

A test for phosphate rock reactivity in which solubility and size are combined in a dissolution rate function

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Abstract

A test for phosphate rock (PR) reactivity has been developed based on a representation of certain fundamental properties of the rocks designated the Dissolution Rate Function. The function and properties have been shown to be those important in models of the dissolution rate of PRs in soil. The properties are size or mass distribution with size, solubility product, P content and particle density. In practice the solubility product is measured in terms of the P concentration attained in a standard solution, simulating that in an average soil with respect to pH, Ca and ionic strength.

The test compares favourably with those using citric and formic acids, using published results for the relative agronomic effectiveness of 11 PRs, both unground and ground. The agronomic data also indicated that particle sizes < 0.15 mm can be regarded as equivalent to the size range of 0.10 to 0.15 mm.

Introduction

With the development of mechanistic models for the dissolution rate of phosphate rock (PR) in soil (Kirk and Nye, 1986a, b; Watkinson, 1994a), it is now appropriate to develop from these a laboratory test for estimating the relative rates of PR dissolution in soil based on the fundamental PR properties which are involved (Sinclair *et al.*, 1992). These properties are: initial diameter(s), solubility product, density and P content of the particles (Kirk and Nye, 1986a, b; Watkinson, 1994a). Since the rate-determining process in the dissolution models is diffusion of dissolved material from the particle surface into the bulk soil, the concentration gradient at the surface is critical, and this is determined largely by the PR solubility product (Kirk and Nye, 1986a, b; Watkinson, 1994a). In New Zealand pastoral soils, the concentration in bulk soil of calcium is several hundred times greater than that of phosphate (Edmeades *et al.*, 1985), so the gradient is controlled more by the phosphate (Watkinson, 1994a). In addition, the total diffusive flux depends on the surface area per unit mass of PR applied to soil, and hence

on the size of particles, or the size distribution if the PR mass comprises a range of sizes (Kirk and Nye, 1986a, b; Watkinson, 1994a). The P content is of some importance because, for example, with smaller values a greater mass of PR must dissolve to produce a given surface concentration of phosphate. The property of least importance is the particle density because it is virtually the same for all PRs at 3.2 g cm^{-3} .

Plant uptake of P has previously been shown to be related to a fundamental crystal property, the unit-cell a (Å) dimension of carbonate apatites (Anderson *et al.*, 1985), which is related to the degree of carbonate substitution, z , (McLellan, 1978) by $a = 9.374 - 0.024z/(6 - z)$. However, this probably arises through their common relationship with the solubility product (Chien and Black, 1976; Kirk and Nye, 1986a).

The current empirical tests for PRs involve dissolution into one of several organic acid or salt solutions (Sinclair *et al.*, 1992). They are conducted under strictly-controlled conditions of concentration, solution ratio, temperature, time and mode of shaking; and attempt to integrate the effects of the two most important properties of particle size and solubility (Rajan *et*

et al., 1992). The conditions must avoid excessive dissolution of the smallest particles, and also the generation of large concentrations of dissolved material. The first effect would accentuate the PR solubility at the expense of size, while the second would inhibit further dissolution. On the other hand, sufficient material must dissolve to permit ranking of the individual PRs, and a large spread of results is seen as an advantage (Rajan *et al.*, 1992). (Acid extractants are partially neutralized by, and give low results for PRs high in carbonate (Sinclair *et al.*, 1992)). An alternative approach would be to measure size and solubility separately as fundamental characteristics, and integrate their effect using the dissolution models (Sinclair *et al.*, 1992).

Particle size distribution

There is general acceptance of dry sieve analysis as the method for measuring mass distribution with size. The use of standard sieves with sizes of 2, 1, 0.5, 0.25, 0.15, 0.075 and 0.038 mm has been found satisfactory (Rajan *et al.*, 1992). Any material outside these limits would be either too dusty to handle, or too large for consideration as a direct application fertilizer.

It is implicit in the sieve method that the distribution of mass with size can be assigned a mean value within each fraction. This assumption was satisfactory for modelling the oxidation of elemental sulfur using similar equations (Watkinson, 1989, 1993). Other properties assumed constant or represented by a mean value within each fraction are the solubility product, P content, and the particle density, as discussed earlier.

Solubility product

The solubility has been measured directly, after first extracting alkaline-earth carbonates with alkaline ammonium citrate (Smith and Lehr, 1966), by equilibrating 1g of solid with 100 ml of dilute hydrochloric acid solutions (pH 4 to 6) for 30 days at 25°C (Chien and Black, 1975, 1976).

If the fraction of carbonate substitution, z , has been measured or calculated from the unit cell a dimension, the solubility product (K_{CA}) may be estimated from the regression (Kirk and Nye, 1986a), $pK_{CA} = 122.2 - 6.3z$, based on the data of Chien and Black (1976).

Possible applications

For the same PR (ie same solubility) ground to different sizes, the products could be ranked agronomically

(Kirk and Nye, 1986b) simply on their size (Rajan *et al.*, 1992). For different PRs ground to the same size, ranking could be made using their solubility products, or some estimate of them such as their unit cell a dimensions (Anderson *et al.*, 1985). These measurements are time consuming and expensive. However, the real difficulty is in providing a means of combining the properties of size, solubility, and P content in a single test property (Chien, 1993) for ease of ranking PRs in order of agronomic importance. This question is addressed in the next section.

