

REVISITING THE WATKINSON DISSOLUTION TEST FOR PREDICTING PHOSPHATE RELEASE FROM DIRECT APPLICATION PHOSPHATE ROCK

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Abstract

Interest in New Zealand in direct application phosphate rock started in the 1980's when rock from a range of sources was available and evaluated. Ultimately the more reactive rocks, those from Sechura and North Carolina were favoured, and Reactive Phosphate Rock was defined as containing not less than 10 % P of which at least 30% is soluble in 2% citric acid. These guidelines are still valid although the flagship RPR's, Sechura and North Carolina, are no longer available with Sechura containing too high cadmium levels and export of North Carolina rock terminated for strategic reasons.

Since the availability of RPR meeting the 30% citric soluble P threshold is limited, the use of "RPR" terminology should be re-considered in favour of "direct application phosphate rock". Although there is a demand for unadulterated phosphate rock in the marketplace, none of the existing qualification criteria provides any indication on the amount of P that will become available over time. Back in 1994, John Watkinson developed a dissolution rate function (DRF) expressing the amount of P dissolved over time that can be used to describe the reactivity of phosphate rocks for direct application. In this model total P content, particle size distribution, density, mean diffusion coefficient based on soil and climatic properties and dissolution of P in a simulated soil solution are factors used to estimate the amount of P released per year.

In the absence of any other method it is suggested that the Watkinson model be used to describe the reactivity of direct application phosphate rock in parallel with the other existing defining parameters.

Introduction

Fertiliser subsidies for New Zealand farmers were terminated in the mid 1980's resulting in an urgent rush to find a cost-effective alternative to single superphosphate fertiliser. At the height of this effort up to 50% of the research budget for the Soil and Fertiliser group at Ruakura was spent on RPR related research. The first FLRC Workshop held in February 1987 was devoted to RPR and to a lesser degree acidulated phosphate rocks as substitutes for soluble phosphate fertilisers. During that period work was also initiated to accurately predict the quantity of phosphate that would become available over time from applied direct application phosphate rocks (DAPR) and at the 1995 workshop Dr JH Watkinson presented on modelling RPR

dissolution in soil (Watkinson, 1995). The dissolution rate function presented (Watkinson, 1994 & 1995) was complex and at a subsequent FLRC workshop a simplified version was presented by Perrott *et al.* (2000). Initial work on RPR resulted in Fertmark setting a chemical standard for RPR: they had to contain at least 10 % Total P of which 30% had to be soluble in 2% citric acid. These qualifying standards suited properties of the then imported Sechura RPR from Peru and it can be reasoned that Sechura was the gold standard used to set the standard.

Historical Total P and citric acid solubility data

Published data by New Zealand and Australian authors (Bolan *et al.*, 1987; Floate *et al.*, 1987; Hedley *et al.*, 1987; Lee & Watkinson, 1987; Mackay, 1990; Mackay *et al.*, 1987; Quin *et al.*, 1987; Rajan, 1987; Rajan *et al.*, 1987; Rajan *et al.*, 1992; Syers *et al.*, 1986; Simpson *et al.*, 1997; Sinclair *et al.*, 1990; Sinclair *et al.*, 1998; Watkinson, 1994) were compiled and grouped into three groups based on origin, viz. firstly, North Carolina (NC) and Sechura, secondly Egypt, Tunisia and Israel and thirdly, the rest of the products with the distinguishing property of not meeting the 30% citric acid solubility criterium. This data presented in Figure 1 show all products except those from Chatham Rise to pass the 10% Total P test. Predominantly the products from North Carolina and Sechura also met the 30% citric solubility criterium while the rest of the products fail this criterium. Products from Egypt, Israel and Tunisia, all countries from the south Mediterranean shores straddled the 30% citric acid solubility line indicating that this group may or may not make the current classification as reactive phosphate rocks.

