RPR REVISITED 6: SWITCHING TO REACTIVE PHOSPHATE ROCK (RPR) BASED FERTILISERS REDUCES ALL FORMS OF DIFFUSE P LOSSES, NOT JUST DRP

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Abstract

Reactive phosphate rock (RPR) is recognised in Overseer® as being less susceptible to loss of dissolved reactive phosphorus (DRP) in run-off from than is soluble P fertiliser, although far less than field trials demonstrate. There is no recognition of lower particulate P losses, and P leaching is essentially ignored by being lumped in with DRP run-off loss without separate calculation.

Typically, 30-70% of P run-off is in the form of particulate P (P adsorbed onto soil particles). It is mistakenly considered by many to be independent of the form of P fertiliser used. However, many field trials show reductions in both DRP and particulate P with RPR. This is consistent with field data demonstrating that RPR maintains maximum pasture growth with considerably lower readily-available Olsen P levels (which includes water-soluble and weakly-adsorbed P) than does soluble P.

The dissolution of RPR particles is dependent on reactivity, particle size, soil pH, soil moisture and soil calcium status. Levels of weakly-adsorbed P achieved with long-term RPR are usually 20-30 ug/gm soil, a good match with concentrations of weakly-adsorbed P and soil solution P levels required for optimum growth of pasture. Levels higher than this can be achieved on very acid soils.

Soluble P fertilisers on the other hand maintain soil concentrations of very weakly adsorbed P up to many hundreds of ppm for several weeks or even months in the dissolution zone surrounding individual particles. Average soil P concentrations are highest near the soil surface, where the dissolving granules largely reside (until moved lower by trampling and worm activity etc). This near-surface particulate P is much more likely to be carried off in run-

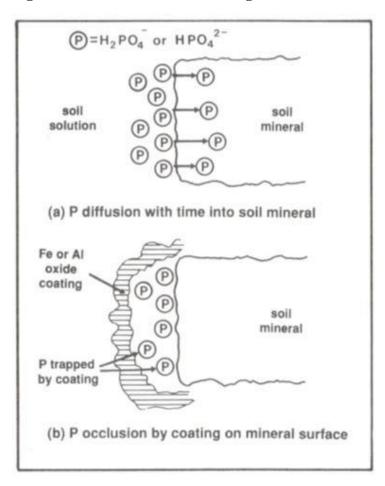
off, and much of it can then be desorbed in mildly-acidic streams, rivers and lakes as the P equilibrium changes with dilution, resulting in eutrophication. Particles of undissolved RPR however are far less likely to reach receiving water than are particles of either soil particles or soluble P fertiliser, because of the much higher density of RPR particles. More intensive P runoff research on farms with a long-term history of RPR should be a priority.

Introduction; Forms of P loss

P leaching

The fundamental drivers of P leaching from soils are the degree of saturation of the soil's P sorption capacity (not the P sorption capacity alone), and the volume of drainage. The higher the percentage of saturation of the P sorption capacity (Pscs%), the greater the concentration of P maintained in the soil solution, and therefore the greater the losses of P in any drainage (Sharpley 1993). This applies to both inorganic and organic P (P_i and P_o). Saturation occurs gradually through either the diffusion of P into a soil mineral like allophane (Fig.1a), and/or its occlusion by being coated by Fe and Al oxides while physically bound to soil mineral surfaces (Fig.1b).

Figure 1: The mechanisms for the gradual saturation of soil solution P sorption capacity.



The Percentage Saturation of the Phosphate Sorption Capacity

The percentage saturation of the phosphate sorption capacity (Pscs%) is very important environmentally, but unlike in countries like the Netherlands and Germany for example, New Zealand soils and farms are not tested for it; only an indirect assessment of the P sorption capacity of the soil is made (the phosphate retention or PR test, which is expressed on a 0-100 scale). Truly enormous quantities of P can be leached from low-P retention acid peat soils, even at Olsen P levels as low as 7 (Simmonds et al 2016).

PR or ASC- what's in a name?