Theoretical

Combination of RPR properties for ranking from dissolution rate models

As a general rule, the agronomic effectiveness of a reactive phosphate rock (RPR) will be governed by the rate of dissolution of the mineral phosphate. This is borne out by the success of the empirical dissolution tests. They combine the effects of surface area, solubility and P content, into a single test value based on the total amount of phosphate dissolved by the extractant under standardized conditions as a fraction of the total P content of the RPR (Rajan *et al.*, 1992). Hence it is appropriate to use as a test function the combination of fundamental RPR properties as they appear in the dissolution rate constant of the mechanistic models for dissolution in soil. Since the Watkinson model (Watkinson, 1994a) contains an explicit rate constant, and gives the same results as the Kirk and Nye model (Kirk and Nye, 1986a, b) under conditions appropriate to New Zealand pastoral soils (Watkinson, 1994a), it is appropriate to take this rate constant for the development of a test function. From Watkinson (1994a) the dissolution rate equation for particles of the same initial radius, r_0 , is given as,

$$(m/m_0)^{2/3} = 1 - 2Gt \quad (1)$$

Where m/m_0 is the undissolved fraction of RPR in the soil at time t ,

and G is the dissolution rate constant, which is the product of soil (G_S) and RPR (G_{RPR}) factors,

$$\begin{aligned} \text{i.e. } G &= [G_S][G_{RPR}] \\ &= [D_m][(\Delta C/F)/(\rho r_0^2)] \\ &= D_m(C_R/F)/(\rho r_0^2) \end{aligned} \quad (2)$$

Where	D_m	is the mean diffusion coefficient for phosphate in the soil (the soil property)
	ΔC	is the difference in phosphate concentration between that at the RPR surface, C_R , and that in bulk soil, C_S ; and is approximately C_R since $C_R \gg C_S$.
	ρ	is the RPR particle density, approximately 3.2 g cm^{-3} .
	r_0	is the initial radius of RPR particles, considered as "equivalent spheres" (Watkinson, 1989).
	F	is the fractional P content of the RPR.

The ratio of C_R/F is the factor from the chemical properties of the RPR, while $1/(\rho r_0^2)$ is the factor from physical properties. Hence, for RPRs of the same size, C_R/F can be used for ranking; while for a single RPR having different sizes, $1/r_0^2$ can be used for ranking. (Note that r_0^2 , which is proportional to the initial surface area, rather than r_0 , is the ranking parameter).

Comparing RPRs of a mixture of sizes is handled as follows: Firstly, a dissolution rate equation based on Equation 1 for a range of sizes is taken from Watkinson (1994b), to calculate m/m_0 at t using a standard value for D_m , eg the average for several representative New Zealand soils. From measured values of C_R , F , ρ , the dissolution rate constant, a , can be calculated, since $a \approx 8 D_m (C_R/F)/\rho$ (Watkinson, 1994b). It can be considered the equivalent diffusion coefficient for the dissolution of the particular RPR in the particular soil (Watkinson, 1994b). The dissolution rate for each sieve fraction can then be calculated using the dissolution rate equation (Watkinson, 1994b). Finally, the overall dissolution rate is derived from the sum of dissolved RPR from all sieve fractions. The amount of phosphate dissolved by different RPRs in a given time, eg one year, can then be compared. Or, the times taken by different RPRs to dissolve a given percentage, e.g. 90%, can be compared.

Dissolution rate of a mixture of particle sizes in soil

The dissolution rate in soil of equivalent spheres of RPR particles of the same size (Eq. 1), with rate constant equal to "a", has been extended to a mixture of different sizes (Watkinson, 1994b). Suppose a sieve analysis of a mixture gives n successive sieve fractions,

each of size range b_{i-1} to b_i and of weight fraction w_i , where $\sum_{i=1}^n w_i = 1$, and the mixture is added to a soil. The total mass of undissolved RPR at a given time will then be the sum of the undissolved mass of the fractions. The undissolved RPR is given by several equations, each covering a different time interval relating to the dissolution of specified particle sizes (Watkinson, 1994b). The first of these equations covers the period for the finest particles, b_0 , to dissolve. The next period and equation cover the time between dissolution of the finest and coarsest particles in the finest size fraction. This is followed by the equation and time between dissolution of the next smallest sieve fraction, and so on in turn until the coarsest fraction is dissolved. The following equations apply (Watkinson, 1994b):

1. Time interval for dissolving the smallest particles, b_0 , $0 \leq t \leq b_0^2/a$

$$m/m_0 = \sum_{i=1}^n w_i [(2 + at/b_i^2)(b_i^2 - at)^{1/2} - (2 + at/b_{i-1}^2)(b_{i-1}^2 - at)^{1/2} + (3\sqrt{at})(\sin^{-1}(\sqrt{at}/b_i) - \sin^{-1}(\sqrt{at}/b_{i-1}))]/2(b_i - b_{i-1}) \quad (3)$$

2. Time interval between dissolution of smallest, b_0 , and largest particles, b_1 , in the smallest fraction, $b_0^2/a \leq t \leq b_1^2/a$

$$m/m_0 = w_1 [(2 + at/b_1^2)(b_1^2 - at)^{1/2} + (3\sqrt{at})(\sin^{-1}(\sqrt{at}/b_1) - \pi/2)]/2(b_1 - b_0) + \sum_{i=2}^n w_i [(2 + at/b_i^2)(b_i^2 - at)^{1/2} - (2 + at/b_{i-1}^2)(b_{i-1}^2 - at)^{1/2} + (3\sqrt{at})(\sin^{-1}(\sqrt{at}/b_i) - \sin^{-1}(\sqrt{at}/b_{i-1}))]/2(b_i - b_{i-1}) \quad (4)$$

And so on, as the remaining finest fraction dissolves successively.

