment}_j + \text{replicate} \times \text{treatment}_{ij} + \text{runoff event}_k + \text{replicate} \times \text{runoff event}_{ik} + \text{runoff event} \times \text{treatment}_{jk} + \varepsilon_{ijk}$$

where  $\mu$  is the intercept,  $\text{replicate}_i$  is the random effect of the  $i$ th replicate ( $i = 1, \dots, 4$ ), and  $\text{treatment}_j$  is the fixed effect of the  $j$ th treatment (factorial treatment structure, two experimental sites  $\times$  five actual treatments). The term  $\text{replicate} \times \text{treatment}_{ij}$  is the error term when differences between the treatments were compared,  $\text{runoff event}_k$  is the fixed effect of the  $k$ th runoff event (number of the rainfall simulations), and  $\text{replicate} \times \text{runoff event}_{ik}$  is the error term when differences between the simulations were compared. The term  $\text{runoff event} \times \text{treatment}_{jk}$  is the fixed effect of time-by-treatment interaction, and  $\varepsilon_{ijk}$  is the residual error.

A  $\log_c$  transformation was needed to bring the distribution of the response variables to an approximately normal distribution. The data were analyzed using the SAS/MIXED procedure (version 9.1) and Restricted Maximum Likelihood Estimation method (SAS Institute, 2004). The estimates mentioned in the text and tables are slightly smaller than the arithmetic means due to the  $\log_c$  transformation.

## Results

### The Effect of Freezing on Phosphorus Concentrations in Surface Runoff

In the first rainfall simulation (of unfrozen soil blocks), DRP concentrations in surface runoff were 0.19 and 0.46 mg L<sup>-1</sup> for the Jokioinen and Pöytyä controls, respectively (Fig. 1), the difference in concentration reflecting the water-extractable P readings of the surface soil layer (~6 and 26 mg kg<sup>-1</sup>,

**Table 2. Characteristics of the air-dry amendments, their application rates, and the amounts of Ca and Fe added with the amendments.**

Amendment	Form	Moisture wt (%)	Application rate tn ha <sup>-1</sup>	Ca and Fe applied kg ha <sup>-1</sup>	
				Ca applied	Fe applied
Gypsum	Powder	17.0	6	1300	5
CaCO <sub>3</sub>	Powder	13.0	3.3	1300	0
Fe-gypsum	Dried powder (<2 mm)	14.9	6	880	710
Ferix-3	Granulated (<5 mm)	-	0.7	0	130

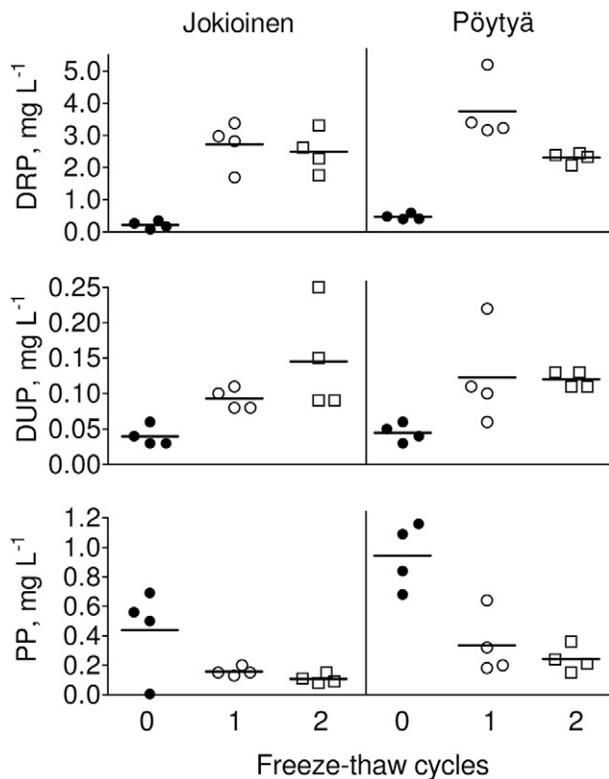


Fig. 1. Concentrations of dissolved reactive (DRP), dissolved unreactive (DUP), and particulate phosphorus (PP) in simulated surface runoff water from the permanently vegetated soils sampled at Jokioinen and Pöytyä. The black markers represent concentrations in surface runoff from unfrozen soil and the white markers the concentrations after the first and second freeze–thaw cycles of the soil blocks.

