



Evaluating the benefits of legacy phosphate

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Abstract

Aims Many soils in the developed world have been fertilized with phosphate for several decades. Appreciable phosphate has accumulated in such soils. This is referred to as “legacy P”. The benefits of legacy P are not widely appreciated. Here, we report the effects of legacy P on buffering capacity and the consequent effects on the effectiveness of plant growth, and its effects on the continuing reaction between soil and P and the consequent effects in decreasing the decline of P effectiveness with time.

Methods We produced five levels of legacy P by incubating the soil with added phosphate at high temperatures for 30 days. We then measured the effect on sorption/desorption and on plant growth in response to further additions of phosphate.

Results Legacy P decreased soil buffering capacity, decreased hysteresis of desorption, and increased the amount of P in a similar state to that of the recently sorbed P. There were analogous effects of plant

growth; effectiveness of P fertiliser increased; the decline in effectiveness with time decreased; and the amount of soil P accessible to plants increased. We think that soil tests reflect only the amount of soil P accessible to plants. Soil testing services which include estimates of phosphate buffering reflect its decrease and the consequent increase in fertilizer effectiveness. We propose a simple test to reflect the rate of decline in effectiveness with time.

Conclusions Managing phosphate applications using soil tests alone underestimates phosphate status and leads to over application of phosphate. It is necessary to also include estimates of the change in phosphate buffering and the change in the rate of decline in effectiveness with time. A simple way to estimate the rate of decline is suggested.

Keywords Phosphate · Residual value · Hysteresis · P sorption · P desorption · Soil tests · Buffering capacity

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Introduction

It is widely believed that it is necessary to apply more phosphate (P) than is needed by subsequent crops. This has led to large accumulations of P especially in soils of the developed world (Syers et al. 2008; Condrón et al. 2013; Doydora et al. 2020, Pavinato et al. 2020). This accumulated P is commonly referred to as legacy P. Much thought

has been devoted to ways in which this legacy P could be accessed, with the aim of decreasing further inputs of P (Menezes-Blackburn et al. 2018; Condrón et al. 2013; Doydora et al. 2020; Pavinato et al. 2020). The methods suggested involve modification of root architecture or biochemistry or modification of the soil. It is often suggested that plants that secrete organic acids, such as citrate, might be better able to use legacy P. This does not appear to be the case. *Lupinus cosentinii* bears cluster roots which secrete citric acid. It was more effective in utilising soil P than were the non-cluster-rooted *L. luteus*, *L. angustifolius* or subterranean clover, but had no significant advantage in accessing legacy P (Barrow and Mendoza 1990).

Our approach is different; we think that the accumulated legacy P has changed soil properties in such a way that further applications of P are more effective; a better way to decrease further inputs is to understand these effects and develop ways of measuring them so that this understanding can be applied.

In order to explain this point, we need to rehearse the way that phosphate reacts with soil. It is initially adsorbed on heterogeneous variable-charge surfaces of soil particles; it then penetrates the soil particles by solid-state diffusion (Barrow 1999; Barrow et al. 2021). These reactions increase the negative charge on the soil particles (Barrow and Debnath 2014; Barrow et al. 2020a). One consequence of this is that it becomes more difficult for subsequent applications of phosphate to be adsorbed; the phosphate buffering capacity is therefore decreased (Barrow and Debnath 2014; Barrow 2015; Barrow et al. 2018); each further application of P therefore becomes more effective; and less is needed (Barrow et al. 2018). The second consequence is that the diffusive penetration becomes slower and eventually stops (Barrow et al. 2018). Once this happens, to maintain the status, it is only necessary to replace the P removed in the previous crop.

In this work we show how the effects of accumulated legacy P can be assessed by measuring soil sorption/desorption behaviour and that the characteristics of these effects so measured are closely related to the characteristics of the response of plants to further additions. We also show how these characteristics can be approximated by simple single-point measurements; we propose these would provide the tools needed to make better management decisions.

We regard the work reported here is an improvement of that reported by Barrow et al. (2018). We think that in that work we did not adequately explore the effects of legacy P on further reaction with P. Here we show that legacy P slows, and eventually stops further reaction, and therefore increases the effectiveness of further applications of P.

Outline of the experiment

We established five levels of legacy P (including zero) by incubating soil with phosphate at 70 °C for 30 days. In work with a similar soil (Barrow et al. 2018) it was estimated that the rate of the reaction at 70 °C was about 65 times that at 20 °C. That means that incubation for 30 days was equivalent to about five years at 20 °C.