3. Time interval between dissolution of smallest, b_{n-1} , and largest particles, b_n , in the coarsest fraction, $b_{n-1}^2/a \leq t \leq b_n^2/a$

$$m/m_0 = w_n [(2 + at/b_n^2)(b_n^2 - at)^{1/2} + (3\sqrt{at})(\sin^{-1}(\sqrt{at}/b_n) - \pi/2)]/2(b_n - b_{n-1}) \quad (5)$$

Note that the angles are measured in radians.

Dissolution Rate Function

Summations in the form of Equations 3, 4 and 5 can be used to define the dissolution rates, under standard conditions, of different RPRs having a mixture of sizes. In this case the fraction dissolved after time, t , is defined as the Dissolution Rate Function or DRF, where $DRF = 1 - m/m_0$. If the RPR has measured values of C_R , F , ρ and particle size distribution as above, and D_m is the mean phosphate diffusion coefficient for several soils (Eq. 2), then $a = 8 D_m (C_R / F) / \rho$. DRF can then be calculated for each successive time interval. If the fractions dissolved after one year are to be compared, then only the value of DRF where $b_{i-1}^2/a \leq t \leq b_i^2/a$ needs be calculated.

To test the foregoing theory, DRF values for RPRs having a range of reactivities were compared with published values (Rajan *et al.*, 1992) for both their agronomic performance in pot experiments, and for their solubility in organic acids. Measured values of solubility (C_R) and published values (Rajan *et al.*, 1992) for P content (F) and size distribution were used to calculate the DRF values.

Materials and methods

PR samples

A range of PRs was investigated. They included a set of PRs whose dissolution rate in field soil had been measured (Rajan, 1987; Watkinson, 1994a); and another set which had been assessed for their relative agronomic effectiveness (RAE) in a greenhouse study using three soils and the test plant ryegrass (*Lolium perenne*) (Rajan *et al.*, 1992). For the latter samples, the total P, reactivity by citric and formic acids, and the mass particle size distribution had been measured (Rajan *et al.*, 1992). The unground rock had been dry sieved at sieve sizes of 0.075, 0.15, 0.25, 0.5, 1 and 2mm; while the ground rock had been sized by laser diffraction (Malvern Particle Sizer) (Rajan *et al.*, 1992).

Measurement of PR chemical properties

(1) Total P content

Where required, total P (F) was measured by the AOAC method (AOAC, 1980; Rajan *et al.*, 1992).

(2) Solubility

Test solution To provide dissolution conditions for obtaining an estimate for C_R in Equation 2 (Watkinson, 1994a) and approximating those in New Zealand pastoral soils, the RPRs were suspended in a solution of ionic strength 5 mM and calcium concentration of 0.5 mM (Edmeades *et al.*, 1985). Phosphate was not included because its concentration is <0.01 mM in soil solution (Edmeades *et al.*, 1985). The pH was held constant at 5.5 by automatically neutralizing the alkali from hydrolysis of the dissolving lattice PO_4^{3-} and CO_3^{2-} . Too high a pH would increase measurement errors because of the low concentrations at decreased solubility, while at pH < 4 the solubility product was found less stable (Chien and Black, 1976). (The relative solubility values for RPRs do not seem to change within a pH range of at least 5 to 6.5). A low concentration, 1 mM acetate buffer at pH 5.5 was included to ensure the pH was kept constant immediately following addition of RPR. Acetate is only a weak chelating agent for Ca^{2+} , and did not give results any different from the non-chelating but more expensive biological buffer, MES (2-(N-Morpholino)ethanesulfonic acid, $pK_a=6.1$).

To determine the effect of the calcium concentration in soil solution (Edmeades *et al.*, 1985) on the concentration of phosphate from the RPR dissolution, calcium was replaced with sodium in the test solution, keeping the initial ionic strength at 5 mM.

Procedure The RPR was added to the stirred test solution at a ratio of 1:500 (0.5 g to 250 ml). (This high ratio was used to ensure secondary reactions were negligible (Smith *et al.*, 1974).) The pH was held constant at pH 5.5 (or sometimes 5.0) using an automatic titrator (Mettler model DL25) in the pH stat mode. The phosphate (by the Murphy-Riley method (Murphy and Riley, 1962)) and calcium (by atomic absorption) concentrations increased rapidly. The rate was consistent with control by Nernst film diffusion at the particle surface (Helfferich, 1962), with the phosphate reaching a relatively steady value after two to three hours. This value is taken as representing the equilibrium value at the RPR surface (i.e. C_R). Calcium continued to increase slowly as a result of continuing calcite dissolution at pH 5.5.

RPR test functions

(1) RPRs of the same size, and C_R/F

As shown in Equation 2, for RPRs of the same particle density, ρ , and radius, r_0 , the RPR chemical component of the dissolution rate constant is measured as the ratio C_R/F , where C_R is the value measured in the test solution.

