

Effectiveness of Different Precipitated Phosphates as Phosphorus Sources for Plants

A. E. JOHNSTON^{1*} and I. R. RICHARDS²

1 IACR-Rothamsted, Harpenden, Hertfordshire, AL5 2JQ, UK

2 Ecopt, Ufford Road, Bredfield, Suffolk, IP13 6AR, UK

* Corresponding author e-mail johnny.johnston@bbsrc.ac.uk

Abstract

Eleven precipitated phosphates were evaluated as sources of phosphorus (P) for plant growth by comparing their effectiveness with that of monocalcium phosphate, a source of water-soluble P that is generally considered to be fully plant available. The precipitated phosphates comprised struvites recovered from waste water discharges (mainly magnesium ammonium phosphate), laboratory synthesised struvites, a synthetic iron phosphate and a recovered calcium phosphate. Precipitating phosphates in these forms could be a way for removing P from waste water before it is discharged to rivers, so reducing the risk of eutrophication. Application to agricultural land would be one potential use for such phosphates. Evaluation was by pot experiments with a sandy loam soil and with a sandy clay loam soil using perennial ryegrass as the test crop. The soils differed in pH (6.6 and 7.1) and in Olsen P (28 and 11 mg L⁻¹). Measured variables were grass dry-matter (DM) yield and grass P concentration which were used to calculate offtake of P in the harvested grass. DM yields of ryegrass and P offtakes given by the synthetic and recovered struvites were not significantly different statistically either between themselves or to MCP applied at the same rate. On this basis these struvites could be used to recycle P to similar soils and the effect of the P on crop yield should be similar to that of MCP

Key words: struvite, P availability, pot experiment, ryegrass

INTRODUCTION

In recent decades waste water discharges have become an issue because the P they contain is one of the sources responsible for the disturbance of the biological balance in some surface fresh waters. Steps can be taken to lessen the amount of soluble P in discharges by precipitating it in various chemical forms. These include magnesium ammonium phosphate (MgNH₄PO₄) and magnesium potassium phosphate (MgKPO₄), members of a group of related compounds called struvites. Additionally P can be precipitated as calcium, iron and aluminium phosphates. The small concentration of N (5.6%) relative to P (12.5%) in magnesium ammonium phosphate indicates that, if this material is to be used on arable crops or grassland, the availability of the P becomes the more important agronomic factor. The use of struvites as nutrient sources was first proposed by Murray (1858). Much of the recent literature on phosphates, particularly struvites, recovered from waste water has been concerned with their production and potential use in agriculture (Gaterell *et al.* 2000) but there are few reports of agronomic effectiveness. Koritskaya and Remen (1962) published some results on field crops. Ghosh *et al.* (1996) reported that struvite was as effective as diammonium phosphate as a P source for gram in India. Goto (1998) in Japan also gave data showing that finely divided struvite was as effective as superphosphate.

Unlike superphosphate, these precipitated phosphates do not contain water-soluble P. High water solubility and the beneficial effects of superphosphates in increasing crop yields are well recognised by farmers. Nevertheless, some phosphatic fertilisers, for example nitrophosphates, contain less than 90% of the P in water-soluble forms yet they are very effective in supplying P to crops. Thus the solubility of P in water and the availability of the P to crops are not necessarily closely related. It is important therefore to test the availability of P in products with little water-soluble P. It was decided to determine the availability of the P in a range of recovered phosphates so that appropriate advice could be given to farmers and advisors.

MATERIALS AND METHODS

Precipitated phosphates

The 11 precipitated phosphates tested had a range of P concentrations and were obtained from several sources (Table 1). The two synthetic struvites were made using commercially available ingredients by two different laboratories. The iron phosphate was made in the laboratory using the ferric chloride that would be used by water companies for P removal from waste water. According to the sponsors of the project, who supplied the precipitated phosphates, the principal P source in the synthetic struvites and all recovered struvites, except no. 5, was magnesium ammonium phosphate. Recovered struvite no. 5 was magnesium potassium phosphate. The total P concentration in every material was determined by digestion with mineral acids (HCl/HNO₃) followed by analysis using inductively coupled plasma (ICP). Results were expressed as percentage P in the materials as received, that is without drying. Monocalcium phosphate (MCP) (24.49% P) was purchased commercially (Analar grade).

The precipitated phosphates differed in physical form (Table 1) so, to ensure a fair comparison, all materials were passed through a 0.5 mm (30 mesh) sieve. Some required grinding but others passed through the sieve easily.

Soils used

The two soils, a sandy loam and a sandy clay loam, were collected fresh, passed through a 4 mm sieve and each was thoroughly mixed before use. Soil pH was determined in water (ratio soil:water 1:2.5), readily available P by the Olsen method and organic matter by the Walkley & Black method.