respectively) of the two sites. Freezing and thawing clearly increased the concentrations of DRP in surface runoff (Fig. 1, Table 3). The highest relative increase was 14-fold (from 0.19–2.63 mg L<sup>-1</sup>) for the Jokioinen site samples and the peak DRP concentration recorded was 3.67 mg L<sup>-1</sup> (for the Pöytyä site samples). The surface runoff obtained after the second freezing contained slightly less DRP than after the first one, but the concentrations remained >2 mg L<sup>-1</sup> (Fig. 1).

The concentrations of DUP in surface runoff water were also elevated twofold to threefold as a result of freezing, but their contribution to the total P stock in the runoff was nevertheless small compared with DRP (Fig. 1, Table 3).

The concentrations of PP were greater than those of DRP during the runoff simulation on unfrozen soil blocks (Fig. 1, Table 3), at 0.51 to 0.94 mg L<sup>-1</sup> and 0.36 to 0.58 mg L<sup>-1</sup> for the Pöytyä and Jokioinen samples, respectively. Compared with the other P forms, a clear decrease in PP was observed when the rainfall simulations were repeated after freezing. Freezing thus changed the relative proportions of P forms so that DRP became the dominant P form in surface runoff from the frozen soils, being many times higher than the PP concentrations. The decline in PP likely represents the combined effect of freezing and flushout of dispersed particles present in soils after sampling.

## The Effects of Amendments on Phosphorus Concentrations

The general trend in DRP concentrations was that surface runoff from the soil blocks with Ca-based amendments had levels of

DRP similar to the respective controls (*p* values 0.24–0.69), whereas Fe-based amendments were able to reduce the freezing-induced increase in DRP by 57 to 80% compared with the control (Fig. 2). Surface runoff from the gypsum-amended soil blocks had higher DRP concentrations than the corresponding control samples, because gypsum from the Siilinjärvi–apatite refining process contains residual phosphoric acid. As for the other Ca-based amendment, chalk powder, there was no detectable effect on DRP for either of the sites (Fig. 2). The amendments containing Fe effectively decreased DRP concentrations to the range of 0.01 to 0.04 mg L<sup>-1</sup> before the samples were frozen, but they could only partly alleviate the increase in DRP due to freezing. Relatively high peak concentrations (0.62–1.21 mg L<sup>-1</sup>) were also measured for the runoff samples of the Fe-amended soil blocks after freezing. As compared with the first freezing cycles, there were only minor differences in the concentrations after the second freezing of the soils that had received Fe amendments.

In all samples, the contribution of DUP to the total amount of runoff P was small, with the concentrations being at a level of 0.04 mg L<sup>-1</sup> in surface runoff from unfrozen controls and increased to 0.09 to 0.12 mg L<sup>-1</sup> after freezing (Table 3). Practically, the amendment applications didn't have any effect on DUP concentrations in surface runoff (Table 3). The highest DUP concentrations were measured in the samples amended with Ferix-3 and this DUP was probably more very fine sized colloidal Fe–P associations formed during dissolution of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and its reaction with DRP, rather than organic P.

The PP concentrations were generally unaffected by the amendment applications (Table 3). For the Ca amendments, we could not find any statistically significant effect with any combination of amendment and runoff event (Table 3), whereas Fe amendments decreased PP in surface runoff from the unfrozen Pöytyä soil. After freezing treatments, however, no statistically significant difference was found between the unamended controls and the Fe-amended soil blocks.

Similar to the control blocks, the concentration of TP in surface runoff from the amended soil blocks followed the trend of DRP due to the high dissolved P concentration in the surface runoff after the freezing treatments. Significantly lower concentrations of TP were measured for the Ferix-3 and Fe-gypsum treatments in all runoff events.