(2) RPRs of different size ranges, and the Dissolution Rate Function

For the PR samples investigated by Rajan *et al.* (1992), the values for C_R were determined from the dissolution test and then combined with the values for total P and particle size distribution (Rajan *et al.*, 1992) using the Dissolution Rate Function.

Results and discussion

RPR dissolution rate constant (G) in field soil, and solubility (C_R/F)

From Equations 1 and 2, the dissolution rate constant, G , for an RPR of initial particle size, r_0 , is directly related to $(1/\rho r_0^2)(C_R/F)$. Equation 1 has been fitted (Watkinson, 1994a) to data from the dissolution of three PRs, Chatham Rise, Florida, and North Carolina (Rajan, 1987) (the only data available), so that values for G can be calculated. Values for C_R were measured (in this case pH 5.0), so that with published values for F (Table 1) (Rajan, 1987), the ratio C_R/F can be calculated. Figure 1 shows the data relating G and C_R/F for the three PRs. The values for North Carolina and Florida are consistent with Equations 1 and 2 for RPRs of the same size, since a line through them passes through the origin. Although the three rocks were ground to approximately the same size (88% passed a 150 μm sieve (Rajan, 1987)), the Chatham Rise is probably smaller since its hard nodules grind more rapidly into a powder. If most of the Florida and North Carolina is estimated to be in the size range 75 to 150 μm (geometric mean 106 μm), then the size for Chatham Rise would be smaller at, say, 38 to 150 μm (geometric mean 75 μm). The value of G for Chatham Rise, 0.162 year^{-1} , would then be adjusted (Equation 2) by the size factor $75^2/106^2 = 0.5$ to 0.08 year^{-1} , as shown in Figure 1. However, it is evident that more data are needed, and particle size measurements would need to be made in any future work.

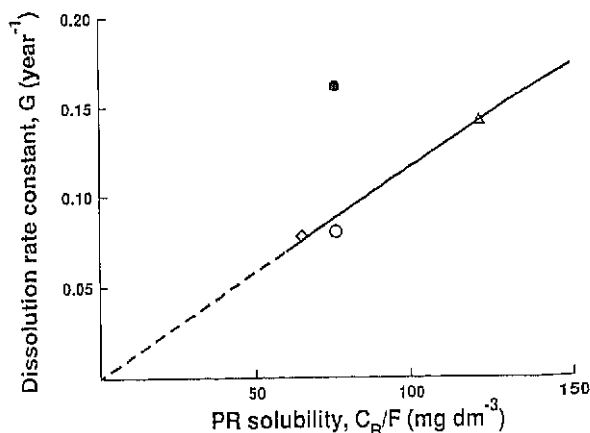


Fig. 1. Comparison of PR solubility, C_R/F , with dissolution rate constants in field soil for Florida (◇), Chatham Rise (●) (and corrected for size, ○), and North Carolina (△) (Rajan, 1987; Watkinson, 1994a).

RAEs for PRs of the same size, and solubility (C_R/F)

The RAEs of RPRs in the same soil depend largely on the amount of PR phosphate dissolved in soil (Rajan, 1987). The latter can be estimated by the amount of phosphate dissolved in an organic acid extraction test (Rajan *et al.*, 1992). Alternatively, the phosphate dissolved can be measured in terms of the dissolution rate constant G which, for RPRs of the same initial size, is proportional to C_R/F (previous section). Rajan *et al.* (1992) have published RAE values for 11 PRs, unground and ground, using ryegrass as the test plant, averaged over three soils. The ground PRs had a similar initial size (Rajan *et al.*, 1992), as also had the unground PRs, except for Nauru. The values for their P concentration (C_R) in the test solution, and C_R/F are listed in Table 1. Figures 2a and b show the relationship between RAE and C_R/F for all the 11 ground, and unground PRs (9 francolites and 2 fluorapatites) used by Rajan *et al.*, (1992), with and without added Ca (0.5 mM) in the test solution. The smaller size of the ground PRs results in the RAEs averaging about 40% greater values than the unground (Rajan *et al.*, 1992). The much larger size of the Nauru PR particles in the set of unground PRs shows itself as a lower RAE for the measured C_R/F compared with the other PRs. When ground to the same size as the other PRs in the ground set, the deviation is less. While added Ca lowers the P in solution and hence C_R/F , it does not have a major effect on the coefficient of determination of the relationship. On adding Ca, r^2 increases from 0.82

Table 1. Concentration of P (C_R) in the test solution (0.5 mM Ca, 5 mM ionic strength, pH 5.5) from the phosphate rocks investigated by Rajan *et al.* (1992), and their total P (F) (Rajan *et al.*, 1992)

Phosphate rock	C_R (mg dm ⁻³)	Total P (%)	C_R/F (mg dm ⁻³)
<i>Francolites</i>			
Sechura (OH substitution for F)	5.5	13.1	42.0
North Carolina	4.4	13.0	33.8
Gafsa	4.1	12.8	32.0
Khouribga	3.0	14.5	20.7
Youssoufia	2.7	13.4	20.2
Jordan	2.7	14.1	19.1
Arad	2.2	14.3	15.4
Zin	1.9	13.8	13.8
Mexico	1.3	12.8	10.2
<i>Fluorapatites</i>			
Nauru	1.8	16.7	10.8
Florida	0.6	14.0	4.3

to 0.91 for unground PRs, but decreases from 0.90 to 0.87 for ground PRs.