Soil 1, a sandy loam, had a pH of 6.6 and contained 28 mg L⁻¹ of Olsen P and 1.0% organic carbon (equivalent to 1.7% organic matter). Soil 2, a sandy clay loam, had a pH of 7.1 and contained 11 mg L⁻¹ of Olsen P and 1.8% organic carbon (equivalent to 3.1% organic matter). These levels of Olsen P would be regarded as medium and low for soils 1 and 2 respectively. Details of the soils are shown in Table 2.

Pot experiments

There were two experiments, of identical design, one for each soil. The 11 precipitated phosphates (Table 1) were applied at a rate equivalent to 0.087 g P per pot based on the total P content of the material as received. MCP was included at 5 rates (0.044, 0.065, 0.087, 0.109 and 0.131 g P per pot, equivalent to 0.10, 0.15, 0.20, 0.25 and 0.30 g P₂O₅ per pot), together with a control treatment which received no P. The P sources were mixed with the soil (1 kg) for each pot immediately before sowing perennial ryegrass, *cv.* Vigor (RvP) at 0.37g per pot. The total number of treatments was 17 and these were replicated 3 times in a randomised block design giving 51 pots for each soil.

Table 1: Description of the precipitated phosphates evaluated in the pot experiments

Material	Source	Phosphorus content %P	Physical form
Synthetic struvite no. 1	Laboratory synthesised 'pure' struvite provided by Rhodia	12.8	White powder, some clumping into lumps that easily broke down
Synthetic struvite no. 2	Laboratory synthesised 'pure' struvite provided by Cranfield University, UK	13.4	White cores, approx 3mm diameter, crumble to white powder
Recovered struvite no. 1a	Struvite recovered by the full scale Unitika process from municipal sewage works in Japan (Uneo & Fujii 2001, Taruya <i>et al.</i> 2000)	12.9	Cream coloured small particles, free flowing
Recovered struvite no. 1b	Struvite recovered by the full scale Unitika process from municipal sewage works in Japan (Uneo & Fujii 2001, Taruya <i>et al.</i> 2000)	12.8	Cream coloured small particles, free flowing
Recovered struvite no. 2	Struvite recovered from corn steep liquor by the Audobon Sugar Institute/Louisiana State University Agricultural Center, USA, AECI-Bio pilot process	13.1	Fine white powder, some formation of lumps that easily broke down
Recovered struvite no. 3	Struvite recovered from the Kiakyushu City municipal sewage treatment plant, Japan, using seawater as a magnesium source (Nishihara Co pilot plant) (Matsumiya <i>et al.</i> 2000)	12.8	Similar to Unitika material, cream coloured small particles, free flowing
Recovered struvite no. 4	Struvite recovered from carmin red dye industry waste liquors (CHR Hansen SA/University of Barcelona) (Villalba <i>et al.</i> 2001)	8.3	Very fine, pale brown powder, free flowing
Recovered struvite no. 5	Potassium struvite recovered from veal manure at the full scale plant of yje Putten agricultural co-operative, The Netherlands (Schuiling & Andrade 1999)	8.6	Yellow/brown moist powder with lumps
Recovered struvite no. 6	Spontaneously occurring deposit material (mainly struvite) from digester outflow pipes at the Wassmansdorff municipal sewage works, Berlin Wasser Betriebe (Heinzmann 2001)	12.4	Large crystalline chips (up to 8mm) with some smaller dark particles
Sewage recovered calcium phosphate	Calcium phosphate recovered by the full-scale Crystallactor process at the Geestmerambacht municipal sewage treatment works, The Netherlands (Gaastra <i>et al.</i> 1998, Giesen 1999)	8.3	Dark brown moist powder, strong foul, unidentified smell
Synthetic iron phosphate	Laboratory synthesised by Cranfield University, UK using commercial water treatment iron chloride (Analar grade) and pure hydrogen phosphate solution	14.1	Pale brown powder

Table 2: Properties of the two soils used in the pot experiments

	Units	Soil 1	Soil 2
pH		6.61	7.08
Phosphorus (Olsen)	mg P L ⁻¹	28.0	11.2
Potassium (AN extraction)	mg K L ⁻¹	265	92
Magnesium (AN extraction)	mg Mg L ⁻¹	155	59
Organic carbon ©	%C	1.0	1.8
Sand	%	61	60
Silt	%	23	11
Clay	%	16	29
Texture		Sandy loam	Sandy clay loam