The PR test currently is used only to help assess required maintenance P inputs and soil Olsen P levels to maintain a given level of farm production. It was renamed the Anion Storage Capacity (ASC) about 15 years ago.

The term ASC is a misnomer and should never have been adopted. A 'store' or 'storage' is by definition somewhere you deliberately put something until such time it is needed again.

When soluble P fertiliser is applied however, the farmer little or no control over the rate it which it will be adsorbed (into 'storage'), or how quickly the soil P concentration will reach equilibrium again.

Just as importantly, the rate of desorption into plant available form is rarely capable of maintaining optimum production for more than 2 or 3 years after fertiliser is withheld.

So this sorbed P is not a 'store' at all; it is better described as a bank 'savings' account which unfortunately pays no interest and can only be withdrawn at rates that are far too low to maintain a reasonable state of living.

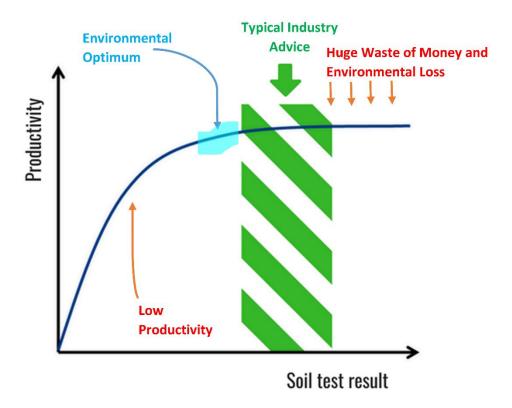
Finding a dual-purpose soil agronomic and environmental management test

In the presence of ongoing applications of soluble P, the concentrations of P in the soil water are generally easily high enough to give rise to eutrophic levels of P in any drainage. Only 0.015 mg/L dissolved reactive P (DRP) is required for drainage water to be eutrophic. This represents only 0.1 kg/ha with an annual drainage of 400mm. This amount of P is of no economic significance, but is enormously important environmentally.

Unfortunately, the Olsen P test, while reasonably useful agronomically, is by itself far to blunt an instrument to be used in environmental management.

Measurements of CaCl₂-P in drainage water have indicated the existence of 'change-points' in Olsen P near the top of the pasture production response curve, above which losses of P in drainage water accelerate (McDowell and Nash 2012). However these 'change-points' have had little applied use, principally because the CaCl₂-P figure is a little use commercially, and therefore not widely measured on farms.

Figure 2: Pasture production related to optimum soil tests for environmental protection.



However, McDowell and Condron (2004) had produced a very useful predictor of DRP from the Olsen P and PR on a range of soils, viz:

$$DRP = 0.069 (Olsen P/PR) + 0.007$$

The Olsen P/PR ratio is essentially an expression of the degree of soil P sorption capacity. Very importantly, it bridges the gap between purely agronomic soil testing and environmental management. It is very disappointing that more has not been done to promote its environmental management potential.

Setting a limit of say 0.35 for the Olsen P/PR ratio for pastoral soil development throughout New Zealand would bring major improvements to water quality, without significantly reducing farm production.

Relevance to RPR

RPR has been proven to maintain any given level of pasture production with considerably lower Olsen P levels on most soils, by many researchers. This is a consequence of the fact that

More of the P uptake is being released more directly, in a drip-feed fashion, directly to root uptake from dissolving particles of RPR.

When soluble P is applied, it undergoes net sorption onto the surfaces of soil particles until equilibrium is established. Soil water P concentrations around dissolving granules can reach hundreds of mg P/L, overloading plant P uptake requirements and soil sorption rates for a period of weeks or months. During this pre-equilibrium period, large leaching losses of DRP are possible from many soils (Eddis et al. 2006, Redding et al. 2006).

This overloading and resulting susceptibility to loss does not occur with RPR.

It is important to note however the fact that not all phosphate rocks can be used as direct application P fertilisers capable of maintaining high levels of pasture production. Only *reactive phosphate rocks* or RPRs, as a function of having at least 20% substitution of phosphate by carbonate in the crystal lattice (which gives them a much higher solubility product in mildly acid soils), can maintain sufficient concentrations of P in the soil solution for vigorous pasture production (Fig.3, Chien 1977).