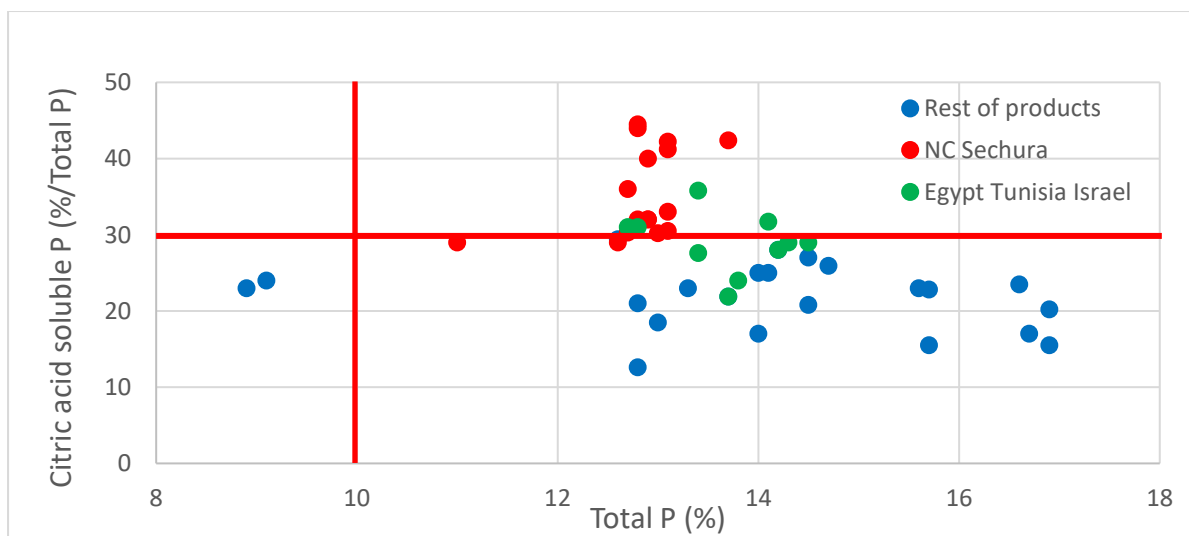


Figure 1. Citric acid soluble P and total P data for a range of direct application phosphate rocks published by New Zealand and Australian authors.

Sechura and North Carolina RPR

Both Sechura (Bech *et al.*, 2010) and North Carolina (McLaughlin *et al.*, 1997) contain levels of Cadmium making them exceed the voluntary standard for Cd in P fertilisers for the New Zealand market. Additionally, there is also a moratorium on export of phosphate rock from the USA based on strategic grounds considering the USA only holds 1.4 % of the world phosphate rock reserves (U.S. Geological Survey, 2020). Therefore, two of the more reactive direct application phosphate rocks are no longer available, with the focus shifting to products from the southern Mediterranean shores.

Refocus

Considering Sechura was the gold standard product according to which the Fertmark standards were set with currently available products not guaranteed to always meet the 30% citric solubility threshold, Doug Edmeades (2016) rightly commented, “The focus should be on the standard, and not the product which initially set the standard”.

Watkinson (1994, 1995) developed the dissolution rate function to predict the percentage of the total P that would be released per year and is backed by data from 90 field trials (Perrott *et al.*, 1996). This dissolution rate function has total P, particle size distribution, density, P solubility in a simulated soil solution and the mean dissolution coefficient of phosphate in soil based on pH, soil type, rainfall, drainage and exchangeable magnesium as inputs and % P released per year as output. In more detail:

$$DRF = 1 - e^{-\sum_{i=1}^n \left(w_i \left(1 - \frac{a}{b_i b_{i-1}} \right)^{\frac{3}{2}} \right)}$$

$$a = 8DmC_R/\rho F$$

Dm = mean diffusion coefficient of phosphate in the soil

C_R = phosphate concentration at the DAPR surface

ρ = density

F = Fractional P content of DAPR

b = sieve size range

w = weight fraction

Site and climatic factors are incorporated in D_m and their effects were determined through field trials and measurement of residual RPR in the soil (Perrott & Kerr, 1994). Significant correlations were found with soil type, pH, exchangeable Mg, rainfall and drainage (Perrott *et al.*, 1996). A range of D_m values were obtained ranging from 0- 0.71 cm² year⁻¹. These factors were incorporated into a model (Perrott and Metherell, 1997; Perrott, 2001) that calculated site D_m values from the inputted environmental data and incorporated the effect of fertilizer properties through the DRF. The RPR model predicts the rate of direct application phosphate rock dissolution into a labile soil P pool and its effect on pasture production over a number of years in comparison to soluble P fertilisers.