RAE and DRF for PRs with a range of sizes

For PRs with a range of sizes their RAE values can be related to the Dissolution Rate Function. In addition to values for RAE and F, Rajan *et al.* (1992) also published data on the particle size distribution (mass w_i for the sieve fraction b_{i-1} to b_i) (before and after grinding) of the 11 PRs studied. This permits comparison of RAE and DRF values. The solubility factor (C_R/F) for each PR is contained in the dissolution rate constant, a , which equals $8 D_m (C_R/F) / \rho$; while the size component is expressed directly as the particle size distribution.

(1) Unground PRs

From values for the 11 PRs for RAE, F, w_i , b_i in Rajan *et al.*, (1992), and C_R from this paper, the DRF can be calculated on arbitrarily setting $D_m = 0.5 \text{ cm}^2 \text{ year}^{-1}$ ($1.6 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$), a realistic value for the mean diffusion coefficient of phosphate in soil (Watkinson, 1994a). In Figure 3, the values for DRF at $t = 1$ year, the amount of PR that would be dissolved after one year in a soil with $D_m = 0.5 \text{ cm}^2 \text{ year}^{-1}$, is plotted against the corresponding RAE value (Rajan *et al.*, 1992) for each PR. Fitting a linear regression gives $r^2 = 0.90$ for

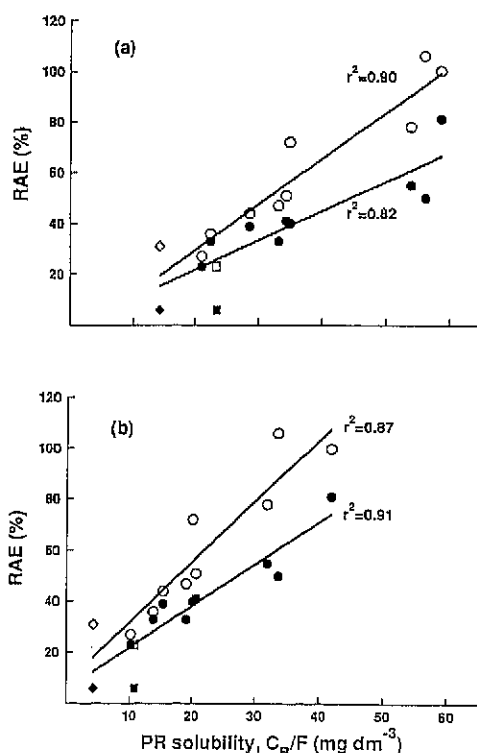


Fig. 2. Comparison of PR solubility, C_R/F (pH 5.5), with RAE values for 11 PRs, ground (\circ) (Florida, \diamond , Nauru, \square) and unground (\bullet) (Florida, \blacklozenge , Nauru, \blacksquare) (Rajan *et al.*, 1992) in the absence of Ca (a) $\text{Ca} = 0 \text{ mM}$, and its presence (b) $\text{Ca} = 0.5 \text{ mM}$

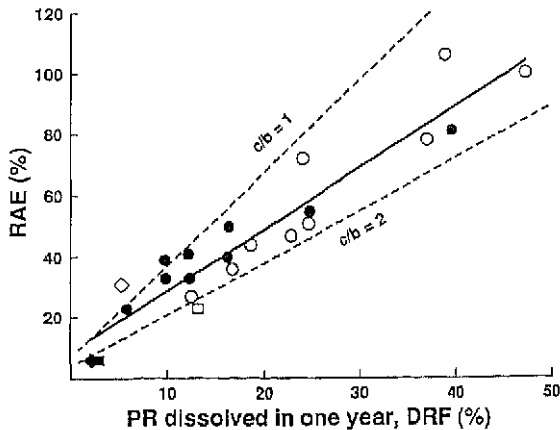


Fig. 3. Regression ($r^2=0.89$) of PR dissolution in one year calculated by the DRF, with RAE values for 11 PRs covering a wide range of sizes (Rajan *et al.*, 1992), both unground (francolites, ●; Florida, ◆, Nauru, ■) and ground (francolites, ○; Florida, ◇, Nauru, □). Ground PRs are treated as having the narrow range of sizes $b=0.10$ to $c=0.15$ mm ($c/b=1.5$). Regressions only are shown (---) for ground PRs of the same size, 0.15 mm ($c/b=1$), and of the wider size range $b=0.075$ to $c=0.15$ mm ($c/b=2$). $D_m = 0.5$ cm² year⁻¹, C_R/F in 0.5 mM Ca.

the 11 PRs ($r^2 = 0.94$ for the 9 francolites). Since the DRF takes into account particle size, the larger sized Nauru PR is no longer the anomaly that was evident when comparing RAE with C_R/F in Figure 2.