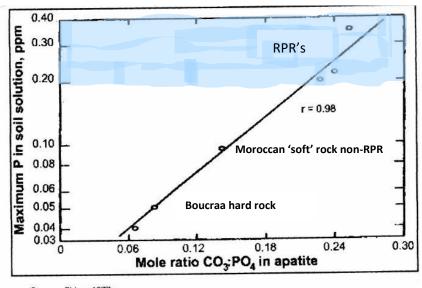


Figure 3: Use of phosphate rocks for sustainable agriculture

Source: Chien, 1977a.

This is a completely different issue from the presence of free lime or dolomite as a free or 'accessory' mineral in the deposit. The presence of these can reduce the solubility of RPRs in citric acid tests (regardless of having no adverse effect of field performance), by preferentially reacting with the citric acid, leaving less acid to dissolve P from the RP (Chien 1993).

P run-off losses with soluble P vs RPR

Dissolved Reactive P (DRP). The concentration of DRP in run-off is driven very largely by specific fertiliser applications and by the form of P applied. Many studies around the world, including several in New Zealand (eg McDowell and Catto 2005), have demonstrated the very high levels of DRP that can occur in the first 2 or 3 run-off events after application of soluble P (Fig.4). This simply reflects the very high levels of soluble fertiliser P in the near-surface soil water.

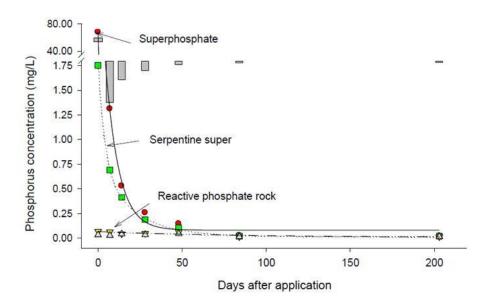


Figure 4. P concentrations in surface runoff: Water soluble P versus non water soluble P

Up to 10 kg P/ha can be lost in single run-off events (Table 1, Hart et al. 2004). These can occur even when the first run-off event does not occur until months after application, particularly if prior soil moisture levels have been too low for complete dissolution of fertiliser granules and the movement and sorption of the P. These losses do not occur to any significant extent with RPR (Tables 1 and 2; also McDowell et a.2003, Weatherley et al. 2004).

Despite the raft of evidence, that should have lead to RPR being strongly recommended for use in all sensitive catchments by independent soil fertility research scientists, the potential role of RPR has been inexplicably reduced in many more recent local publications; for example to its use on acid peat soils (Simmonds and McDowell 2016).

RPR's overall 'ranking' as a mitigation option was reduced to '0-20%' by McDowell and Nash (2012), lower than many of other mitigations listed, including flood irrigation management (almost non-existent now), sorbents in and near stream, dams and water recycling, applying alum and red mud to pasture etc pure clover swards in sensitive areas, not applying fertiliser P to 'hot-spots' etc. The only explanation given has been a 'lack of uptake of RPR. Disturbingly, this change took place as the superphosphate industry withdrew support for RPR in NZ.

Table 1. Phosphorus (P) losses from different land uses, related to P fertilizer application.