This dissolution rate function has never been implemented in its full extent, probably as a result of having highly reactive phosphate rock commercially available. Implementation of the laboratory test for C_R and the dissolution function has the potential to add valuable information regarding reactivity and ultimately the predicted amount of P that can be released during the first year after application. Having this information available can assist end users in making sound commercial decisions.

In the process of establishing DRF as a routine laboratory test, as many as possible different direct application phosphate rock products were obtained through collaboration with other laboratories. These products were analysed for all the different parameters required to model the dissolution rate.

In the relationship between citric acid solubility and the modelled dissolution rate (Figure 2) there is a clear distinction between the Sechura products and the rest including a sample of North Carolina rock. This separation between the groups is also more pronounced than in the relationship between citric acid solubility and total P content (Figure 1).

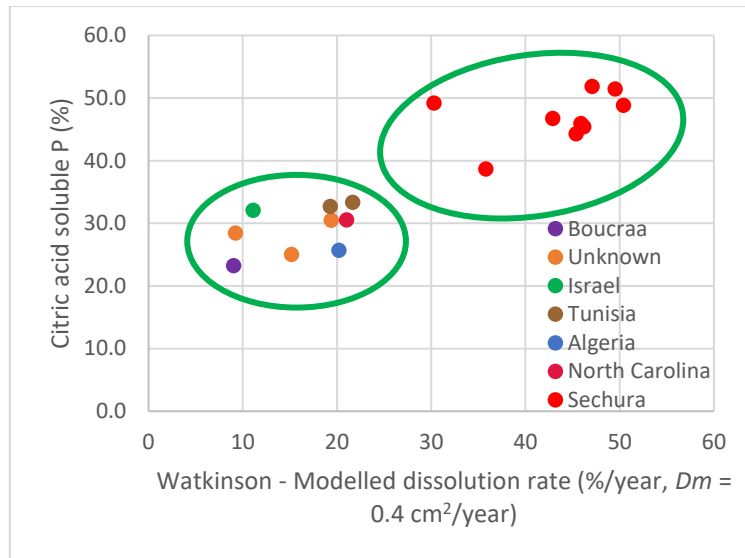


Figure 2. Relationship between the Watkinson modelled P dissolution rate (*DRF*) and citric acid soluble P % for a range of direct application phosphate rocks. *Dm* was chosen as 0.4 cm² year⁻¹.

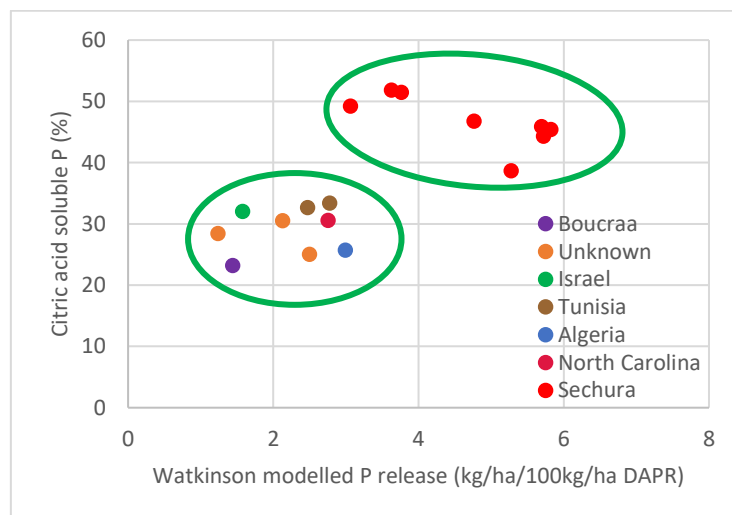


Figure 3. Relationship between the Watkinson modelled P release from DAPR applied at a rate of 100 kg/ha and citric acid soluble P % for a range of direct application phosphate rocks. *Dm* was chosen as 0.4 cm² year⁻¹.

From a customer perspective the quantity of P that can be expected to become available over a year rather than the percentage of total P content that will become available may be more

appropriate. Therefore, the amount of P released from 100 kg/ha direct applied phosphate rock for these samples were calculated for a theoretical site with $D_m = 0.4 \text{ cm}^2 \text{ year}^{-1}$, representing favourable soil and climatic conditions (Figure 3). Sechura still outperformed the other products but an important observation is that despite some products having citric acid solubility values below 30% they outperformed products with greater than 30% citric acid solubility indicating that the *DRF* can discriminate sufficiently between products based on modelled reactivity.