The SS concentrations changed much in the same way as PP, with generally small differences among the controls and treatments (Table 3). However, for the unfrozen soils, a slight decrease in SS concentration as a result of all other amendments than chalk powder was recorded (Table 3). The higher SS in surface runoff from the chalk-amended soils was likely due to suspension of the fine chalk powder itself. If increased dispersion of soil matter would have occurred due to chalk application, it should have been logically accompanied by higher PP concentrations as well, but this was not the case.

The amendments also affected, in a variable degree, pH of runoff water. While gypsum and Fe-gypsum had little, if any, effect on pH, chalk powder elevated it to 7.8 (Table 4). Ferix-3, in turn, has a strong acidic reaction (the pH of the product is <2). In our simulations, pH readings during the first simulations were 4.7 and 5.6 for Jokioinen and Pöytyä surface runoff samples, respectively, compared with a pH value of

slightly more than 7 in the surface runoff from the unamended controls (Table 4). The use of Ferix-3 would thus need careful consideration and accuracy since the product is readily soluble and high application rates might strongly decrease pH of the surface layer of soil and runoff water.

## Discussion

It is a common phenomenon of springtime runoff that the peak of DRP concentration precedes those of particles and turbidity (Rekolainen, 1989). The first snowmelt runoff presumably carries much of the P liberated from dead plant material, whereas particle transport starts only after the soil begins to thaw. The combination of high flow and high DRP concentrations suggests that controlling the concentrations of DRP in

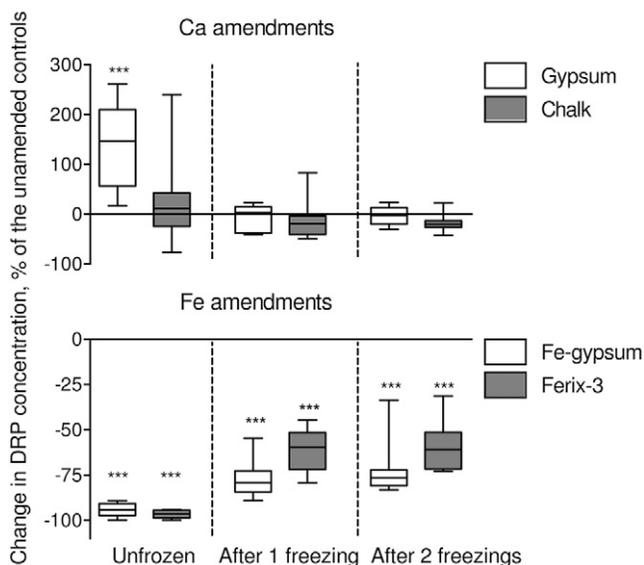
spring would have a clear effect on annual P losses. Less DRP, i.e. the P form with a high degree of bioavailability once in surface waters (e.g., Ekholm, 1998), might also depress growth of algae in springtime when the algal biomass has its maximum in Nordic conditions (e.g., Inkala et al., 1997). This especially calls for options to decrease P losses in springtime runoff.

In our rainfall simulation study, the Fe-containing amendments showed clear DRP mitigation effects. Promising results have also been obtained in earlier studies. Schärer et al. (2007) added ferrous sulfate (25%  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Ca}[\text{OH}]_2$  powder to neutralize acidity), supplying 0.25 kg Fe  $\text{m}^{-2}$  and measured a significant decrease in runoff DRP from a grass field. The effect was still sustained in the second year after application. A longer-term followup was conducted by Agyin-Birikorang et al. (2007),

**Table 3. Concentrations of dissolved reactive P (DRP), dissolved unreactive P (DUP), particulate P (PP), and suspended solids (SS) in surface runoff water from soil blocks at two sites (Jokioinen and Pöytyä), with different amendments during three runoff events. The values in parentheses show 95% confidence intervals of the estimates.**