Land use	Pathway	Scale, type, measurement period		P loss		V-202	
			P sidded and form†	Dissolved	Total	Applied P lost	Reference, location
			k	g ha ⁻¹	%		
Grazed pasture	surface runoff	55-m2 plots,	0	0.91±	1.57		Sharpley and Syers (1976),
		4 mo	50 (SSP)	2.43±	4.64	6.1	New Zealand
Ungrazed pasture	surface runoff	41-m ² plots,	0	0.46‡	0.82		Sharpley and Syers (1976),
		4 mo	50 (SSP)	1.89‡	3.64	5.7	New Zealand
Ungrazed pasture	surface runoff	55-m ² plots,	0	0.47#\$	1.00\$		Sharpley and Syers (1979b)
		3 yr	50 (SSP)	2.1945	4.365	6.7	New Zealand
Retationally grazed	surface runoff	7.8- to 11.1-ha	0	0.02±	0.20		Olness et al. (1980), USA
pasture		catchments, 1 yr	75 (ammonium phosphate)	2.43‡	3.09	2.9	
Continuously grazed	surface runoff	7.8- to 11.1-ha	0	0.01‡	0.76		Olness et al. (1980), USA
pusture		catchments, 1 yr	75 (ammonium phosphate)	3.27‡	4.90	4.1	
Ungrazed pasture	surface runoff	41- to 55-m2	0	0.2881	0.875		Sharpley and Syers (1983),
		plots, 5 mo	50 (solid SSP)	1.7181	3.778	5.8	New Zealand
			50 (liquid SSP)	0.798¶	1.238	2.3	
Grazed hill country	surface and	0.1- to 1.5-ha	11	0.1081	0.95§	-	Lambert et al. (1985),
pusture	subsurface runoff	catchments, 1.5 to 4.5 yr	64 (SSP)	0.14§¶	0.945	172	New Zealand
Ungrazed pasture	surface runoff	240-m2 irrigation	0	- 6.00#	0.000		Austin et al. (1996),
	(first irrigation)	bays, 1 mo	22		6.60	30.0	Australia
			44	8.70#	9.70	22.0	
			66	11.40#	12.90	19.5	
			88 (SSP)	11.50#	11.90	13.5	
Grazed pasture	surface and	1-ha lysimeter	0	20000-20	0.001		Haygarth and Jarvis (1997).
	subsurface runoff	plots, 30 h	16 (TSP)	ores Sho	approx. 0.5	approx. 3	UK
Ungrazed pasture	surface runoff	150-m1 hillslope	0	0.09††	0.09		Heathwaite et al. (1998),
		plots, 1 wk	100 (DAP)	2.50††	3.80	3.8	UK
Grazed pasture	surface runoff	0.37-ha irrigation	0	6.0811	8.18		Bush and Austin (1999),
- 55		bays, 2 yr	44 (SSP)	20.7577	26.78	42	Australia
			44 (Prolong‡‡)	13,15++	17.78	22	
Ungrazed pasture	surface runoff	0.5-m1 hillslope	0	0.02††	0.04		Nguyen et al. (1999),
		plots, 7.5 mo	35 (SSP)	0.59++	0.64	1.8	New Zealand
			35 (TSP)	0.7711	0.84	2.4	
			35 (TSP-DAPR)	0.27	0.32	0.9	
			35 (DAPR)	0.0311	0.06	0.2	
Laboratory microcosm,	surface runoff	0.5-m ¹ sloped	0	0.00811	0.42		Nguyen et al. (2002),
sieved soil		plots, 1 mo	35 (SSP)	0.43011	1.12	2.0	New Zealand
	2.5		35 (DAPR)	0.017++	0.43	0.03	31 BROWN BROWN
Cultivated seedbed	surface runoff (first runoff	32-m² plots, 4 mo	0 90 (TSP)	0.008± 0.62±	0.04 0.67	0.7	Withers et al. (2001), UK
Andread Williams	event)	ne 3 - 1			0.00		B - 1 -1 -1 -2001)
Ungrazed pasture	subsurface and	30-m ² lysimeter	0	-	0.06	22	Preedy et al. (2001),
	surface runoff	plots, 1 wk	29 (TSP)		1.86	6.4	UK
Paddy soil under wheat	subsurface and	30-m² plots,	0	0.0311	0.25	0.7	Zhang et al. (2003),
	surface runoff	3 mo	20	0.04++	0.39		Anzhen, China
			80	0.1011	0.57	0.4	
		an all the	160 (N-P-K + SSP)	0.28††	0.82	0.4	71
Paddy soil under	subsurface and	30-m² plots,	0	0.0411	0.39	0.75	Zhang et al. (2003),
wheat	surface runoff	3 mo	20	0.1977	0.54	0.75	Changshu, China
			80	0.68††	1.36	1.2	
			160 (N-P-K + SSP)	0.94	1.94	1,2	

[†] DAP, diammonium phosphate; DAPR, direct-application phosphate rock; SSP, single superphosphate; TSP, triple superphosphate.
† Total dissolved phosphorus.
\$ Values shown are kg P ha⁻¹ yr⁻¹.