(2) Ground PRs

Rajan *et al.* (1992) also ground the PRs to < 0.15 mm. Unfortunately there is uncertainty for the ground material with respect to both the particle size, and also the relationship between particle size and RAE. Although the size distribution for all ground PRs was similar and values were given, the sizes were determined using laser diffraction, but the correlation with sizing by dry sieve analysis was not given (Rajan *et al.*, 1992). More importantly, however, the relationship between RAE and PR particle size breaks down at sizes less than about 0.15 mm, since finer particles do not give increased plant growth (Hagin and Harrison, 1993; Khasawneh and Doll, 1978). It can be assumed therefore that the particles act as if their size was just below 0.15 mm in their relationship with RAE, since the good regression shown in Figure 2 for ground PRs shows that they act as if they were of similar size. Treating the ground PRs as having a uniform size of 0.15 mm gives a regression *above*, while a size range of 0.075 to 0.15 mm gives a regression *below* that for the unground PRs (Fig. 3). That is, the equivalent size

of the ground PRs in relation to RAE is < 0.15 mm, but > 0.075 mm. Taking the intermediate size range of 0.10 to 0.15 mm and combining the data with that for unground PRs gives a regression with $r^2 = 0.89$ ($n = 22$). Even the less likely size range of 0.075 to 0.15 mm gives $r^2=0.87$. These are similar to the value of 0.87 for the relation between RAE and P extractable into formic acid (Rajan *et al.*, 1992), which was considered by Rajan *et al.* (1992) to be superior to the citric extractable P relation ($r^2 = 0.83$).

In the light of this discussion, the size range < 0.15 mm is treated as having the size range 0.10 to 0.15 mm.

Comparison of C_R/F , and DRF with acid-extractable P

Figures 4a and b, and Table 2 show the relationship between acid extractable P (Rajan *et al.*, 1992) and C_R/F , DRF, respectively.

The acids extracted more P from the ground PRs (Rajan *et al.*, 1992) at a given value of C_R/F than the unground (Fig. 4a). The DRF takes size into account so that in Figure 4 b the ground and unground samples become one population, including the previously anomalous unground Nauru PR with its much larger particle size. One curious exception is that formic acid extracts only as much P from the two fluorapatites as citric acid (Rajan *et al.*, 1992). In contrast, formic acid extracts significantly more P from the francolites than citric (Rajan *et al.*, 1992). (Reanalysis of the Florida and Nauru PRs confirmed that for each PR their citric-P and formic-P values were not significantly different. This difference in P extracted by the two acids could be the basis of a possible test to discriminate between the two types of PR).

Conclusions

A Dissolution Rate Function (DRF) has been developed for assessing the relative agronomic performance of Reactive Phosphate Rocks (RPRs) based on certain of their fundamental properties, in contrast to current empirical tests based on quantities extracted into an organic acid or salt solution. The fundamental properties utilised of solubility, size distribution, total P content, and particle density have been shown to be those of importance in mechanistic models of RPR dissolution in soil (Kirk and Nye, 1986a, b; Watkinson, 1994a, b). The way in which the properties are combined in the

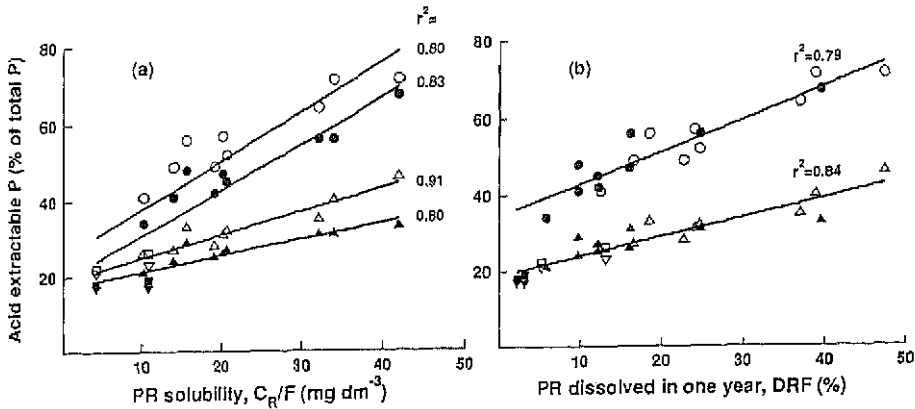


Fig. 4. Relationship between acid extractable P (Rajan *et al.*, 1992) for the 11 PRs and (a) C_R/F . For unground PRs, if Nauru is excluded $r^2=0.83$ (citric-P), $r^2=0.88$ (formic-P) and (b) PR dissolved in one year from the DRF. If fluorapatites are excluded, $r^2=0.87$ (formic-P).

	Citric-P		Formic-P	
	Unground	Ground	Unground	Ground
Francolites	▲	△	●	○
Fluorapatites	▼	▽	■	□

Table 2. Coefficient of determination (r^2) between acid extractable P (Rajan *et al.* 1992), and C_R/F , DRF (Fig. 4 (a), (b)) for the 11 phosphate rocks (Table 1).

Extractant	C_R/F		DRF
	Ground	Unground	Ground and Unground
Citric acid	0.91	0.80 (0.83 ^a)	0.84
Formic acid	0.80	0.83 (0.88 ^a)	0.79 (0.87 ^b)

^a Nauru PR excluded.

^b Fluorapatites excluded.

DRF is also derived from the dissolution rate equation of a mechanistic model (Watkinson 1994a, b). Values generated by the DRF correlate well with published data (Rajan *et al.*, 1992) for plant growth rate in three soils in a greenhouse study. The correlation with Relative Agronomic Effectiveness ($r^2 = 0.89$) is at least as good as that using the formic acid test ($r^2 = 0.87$) proposed by Rajan *et al.* (1992).

Advantages of the DRF over acid extractants are that it is based on fundamental PR properties; has a wider spread of values (the ratio of greatest to least is 30, whereas that for formic and citric acid test values is only 3.9 and 2.7, respectively (Rajan *et al.*, 1992)); and it would more readily handle a test for PRs containing appreciable amounts of free calcite (e.g. Chatham Rise PR (Rajan *et al.*, 1992)). On the other hand a scientific calculator or PC is required for calculating the DRF, and time to program the DRF initially.