Site/Treatment	DRP	DUP	PP	SS
<b>Surface runoff before freezing, mg L<sup>-1</sup></b>				
Jokioinen				
Control	0.19 (0.13–0.29) <sup>b†</sup>	0.04 (0.02–0.06) <sup>ab</sup>	0.44 (0.25–0.63) <sup>a</sup>	253 (146–439) <sup>a</sup>
Gypsum	0.69 (0.46–1.04) <sup>a</sup>	0.06 (0.04–0.10) <sup>a</sup>	0.58 (0.40–0.77) <sup>a</sup>	98 (57–170) <sup>b</sup>
Chalk powder	0.16 (0.11–0.24) <sup>b</sup>	0.04 (0.02–0.07) <sup>ab</sup>	0.36 (0.17–0.54) <sup>a</sup>	294 (170–508) <sup>a</sup>
Fe-gypsum	0.01 (0.01–0.02) <sup>c</sup>	0.03 (0.02–0.05) <sup>b</sup>	0.39 (0.21–0.58) <sup>a</sup>	165 (95–286) <sup>ab</sup>
Ferix-3	0.01 (0.01–0.02) <sup>c</sup>	0.04 (0.02–0.07) <sup>ab</sup>	0.36 (0.17–0.55) <sup>a</sup>	143 (83–248) <sup>ab</sup>
Pöytyä				
Control	0.46 (0.31–0.70) <sup>a</sup>	0.04 (0.03–0.07) <sup>a</sup>	0.94 (0.76–1.13) <sup>a</sup>	289 (167–500) <sup>ab</sup>
Gypsum	0.72 (0.48–1.08) <sup>a</sup>	0.06 (0.04–0.10) <sup>a</sup>	0.73 (0.54–0.92) <sup>abc</sup>	141 (82–245) <sup>b</sup>
Chalk powder	0.64 (0.43–0.96) <sup>a</sup>	0.06 (0.04–0.10) <sup>a</sup>	0.76 (0.58–0.95) <sup>ab</sup>	433 (250–750) <sup>a</sup>
Fe-gypsum	0.04 (0.03–0.06) <sup>b</sup>	0.03 (0.02–0.06) <sup>a</sup>	0.63 (0.44–0.82) <sup>bc</sup>	184 (106–319) <sup>b</sup>
Ferix-3	0.02 (0.01–0.03) <sup>c</sup>	0.04 (0.02–0.06) <sup>a</sup>	0.51 (0.32–0.70) <sup>c</sup>	191 (110–330) <sup>b</sup>
<b>Surface runoff after the first freezing and partial thawing, mg L<sup>-1</sup></b>				
Jokioinen				
Control	2.63 (1.76–3.95) <sup>a</sup>	0.09 (0.06–0.16) <sup>b</sup>	0.16 (0.00–0.34) <sup>a</sup>	49 (28–85) <sup>a</sup>
Gypsum	3.01 (2.01–4.52) <sup>a</sup>	0.04 (0.02–0.06) <sup>c</sup>	0.19 (0.01–0.38) <sup>a</sup>	39 (22–67) <sup>a</sup>
Chalk powder	2.27 (1.51–3.39) <sup>a</sup>	0.09 (0.06–0.15) <sup>b</sup>	0.18 (0.00–0.37) <sup>a</sup>	77 (44–133) <sup>a</sup>
Fe-gypsum	0.62 (0.41–0.93) <sup>c</sup>	0.08 (0.05–0.14) <sup>b</sup>	0.25 (0.06–0.43) <sup>a</sup>	51 (30–89) <sup>a</sup>
Ferix-3	1.14 (0.76–1.71) <sup>b</sup>	0.23 (0.14–0.39) <sup>a</sup>	0.15 (0.00–0.33) <sup>a</sup>	44 (26–77) <sup>a</sup>
Pöytyä				
Control	3.67 (2.45–5.49) <sup>a</sup>	0.11 (0.07–0.18) <sup>a</sup>	0.34 (0.15–0.52) <sup>a</sup>	98 (56–169) <sup>a</sup>
Gypsum	2.67 (1.78–4.00) <sup>a</sup>	0.08 (0.05–0.14) <sup>a</sup>	0.39 (0.20–0.57) <sup>a</sup>	60 (35–104) <sup>ab</sup>
Chalk powder	3.00 (2.00–4.49) <sup>a</sup>	0.09 (0.06–0.15) <sup>a</sup>	0.32 (0.14–0.51) <sup>a</sup>	117 (68–203) <sup>a</sup>
Fe-gypsum	0.73 (0.49–1.10) <sup>b</sup>	0.03 (0.02–0.05) <sup>b</sup>	0.32 (0.14–0.51) <sup>a</sup>	78 (45–135) <sup>a</sup>
Ferix-3	1.21 (0.81–1.81) <sup>b</sup>	0.15 (0.09–0.24) <sup>a</sup>	0.18 (0.00–0.37) <sup>a</sup>	35 (20–61) <sup>b</sup>
<b>Surface runoff after the second freezing and partial thawing, mg L<sup>-1</sup></b>				
Jokioinen				
Control	2.14 (1.30–3.52) <sup>ab</sup>	0.12 (0.07–0.23) <sup>a</sup>	0.06 (0.00–0.29) <sup>a</sup>	32 (16–62) <sup>a</sup>
Gypsum	2.69 (1.72–4.22) <sup>a</sup>	0.08 (0.04–0.14) <sup>a</sup>	0.21 (0.00–0.42) <sup>a</sup>	40 (22–74) <sup>a</sup>
Chalk powder	1.85 (1.18–2.90) <sup>ab</sup>	0.13 (0.08–0.23) <sup>a</sup>	0.21 (0.00–0.42) <sup>a</sup>	66 (36–122) <sup>a</sup>
Fe-gypsum	0.64 (0.41–1.00) <sup>c</sup>	0.10 (0.06–0.17) <sup>a</sup>	0.25 (0.05–0.46) <sup>a</sup>	64 (35–116) <sup>a</sup>
Ferix-3	1.13 (0.68–1.86) <sup>bc</sup>	0.15 (0.08–0.28) <sup>a</sup>	0.17 (0.00–0.40) <sup>a</sup>	58 (29–114) <sup>a</sup>
Pöytyä				
Control	2.44 (1.48–4.01) <sup>a</sup>	0.12 (0.07–0.23) <sup>a</sup>	0.28 (0.05–0.51) <sup>a</sup>	82 (41–161) <sup>a</sup>
Gypsum	2.10 (1.34–3.30) <sup>a</sup>	0.10 (0.06–0.18) <sup>a</sup>	0.04 (0.00–0.24) <sup>a</sup>	33 (18–61) <sup>b</sup>
Chalk powder	2.64 (1.69–4.14) <sup>a</sup>	0.11 (0.06–0.19) <sup>a</sup>	0.17 (0.00–0.38) <sup>a</sup>	59 (32–108) <sup>ab</sup>
Fe-gypsum	0.66 (0.42–1.02) <sup>b</sup>	0.07 (0.04–0.12) <sup>a</sup>	0.28 (0.08–0.48) <sup>a</sup>	64 (35–115) <sup>ab</sup>
Ferix-3	0.72 (0.44–1.19) <sup>b</sup>	0.09 (0.05–0.16) <sup>a</sup>	0.23 (0.00–0.46) <sup>a</sup>	28 (14–55) <sup>b</sup>