¶ Dissolved inorganic phosphorus.

Estimated dissolved reactive phosphorus.

† Prolong is a granulated mixture of SSP and North Carolina phosphate rock, with a soluble P content of approximately 55%,

However, as found in the studies by Nguyen et al. 1999, 2002 (Table 1), more detailed studies have demonstrated much reduced losses of both DRP and PP with RPR (Table 2, Hart et al. 2004).

Table 2. Cumulative mean dissolved reactive phosphorus (DRP) and particulate phosphorus (PP) in 60-min simulated runoff events from unfertilized and fertilized hillslope microplots, Whatawhata, New Zealand.

Treatment†	Day											
	3		10		32		110		232			
	DRP	PP	DRP	PP	DRP	PP	DRP	PP	DRP	PP		
	mg plot ⁻¹											
Control	0.13	0.17	0.24	0.52	0.37	0.84	0.68	1.01	0.83	1.16		
SSP	23.26	0.54	27.09	1.53	28.19	2.35	29.20	2.63	29.40	2.82		
TSP/S	33.82	1.05	37.13	2.62	37.89	3.27	38.45	3.43	38.65	3.60		
DAPR/TSP/S	10.48	0.52	12.09	1.43	12.51	1.99	13.17	2.23	13.38	2.43		
Gafsa/S	0.17	0.22	0.47	0.89	0.76	1.31	1.18	1.52	1.39	1.70		
Kosseir/S	0.23	0.33	0.45	1.02	0.75	1.42	1.13	1.58	1.29	1.73		

[†] Control, unfertilized; SSP, single superphosphate; TSP/S, triple superphosphate and elemental sulfur; DAPR/TSP/S, direct application phosphate rock blend plus triple superphosphate; Gafsa/S, Gafsa DAPR and elemental sulfur; Kosseir/S, Kosseir DAPR and elemental sulfur.

Discussion

The fact that application of unnecessary soluble P *in the first place* is the root cause of virtually all P loss is now not mentioned in published papers by scientists funded under the Mitigator project; nor is it in the 'public' version of Ballance's Mitigator® webpage.

Instead of promoting the one-step practical solution of switching from soluble P to RPR, which alone of all mitigations *saves the farmer money as well*, a raft of expensive and site-unproven 'remedies' that are costly for the farmer to install and maintain are presented. These remedies seem designed purely to 'justify' the continuing use of soluble P.

One excuse for scientists for not giving RPR far stronger promotion as a P loss mitigation is the results from one or two studies showing that while DRP losses are greatly reduced with RPR, particulate P losses are not. Despite DRP making up 30-70% of total P losses in most cases (Hart et al 2004), the attitude now appears to be 'why bother using RPR if particulate P losses are not reduced also?'

This 'logic' ignores the fact that virtually all particulate P loss comparisons between soluble P and RPR have been done on areas with a background of soluble P use only.

The nature and origin of soil particulate P and its susceptibility to run-off cannot hope to be accurately reflected, as far as RPR is concerned, by trials sites that have not had a history of RPR applications. This is a fundamental shortcoming of soluble P vs RPR research to date. Particulate P losses cannot be just assumed to be the same for both P sources, for the following reasons:

- (i) RPR particles are much denser (Bulk Density 1.65) than soluble P (BD 1.0-1.1), and are therefore far less prone to being carried off in run-off. This density difference also means that RPR particles 'sink' into the soil must faster, further reducing their susceptibility to run-off. As seen in Fig. 4, RPR is not capable of producing P concentrations in soil water much greater than 0.2 mg/L.
- (ii) Soluble P applications produce very much higher concentrations of weakly adsorbed 'Olsen' P near the soil surface, often much higher than in the standard 0-75mm sampling depth.
- (iii) Much (>25%) of this loosely-bound P in near-surface soil is easily desorbed when the soil particles enter a body of water, for simple equilibrium reasons, as demonstrated decades ago by Australian researchers (Barrow 1983 and others).