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Appendix

Calculation of Dissolution Rate Function values

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The steps in estimating the Dissolution Rate Function (DRF) for a given RPR are, briefly, measurement of the values of their chemical and physical properties, then

insertion into the DRF for $t=1$, to give the percentage of the RPR dissolved in one year.

The sieve fraction $<.15$ mm is taken as $.1$ to $.15$ mm as indicated in the main text, while the >2 mm fraction is estimated at 2 to 4 mm.

Example

1. Chemical and physical properties

$$C_R = 4.1 \text{ mg dm}^{-3}, F = 12.8\% P$$

$$\text{Therefore } C_R/F \approx 32 \text{ mg dm}^{-3} (\mu\text{g cm}^{-3})$$

b_i to b_{i-1} (cm)	.01-.015	.015-.025	.025-.05	.05-.1	.1-.2	.2-.4	.01-.4 (total)
w_i (mass fraction)	0.20	.40	.19	.11	.07	.03	1.00

2. Value for D_m and calculation of rate constant, a

We use $D_m = 0.5 \text{ cm}^2 \text{ year}^{-1}$ (equation (2)), being the average for a number of New Zealand soils (Edmeades et al., 1992), which is supported by data from a further 97 sites (K.W. Perrott and B.E. Kerr, unpublished).

The rate constant, a , can now be calculated (Watkinson, 1994b), using units of g, cm, and year.

$$\begin{aligned} a &= 8D_m(C_R/F)/\rho \\ &= 8 \times 0.5 \times 32 \times 10^{-6} \div 3.2 \\ &= 4 \times 10^{-5} \text{ cm}^2 \text{ year}^{-1} \end{aligned}$$

3. Validity of equation (3) for DRF

The applicability of equation (3) for $t=1$ year is now checked for the condition $0 \leq t \leq b_0^2/a$, where $b_0 = 0.01$ cm is the smallest particle.

$$\begin{aligned} b_0^2/a &= 0.01^2 \div 4 \times 10^{-5} \\ &= 2.5 \text{ year} \end{aligned}$$

$$\text{i.e. } b_0^2/a > 1 \text{ year}$$

The smallest particles take 2.5 years to dissolve, and therefore equation (3) applies.

4. Calculation of DRF

The DRF = $1 - m/m_0$, and m/m_0 is given by equation (3) for $t=1$ year.

$$\begin{aligned} \frac{m}{m_0} &= \sum_{i=1}^n \frac{w_i}{2(b_i - b_{i-1})} \left[b_i \left(2 + \frac{a}{b_i^2} \right) \left(1 - \frac{a}{b_i^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. - b_{i-1} \left(2 + \frac{a}{b_{i-1}^2} \right) \left(1 - \frac{a}{b_{i-1}^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. + 3\sqrt{a} \left(\sin^{-1} \left(\frac{\sqrt{a}}{b_i} \right) - \sin^{-1} \left(\frac{\sqrt{a}}{b_{i-1}} \right) \right) \right] \end{aligned}$$

There are six sieve fractions ($n=6$), ie each of the sieve fractions is represented by one of the terms in the summation. Summing from the smallest to the greatest sizes (cm),

$$\begin{aligned} \frac{m}{m_0} &= \frac{w_1}{2 \times .005} \left[.015 \left(2 + \frac{a}{.015^2} \right) \left(1 - \frac{a}{.015^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. - .01 \left(2 + \frac{a}{.01^2} \right) \left(1 - \frac{a}{.01^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. + 3\sqrt{a} \left(\sin^{-1} \frac{\sqrt{a}}{.015} - \sin^{-1} \frac{\sqrt{a}}{.01} \right) \right] \\ &+ \frac{w_2}{2 \times .01} \left[.025 \left(2 + \frac{a}{.025^2} \right) \left(1 - \frac{a}{.025^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. - .015 \left(2 + \frac{a}{.015^2} \right) \left(1 - \frac{a}{.015^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. + 3\sqrt{a} \left(\sin^{-1} \frac{\sqrt{a}}{.025} - \sin^{-1} \frac{\sqrt{a}}{.015} \right) \right] \\ &+ \frac{w_3}{2 \times .025} \left[.05 \left(2 + \frac{a}{.05^2} \right) \left(1 - \frac{a}{.05^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. - .025 \left(2 + \frac{a}{.025^2} \right) \left(1 - \frac{a}{.025^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. + 3\sqrt{a} \left(\sin^{-1} \frac{\sqrt{a}}{.05} - \sin^{-1} \frac{\sqrt{a}}{.025} \right) \right] \\ &+ \frac{w_4}{2 \times .05} \left[.1 \left(2 + \frac{a}{.1^2} \right) \left(1 - \frac{a}{.1^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. - .05 \left(2 + \frac{a}{.05^2} \right) \left(1 - \frac{a}{.05^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. + 3\sqrt{a} \left(\sin^{-1} \frac{\sqrt{a}}{.1} - \sin^{-1} \frac{\sqrt{a}}{.05} \right) \right] \\ &+ \frac{w_5}{2 \times .1} \left[.2 \left(2 + \frac{a}{.2^2} \right) \left(1 - \frac{a}{.2^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. - .1 \left(2 + \frac{a}{.1^2} \right) \left(1 - \frac{a}{.1^2} \right)^{\frac{1}{2}} \right. \\ &\quad \left. + 3\sqrt{a} \left(\sin^{-1} \frac{\sqrt{a}}{.2} - \sin^{-1} \frac{\sqrt{a}}{.1} \right) \right] \\ &+ \frac{w_6}{2 \times .2} \left[.4 \left(2 + \frac{a}{.4^2} \right) \left(1 - \frac{a}{.4^2} \right)^{\frac{1}{2}} \right. \end{aligned}$$