† Different letters indicate significant ( $P < 0.05$ ) among between treatments in a given site. All surface runoff events and sites were tested separately.



**Fig. 2.** Percentage change, compared with the unamended controls, in concentration of dissolved reactive P (DRP) in the surface runoff water obtained in rainfall simulations of unfrozen and frozen soil blocks. The data are averaged over the two sites (Jokioinen and Pöytyä). See Fig. 1 and Table 3 for the original concentrations. The asterisks indicate a highly significant ( $P < 0.001$ ) difference compared with the DRP concentration in the surface runoff from the respective unamended controls.

who stated that DRP was reduced by >50% from runoff for 7.5 yr after a single application of Al–water treatment residuals (WTR) on soils with very high soil test P concentrations. However, more modest results have also been reported in conditions of concentrated flow. Wagner et al. (2008) amended BZs with drinking Al–WTR (20  $\text{tn ha}^{-1}$ ) on downslopes of a source field growing grass with biosolids application (102  $\text{kg P ha}^{-1}$ ). They found that WTR-amended BZs were not statistically better than unamended BZs in retaining runoff P and concluded that the contact between the runoff and WTR was insufficient. They suggested that DRP retention by WTRs would be obtained in sheet flow conditions. However, during peak flows in spring and on steeper slopes, it is likely that flow will concentrate and contact may be insufficient.