Conclusions

- There is overwhelming evidence that the use of RPR instead of soluble P would greatly reduce P leaching and the loss of soluble P in run-off events. These losses can occur for weeks and even months after soluble P application.
- The advantage of RPR seems very likely to apply to particulate P losses as well, in real situations where RPR has been used for a period of years.

- There needs to be a much greater focus on introducing P soil tests that are useful for both environmental management as well as productivity advice. The introduction of limits on the Olsen P to PR ratio, for example a ratio of 0.35, would have very considerable environmental benefits.
- Ways must be found to create a soil fertility research environment that is far more open
 to discussion and scrutiny than the current situation, where research topics, the
 publishing of trial data, and the availability of environmentally-protective products are
 under the almost total control of the management staff of the two superphosphatemanufacturing cooperatives.
- Research scientists who regard themselves as even slightly independent should be promoting what they talk about in private discussions with the industry, *viz.* that the most effective mitigation by far, and one that unlike all other mitigations actually saves the farmer money, is to change to using RPR.

References

- Barrow, N.J. (1983). A mechanistic model for describing the sorption and desorption of phosphate by soil. *J.Soil Sci.* 34(4).
- Chien, S.H. (1977). Thermodynamic considerations on the solubility of phosphate rock. *Soil Sci. 123*: 117-121.
- Chien, S,H. (1993). Solubility assessment of fertilizer containing phosphate rock. *Fert. Res.* 35: 93-99.
- Chien, S.H. (1977). Thermodynamic considerations on the solubility of phosphate rock. *Soil Sci. 123*: 117-121.
- Edis, R.B., Bramley, R.G.V., White, R.E., Wood, R.E. (2002). Desorption of phosphate from sugarcane soils into simulated natural waters. *Marine Freshwater Res.* 53:961-970.
- Hart, M.R., Quin, B.F., Nguyen, M-L. (2004). Phosphorus runoff from agricultural land and direct fertilizer effects: a review. *J. Environ. Qual. 33*: 1954-1972.
- McDowell, R.W., Monaghan, R.M., Carey, P.L. (2003). Potential phosphorus losses in overland flow from pastoral soils receiving long-term applications of either superphosphate or reactive phosphate rock. *NZJ Agric. Res.* 46: 329-337.
- McDowell, W., Catto, W. (2005). Alternative fertilisers and management to decrease incidental phosphorus loss. *Environ Chem Lett* 2: 169-174.
- McDowell, R.W., Nash, D. (2012). A review of the cost-effectiveness and suitability of mitigation strategies to prevent phosphorus loss from dairy farms in New Zealand and Australia. *J.Env. Qual.* 41: 680-693.
- Redding, M.R., Ghani, A., Kear, M., O'Connor, M., Catto, W. (2006). Phosphorus leaching from pastures can be an environmental risk and even a significant fertiliser expense. *Proc. NZ Grasslands Ass.* 68: 293-296.
- Sharpley, A.N. (1993). Assessing phosphorus bioavailability of phosphorus in agricultural soils and runoff. *Fert Res* 36: 1375-1384.

- Simmonds, B., McDowell, R.W., Condron, L.M., Cox, N. (2016). Can phosphorus fertilizers sparingly soluble in water decrease phosphorus leaching loss from an acid peat soil? *Soil Use andManagement, British Society of Soil Science*. doi: 10.1111/3um.12274. 7 pages.
- Weatherley, A.J., Quin, B.F., Dassanayake, K.B., Rowarth, J.S. (2011). Runoff losses from irrigated dairy pastures treated with phosphorus fertilisers of different solubility in southeastern Australia. *Soil Research* 49: 633-641.