$$-2 \left(2 + \frac{a}{.2^2} \right) \left(1 - \frac{a}{.2^2} \right)^{\frac{1}{2}} + 3\sqrt{a} \left(\sin^{-1} \frac{\sqrt{a}}{.4} - \sin^{-1} \frac{\sqrt{a}}{.2} \right)$$

Inserting values above for "a", w_i and calculating angles in radians

$$\text{DRF} = 1 - m/m_0 = 0.148$$

The above summations can be performed on a calculator, but more readily by computer using a spreadsheet program eg MS Excel, set out with input/output columns as follows.

5. Use of MS Excel for calculating DRF

Using a database such as in Excel, simplifies the calculations. The equation for m/m_0 is split into six equations; one for each size fraction, which are inserted into adjoining cells. Putting the weight fraction in place of W_i in each equation, and the rate constant, a, as \$C24 we have,

$$\text{MF}_1 = (W_1 / (2 * 0.005)) * ((0.015 * (2 + (\$C24 / 0.015^2)) * ((1 - (\$C24 / 0.015^2)) \wedge 0.5)) - (0.01 * (2 + (\$C24 / 0.01^2)) * ((1 - (\$C24 / 0.01^2)) \wedge 0.5))) + (3 * \text{SQRT}(\$C24)) * ((\text{ASIN}((\text{SQRT}(\$C24)) / 0.015)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.01))))$$

$$\text{MF}_2 = (W_2 / (2 * 0.01)) * ((0.025 * (2 + (\$C24 / 0.025^2)) * ((1 - (\$C24 / 0.025^2)) \wedge 0.5)) - (0.015 * (2 + (\$C24 / 0.015^2)) * ((1 - (\$C24 / 0.015^2)) \wedge 0.5))) + (3 * \text{SQRT}(\$C24)) * ((\text{ASIN}((\text{SQRT}(\$C24)) / 0.025)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.015))))$$

$$\text{MF}_3 = (W_3 / (2 * 0.025)) * ((0.05 * (2 + (\$C24 / 0.05^2)) * ((1 - (\$C24 / 0.05^2)) \wedge 0.5)) - (0.025 * (2 + (\$C24 / 0.025^2)) * ((1 - (\$C24 / 0.025^2)) \wedge 0.5))) + (3 * \text{SQRT}(\$C24)) * ((\text{ASIN}((\text{SQRT}(\$C24)) / 0.05)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.025))))$$

$$\text{MF}_4 = (W_4 / (2 * 0.05)) * ((0.1 * (2 + (\$C24 / 0.1^2)) * ((1 - (\$C24 / 0.1^2)) \wedge 0.5)) - (0.05 * (2 + (\$C24 / 0.05^2)) * ((1 - (\$C24 / 0.05^2)) \wedge 0.5))) + (3 * \text{SQRT}(\$C24)) * ((\text{ASIN}((\text{SQRT}(\$C24)) / 0.1)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.05))))$$

$$\text{MF}_5 = (W_5 / (2 * 0.1)) * ((0.2 * (2 + (\$C24 / 0.2^2)) * ((1 - (\$C24 / 0.2^2)) \wedge 0.5)) - (0.1 * (2 + (\$C24 / 0.1^2)) * ((1 - (\$C24 / 0.1^2)) \wedge 0.5))) + (3 * \text{SQRT}(\$C24)) * ((\text{ASIN}((\text{SQRT}(\$C24)) / 0.2)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.1))))$$

$$\text{MF}_6 = (W_6 / (2 * 0.2)) * ((0.4 * (2 + (\$C24 / 0.4^2)) * ((1 - (\$C24 / 0.4^2)) \wedge 0.5)) - (0.2 * (2 + (\$C24 / 0.2^2)) * ((1 - (\$C24 / 0.2^2)) \wedge 0.5))) + (3 * \text{SQRT}(\$C24)) * ((\text{ASIN}((\text{SQRT}(\$C24)) / 0.4)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.2))))$$

$$((\text{ASIN}((\text{SQRT}(\$C24)) / 0.4)) - (\text{ASIN}((\text{SQRT}(\$C24)) / 0.2))))$$

The sum of the MF values for each weight fraction gives m/m_0 and the DRF is simply calculated from $1 - m/m_0$.

6. Calculations for any time

For each sieve fraction, i , calculate b_{i-1}^2/a and b_i^2/a .

- For times $0 \leq t \leq b_{i-1}^2/a$, use equation (3)
- For times $b_{i-1}^2/a \leq t \leq b_i^2/a$, use equation (4)
- For times $t > b_i^2/a$, $m_i/m_0 = 0$, so $1 - m_i/m_0 = 1$

Summing the values for all sieve fractions permits calculation of the dissolution curve, which covers times $0 \leq t \leq b_n^2/a$.

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