In our work, Ca-based amendments showed little, if any, effect on P mitigation. It is probable that the precipitation of Ca phosphates was very limited, which may be due to the low pH of our soils (5.5 or 6.1 in the surface layer). Moreover, the time from the amendment applications to rainfall simulations was relatively short. In a recent study by Watts and Torbert (2009), the authors found that adding gypsum at 1.0 to 5.6

$\text{tn ha}^{-1}$  to BZs initially decreased DRP concentrations by 32 to 40%, doubling the DRP retention efficiency. However, in a second runoff event of their study, 1 mo later, the effect of the gypsum amendment had disappeared.

The study by Watts and Torbert (2009) included poultry litter application to the source field and addition of gypsum to a grassed BZ. Phosphorus concentrations in field runoff, in turn, are low compared with those of wastewaters, which are successfully purified by Ca precipitation. It can be hypothesized that soluble, Ca-based amendments perform better if they are brought into contact with high P concentrations (like in manure) and P forms that are already initially controlled by the soluble Ca concentrations (poultry litter), or in a high pH environment (gypsum itself does not elevate pH). Such prerequisites for Ca–phosphate precipitation did not prevail in our study, which was done on noncalcareous soils. Our study mostly likely involved orthophosphate compounds and rapidly degradable organic P associations from frost-injured plants. In the present study, application of chalk powder did not have an effect on any of the P forms, either, despite the increase in initial pH values from 7.2 to 7.4 of the control treatment to 7.7 to 7.8 in the surface runoff water as a result of the application (Table 4). In practice, effective P stripping in wastewater treatment plants is obtained with a high supersaturation of Ca–phosphates and typically in high-alkaline (pH 9–12) conditions (see, e.g., Berné and Richard, 1991), and such settings are not easily created in field conditions.

In Finland, BZs are a widely used option to mitigate P losses from agricultural fields. However, they tend to increase the losses of DRP in surface runoff outside the growing season, especially after frost periods. Although the increase in the losses of dissolved P species may be partly mitigated by mowing the grass and removing swaths annually, additional measures are needed for old BZs where the topsoil has become enriched with P. The findings of our study suggest that Fe compounds, such as Fe–gypsum or ferric sulfate, applied to the surface of BZs, can reduce DRP losses from the BZs themselves.

Since the present study was conducted indoors by rainfall simulations, only a limited number of variables present in field conditions could be taken into account. However, the concentration of DRP in our rainfall simulation of unfrozen Jokioinen soil blocks was very similar to that measured in the Lintupaju field at the time of soil sampling in November 2008 (mean 0.19  $\text{mg L}^{-1}$ ). Also, for the frozen soil blocks, the DRP concentration was as high as measured for the field surface runoff (up to 2.4  $\text{mg L}^{-1}$ ) when the source fields of the Lintupaju BZs were under grass in spring 2003 (Uusi-Kämpä

**Table 4.** Eventwise pH values of surface runoff water at two sites (Jokioinen and Pöytyä).

Runoff event/Site	Control	Gypsum	CaCO <sub>3</sub>	Fe–gypsum	Ferix–3
Before freezing					
Jokioinen	7.4	6.6	7.8	7.1	4.7
Pöytyä	7.2	7.0	7.7	7.2	5.6
After the first freezing and partial thawing					
Jokioinen	6.9	6.4	7.5	6.8	5.9
Pöytyä	7.0	6.9	7.4	6.9	6.1
After the second freezing and partial thawing					
Jokioinen	6.9	6.4	7.5	6.7	6.4
Pöytyä	7.2	6.8	7.5	7.0	6.4

and Jauhiainen, 2010). This suggests that indoor rainfall simulations can provide useful information on the concentrations and P forms in the field, but further, larger-scale studies on field plots and BZs are needed to account for natural runoff variations and surface runoff from the source fields.

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