C_R measurement

Of all the parameters utilised in *DRF* it is only C_R measured as the P solubility in a simulated soil solution that is a new laboratory test that needs to be implemented. This test involves 0.5g DAPR to be impeller stirred for 30 minutes in a 250 ml solution while keeping the pH at 5.5 by adding 0.1 M HCl. The simulated soil solution consists of sodium chloride (0.7305g), anhydrous sodium acetate (0.4103g), 100 mmol/L calcium chloride solution (25ml) added to 4.8 L of water, adjusted to pH5.5 with acetic acid and made up to 5L.

From the limited number of DAPR samples tested the uncertainty of measurement was calculated to be $\pm 0.6 \text{ mg/L P}$. Limiting the parameters to that typical of products from Tunisia, Israel, and Algeria, three fictitious products with total P of 13.5%, three arbitrary chosen particle size groups, fine, medium and coarse, the P release over dissolution rate (C_R) values 2.5-5 mg/L P were calculated (Figure 4). The difference in *DRF* over an C_R range of 3 to 4.2 mg/L P, the uncertainty of measurement range for a value of 3.6 mg/L P, varies between 2.5 and 8.1 % P for the coarse and fine fictitious products respectively, or 0.3 to 1.1 kg/ha P per year for each 100kg/ha DAPR applied.

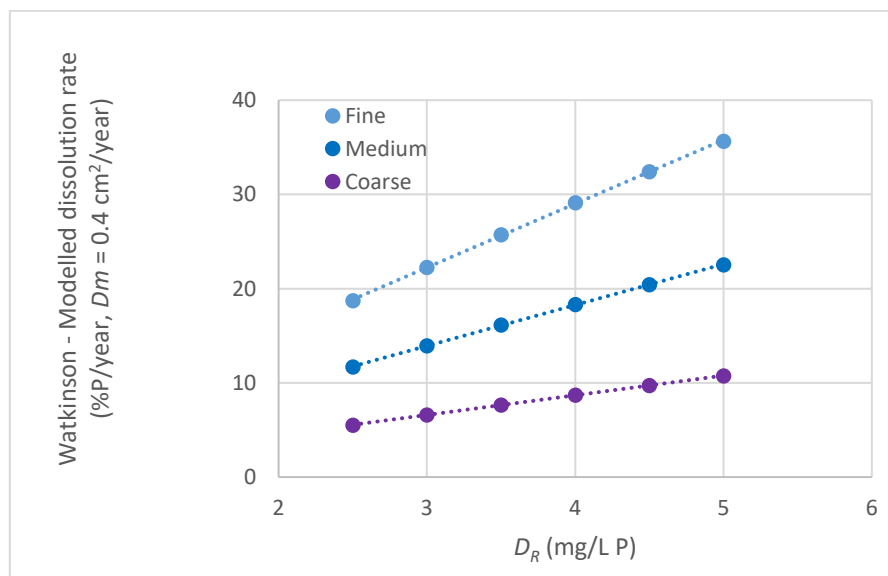


Figure 4. Sensitivity analysis illustrating the effect of C_R on *DRF* for three hypothetical DAPR products with total P 13.5% and a selection of fine, medium and coarse particle sizes.

The products from Israel and Tunisia have *DRF* values differing with 4.4 and 4.8 %P over the uncertainty of measurement range, equating to 0.6 kg/ha P released for both products per 100

kg/ha DAPR applied. Considering the potential range of DAPR products available it can be deduced that the reactivity range is limited, and that citric acid solubility and total P are inferior parameters for predicting DAPR reactivity, especially from a customer perspective. Despite the additional C_R measurement involved in the Watkinson dissolution rate function the implementation of this measure of reactivity will empower customers to make better informed decisions around DAPR.

Summary and suggestions

- The gold standard product that defined the RPR definition is no longer available.
- Products available may or may not fail the citric acid criterium. Over time the DAPR landscape has changed with the 30% citric solubility standard becoming misaligned with products currently available.
- Either the definition must change or the name RPR must be replaced by DAPR. To prevent confusion, it would be advantageous to change the definition and the name.
- To enable customers to make informed decisions the modelled P release according to the Watkinson dissolution function should be used for comparing products.

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