We then measured sorption and desorption properties by mixing samples of the treated soils with solutions containing several different levels of phosphate. After the designated period, we removed the solution and replaced it with a solution containing no phosphate and mixed for the same period. The following equations were used to describe the results.

$$S_s = a_s c_s^b - q_s \quad (1)$$

$$S_d = a_d c_d^b - q_d \quad (2)$$

where the subscript *s* indicates the sorption phase and subscript *d* indicates the desorption phase, *S* indicates phosphate sorbed by the soil, *c* indicates the phosphate concentration in solution and the other terms are parameters to be fitted. Because sorption is calculated from the observed change in concentration, the terms in the above equations are not independent. This problem is overcome (Barrow 2008) by treating the equations above as simultaneous with:

$$S_s = (c_i - c_s) S_{sr} \quad (3)$$

$$S_d = S_s - c_d S_{sr} \quad (4)$$

Equation (3) means that during the sorption phase, sorption is calculated from the change in concentration ($c_i - c_s$), multiplied by the solution:soil ratio, S_{sr} . During the desorption phase (Eq. (3)), sorption, S_d , is calculated by subtracting the product of the desorption phase solution concentration, c_d , and the

solution:soil ratio. Parameters of these equations were used to indicate the three benefits of legacy phosphate. Because the parameter b could be assumed to be common (see Fig. 1), the parameter a_s was used to assess the effect of legacy P on buffering capacity. The ratio of slopes a_s/a_d measures the hysteresis of sorption; when this is large it indicates that diffusive penetration is marked; the change of the ratio with increasing levels of legacy P reflects the extent to which the rate of diffusive penetration has decreased. Finally the parameter q_s reflects the amount of phosphate in a similar status to that of the recently sorbed phosphate. It might therefore be assumed to be proportional to the phosphate supplied by soil when plants are grown.

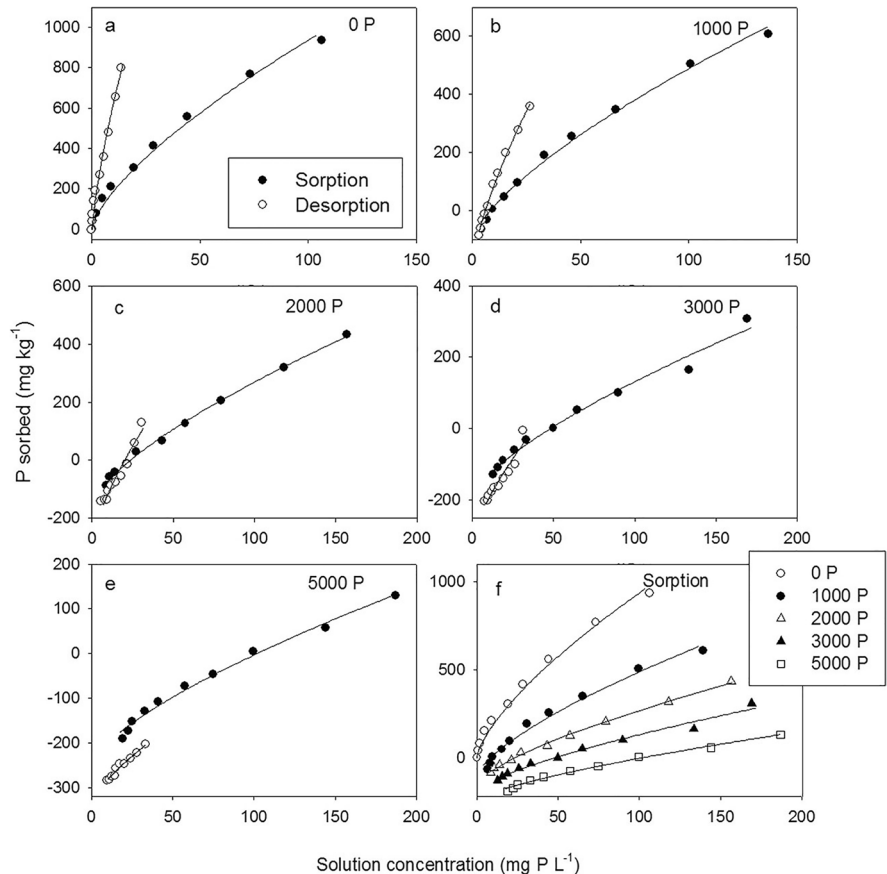
We also assessed the effect of the legacy P on response to fertilizer. At each level of legacy P, we prepared five sets of soil samples each containing 10 different levels of phosphate. The five sets were subjected to further incubations at 70 °C for 0, 1, 3, 10, and 30 days. The samples so treated were then used

as a source of P for plant growth. The responses were measured using the following equation.