Before sowing the seed, basal nutrients, 0.05 g N per pot and 0.1 g Mg per pot, were mixed with the soil as ammonium nitrate and magnesium sulphate. This was followed by top-dressing with 0.15 g N per pot and 0.08 g K per pot after every harvest as ammonium nitrate and potassium sulphate and by top-dressing with 0.05 g Mg per pot as magnesium sulphate after harvests 2 and 4. The pots were watered with rain water applied to the surface as required. The amount was such that the grass never wilted but through-drainage into the saucers in which the pots stood was kept to a minimum. Any leachate was returned to the pot. The grass was harvested at 20, 38, 49/50, 66, 85 and 100 days after sowing. Grass samples were dried overnight at 100°C, weighed and then milled before chemical analysis for total P concentration. P offtake was calculated on a pot basis by multiplying DM yield by % P. Samples taken at 100 days were not analysed for P as, by harvest 6, dry DM yield responses had declined on both soils and there were no significant treatment differences in grass % P at harvest 5.

RESULTS AND DISCUSSION

The data sets comprised grass DM yield at harvests 1 to 6 and P offtake at harvests 1 to 5. Results presented in Table 3 are for total DM yield and for total P offtake. P concentration in the DM, which is not shown, tended to decline during the experiment from 7000 to 9000 mg P kg⁻¹ for soil 1 and 4000 to 7000 mg P kg⁻¹ for soil 2 at harvest 1 to between 3700 and 5300 mg P kg⁻¹ for both soils at harvest 5. There were few significant treatment differences in % P, mainly lower concentrations with the sewage recovered calcium phosphate and the synthetic iron phosphate. However, these did not lead to significant differences in P offtake. Although a well tested pot experiment technique was used, experimental error reflected in the standard error per pot tended to be somewhat higher than normally expected. We can offer no explanation for this.

Dry matter yield and P offtake

At the lower amounts of P applied as MCP, both DM yield and P offtake were smaller on soil 2 which had the least Olsen P. Differences between the two soils were less at the higher levels of applied P. This suggests that the small difference in pH and the larger difference in Olsen P between the soils did not affect the DM yield and P offtake that could be achieved under the conditions of these pot experiments. This conclusion is supported by DM yields and P offtakes with MCP at 0.109 and 0.131 g P per pot. Both were a little lower with 0.131 than with 0.109 g P per pot but the differences were not significant suggesting that the maximum DM yield and P offtake had been reached.

Table 3: Total dry-matter yield of ryegrass and total P offtake in the grass for MCP and precipitated phosphates

	Total dry-matter yield (g per pot)			Total P offtake (mg per pot)		
	Soil 1	Soil 2	Mean	Soil 1	Soil 2	Mean
Control	3.25	2.56	2.91	16.35	9.38	12.87
MCP 0.044 g P per pot	6.53	3.66	5.10	23.94	12.55	18.25
MCP 0.065 g P per pot	6.92	5.19	6.06	25.79	18.53	22.16
MCP 0.087 g P per pot	6.19	5.23	5.71	27.36	22.46	24.91
MCP 0.109 g P per pot	6.66	7.00	6.83	27.66	32.22	29.94
MCP 0.131 g P per pot	5.63	6.10	5.86	26.80	26.10	26.45
MCP 0.087 g P per pot (from response curve)	6.66	5.97	6.28	27.14	25.35	26.28
Precipitated phosphates at 0.087 g P per pot:						
Synthetic struvite no. 1	6.40	7.25	6.83	29.68	29.75	29.72
Synthetic struvite no. 2	6.58	7.40	6.99	28.75	30.01	29.38
Struvites recovered from:						
Sewage (no. 1a)	7.00	5.87	6.44	30.44	24.10	27.27
Sewage (no. 1b)	6.40	6.11	6.26	27.09	24.84	25.97
Sewage (no. 3)	6.68	5.88	6.28	29.70	23.92	26.81
Corn steep (no. 2)	6.00	6.18	6.09	26.01	26.48	26.25
Dye industry (no. 4)	6.35	5.89	6.12	28.53	24.75	26.64
Veal manure (potassium struvite no. 5)	6.91	5.99	6.45	31.13	22.22	26.68
Sewage deposit (no. 6)	6.62	5.11	5.87	28.97	20.46	24.72
Recovered calcium phosphate	6.09	6.83	6.46	21.64	20.45	21.05
Synthetic iron phosphate	6.94	7.09	7.02	25.20	22.68	23.94
SE/plot (33 D.F.)	1.126	1.557	1.359	4.295	5.089	4.709

Yield and P offtake responses to P applied as MCP

Curvilinear relationships between total DM yield and P applied and between total P offtake and P applied were apparent for each soil and for mean data from the two soils. Cubic regression functions, fitted to the data in Table 3, were used to describe these relationships. Values for total DM yield and total P offtake for MCP applied at 0.087 g P per pot calculated from the regression equations, provided a more representative basis for comparing MCP and the precipitated phosphates than did the measured values for MCP at 0.087 g P per pot.