$$Y = M_{ax} (1 - \exp(-\gamma (x + d))) \tag{5}$$

where Y indicates the weight of plants, x the level of phosphate applied, and the other terms are parameters to be fitted. Equation (5) is a modified form of the Mitscherlich equation. The more common form of the Mitscherlich equation indicates the maximum and the intercept with the vertical axis. The form used here indicates the intercept with the horizontal axis. This value estimates the P sourced from the soil plus that from the seed. The parameter γ indicates the slopes of the response curves. The values for the set of soils that had not been subject to a second incubation indicate the effect of legacy P on the soil P buffering capacity and therefore on phosphate effectiveness. The change in γ with increasing period of second incubation indicates the effect of legacy P on the diffusive penetration of phosphate and thus on its

Fig. 1 Adsorption and desorption plots. Parts a to e show individual plots for each amount of legacy P as indicated. Part f shows the individual sorption plots. The equations fitted were: $S_s = a_s c^b - q_s$ (1), $S_d = a_d c^b - q_d$ (2), where the subscript s indicates the sorption phase and subscript d indicates the desorption phase, S indicates phosphate sorbed by the soil, c indicates the phosphate concentration in solution and the other terms are fitted parameters. The leastsquares value of the parameter b was 0.70 when a common value was used for all treatments. Using a common value did not significantly increase the residual sums of squares. The values of the parameters $a_s, a_d,$ and q_s are used in Fig. 4



residual effectiveness. As there was little phosphate present in the seed, the parameter d reflects the effect of legacy P to which the plants have access. As it was infeasible to incubate all the soil to be used in the pot experiment at a constant temperature, we applied P to 200 g of soil for each treatment (one fifth of the pot soil).

We also measured the effects of legacy P on three commonly used soil tests for P.

Details of methods

We used a soil from the Regional Research Station of Bidhan Chandra Krishi Viswavidyalaya at Jhargram in West Bengal, India ($22^{\circ}26' \times 86^{\circ}59' \times 49.23' \text{E}$). It was low in P and had high buffering capacity for P. The site was well drained and uncultivated. This soil was previously used by Barrow et al. (2020a, b, 2022). The average annual rainfall of this location is 1400 mm; 81% of this falls between June and early October. The average maximum summer temperature is 37 °C and average minimum in winter is 15 °C. We collected 50 kg soil in the dry season, in December 2019, to a depth of 20 cm; thoroughly mixed and ground well. A portion of soil was passed through a 2 mm sieve for laboratory experiments and stored at 25 °C prior to use. The soil is classified as a coarse loamy Typic Haplustulf (USDA Soil Staff Survey 1999) or an Orthic Acrisol (FAO WRB 2006) in the red and lateritic soil zone. Some properties are: Colwell P, 11.36 mg kg⁻¹ (Colwell 1963); Bray P, 3.17 mg kg⁻¹ (Bray and Kurtz 1945); cation exchange capacity, 9.2 cmol (p⁺) kg⁻¹ (Dewis and Freitas 1984); water-holding capacity, 28% (Piper 1966); and organic C content, 3.1 g kg⁻¹ (Walkley and Black 1934).

Legacy P

We established five different levels of legacy by adding to samples of soil 0, 1000, 2000, 3000, and 5000 mg P kg⁻¹ in solutions containing KH₂PO₄. The samples were then incubated moist at 70 °C for 30 days. As indicated above, this is equivalent to about five years at 20 °C.

P sorption study

We mixed 5 g soil of different levels of legacy P in centrifuge tubes with 50 mL 0.01 M CaCl₂ solution containing the following concentrations of P: 0, 5, 10, 20, 30, 50, 70, 100, 150, and 200 mg P L⁻¹ as KH₂PO₄. The tubes were gently shaken for 48 h in a reciprocal shaker at 25 °C, centrifuged at 2146 g and P in the solution was measured by the method of Murphy and Riley (1962). To study phosphate desorption, the soil from the sorption run (after decanting the supernatant) was re-suspended with 0.01 M CaCl₂ and shaken for the same period as for the sorption run. Phosphorus in the solution was determined.

Cultivating plants

For each of the levels of legacy P, 10 levels of P were applied in solution to 200 g subsamples to give the following P concentrations: 0, 10, 20, 30, 60, 100, 200, 300, 500, and 1000 mg P kg⁻¹ soil. These treatments were applied to five different sets of soils. The five sets were then incubated moist at 70 °C for 0, 1, 3, 10, or 30 days.