P offtake response (the difference in P offtake between a treatment and the untreated control) tended to increase during the course of the pot experiments. Apparent P recovery calculated from total P offtake, was 12.7% for soil 1 and 15.0% for soil 2, typical for pot experiments using ryegrass as the test crop and for many arable crops in field experiments.

Yield and P offtake response with P applied as precipitated phosphates

There were no significant ($P < 0.05$) differences in total DM yield between the different precipitated phosphates or between any of the precipitated phosphates and MCP applied at 0.087 g P per pot (Table 3). For the precipitated phosphates, total P offtake response over 5 harvests ranged from 5.3 to 14.8 mg P per pot for soil 1, equivalent to an apparent recovery of 6 to 17% of the applied P. For soil 2, total P offtake response ranged from 11.1 to 20.6 mg P per pot, equivalent to an apparent recovery of 13 to 24% of the applied P.

P offtake for both synthetic struvites was higher than that for MCP at 0.087 g P per pot though not significantly so. For the recovered struvites, P offtake was similar to that for MCP at 0.087 g P per pot although in soil 2, P offtake recorded for recovered struvite no. 6 was lower than that for MCP (though the difference was not statistically significant). The potassium struvite (recovered struvite no. 5) gave a P offtake apparently higher than that for MCP in soil 1 but similar to MCP in soil 2. The sewage recovered calcium phosphate gave the lowest P offtake in both soils, significantly ($P < 0.05$) lower than that for MCP in soil 1.

For the precipitated phosphates, there were some small differences in DM yield and P offtake between the two soils. However, these differences were not consistently in favour of one soil or the other and fell within the range of experimental error. It is, therefore, appropriate to consider the mean of the two soils. The apparent effectiveness (E) of the precipitated phosphates relative to that of MCP was expressed as a percentage by $E = (M/0.087) \times 100$ where M is the rate of P applied as MCP (from the regression equation) corresponding to the same total P offtake given by the precipitated phosphate.

Both synthetic struvites applied at 0.087 g P per pot gave very similar DM yields and P offtakes which were larger than those recorded for MCP at the same rate of application but the differences were not statistically significant. The value of E for these materials could not be calculated as the recorded P offtakes were slightly greater than the maximum values from the regression equations.

DM yields and P offtakes were similar for the three struvites recovered from municipal sewage (nos 1a, 1b and 3) and in the ranges 6.26 to 6.44 g DM per pot and 25.97 to 27.27 mg P per pot. These values were not significantly different to those for MCP at 0.087 g P per pot predicted using the regression equations. Values of E for these materials were 98% to 109%.

DM yields given by the struvites recovered from corn steep (no. 2) and the dye industry (no. 4) were only a very little smaller than those given by struvites recovered from sewage and P offtakes were the same. Values of E were 104% and 103% respectively.

Potassium struvite derived from veal manure (no. 5) gave very similar DM yields and P offtakes to the other recovered struvites and a value of 103% for E.

The spontaneously occurring deposit from sewage (no. 6), mainly struvite judged by its total P content, gave slightly lower DM yields and P offtakes than did the other recovered struvites. The E value was somewhat lower at 90%.

The recovered struvites gave consistently smaller DM yields than the synthetic struvites but the differences were not statistically significant. This suggests that the recovered struvites might have slightly lower P availability than the synthetic struvites, a conclusion supported by the lower yields given by the spontaneously occurring struvite deposit. These small differences may be due to crystal size. If so, this would suggest that struvite precipitation from waste water streams should be carefully controlled. Nevertheless, the effectiveness of these struvites as sources of P for plants was very similar to that of MCP.

The recovered calcium phosphate gave the lowest recorded total P offtake of the precipitated phosphates and a value of 69% for E.

The iron phosphate gave somewhat larger DM yields but slightly smaller P offtakes to those given by MCP at 0.087 g P per pot with a value of 85% for E. It has generally been considered that iron phosphates are insoluble and that the P they contain is unavailable to plants. This was not so for this synthetic iron phosphate. Recently, Richards and Johnston (personal communication) found that a part at least of the water-insoluble P fraction of triple superphosphate was available to plants. This fraction also was probably largely iron phosphates. Some research is needed on iron phosphates precipitated from waste water using ferrous or ferric salts. The plant availability of the P may depend on the degree of hydration and perhaps the extent of ageing and slow transformations of the iron phosphate.

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