The pots were prepared as follows. Bulk soil weighing 700 g was placed into pots with a surface diameter of 115 mm. The 200 g test soil samples were then added followed by 50 g of bulk soil; ten seeds of mustard (*Brassica campestris* L. 'B9') and a further 50 g of bulk soil. As the test soils comprised 20% of the total soil in the pot, these values may be divided by 5 to give mg pot⁻¹. The advantage of this method is that only a small amount of soil had been incubated at high temperature and therefore the bulk soil was not subjected to this treatment. After germination, five healthy plants were kept, maintaining equal spaces as far as possible. The weight per 100 seeds was 218 mg with a P concentration of 1.005 mg g⁻¹. Five seeds would therefore supply only 10.95 µg P. Seven days after emergence we added a basal nutrient solution containing the following nutrients (mg nutrient kg⁻¹ soil): Mn 4, Mo 1, Cu 1, B 0.2, Zn 10, K 100, Mg 6, and N 100. Plants were grown for 30 d in the open air on a rooftop. Night temperatures were as low as 18°C and maximum day temperatures averaged 27°C. All pots received the same amount of light. The aboveground parts of plants were collected and washed with dilute H₂SO₄. This was to remove any greasy material that might have left on the leaves.

They were then washed with distilled water, air dried, then oven dried at 60°C until a constant weight was reached.

Soil tests

Before cultivating plants, we extracted the soils that had been treated to give different levels of legacy P using three methods: Bray and Kurtz (1945), Colwell (1963) and Olsen et al. (1954).

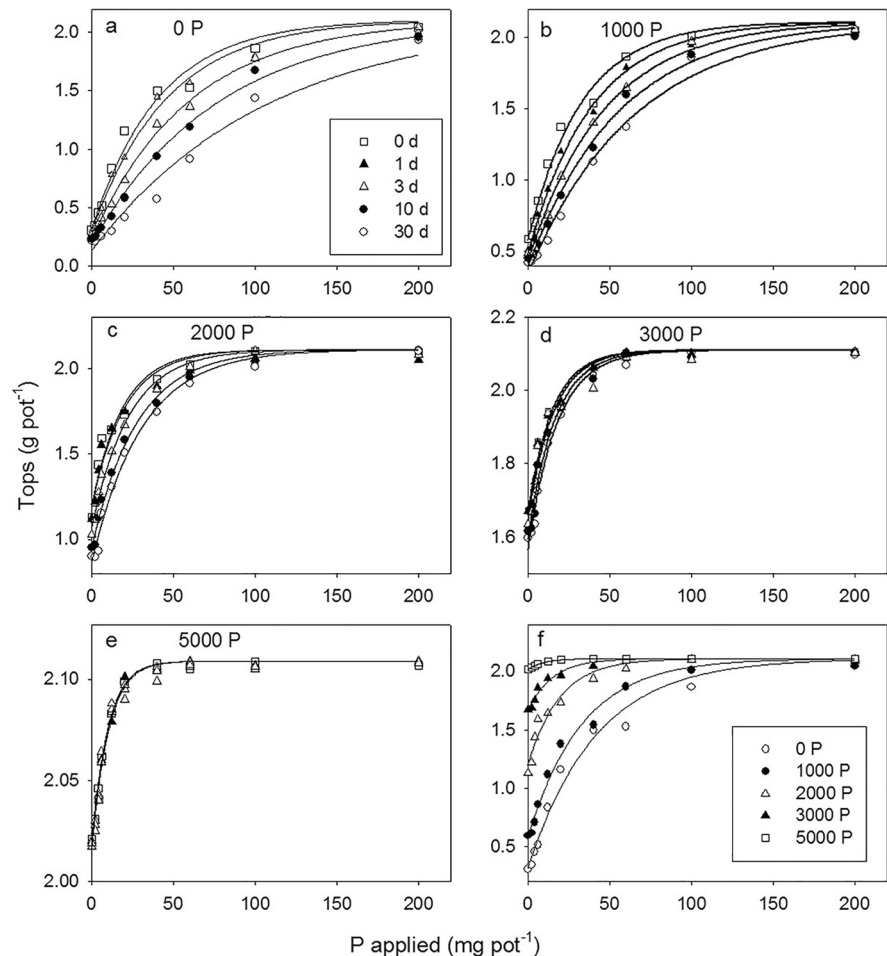
Results

With increasing levels of legacy P, the slope of the sorption curves decreased to about a quarter of the value for the zero P treatment. Thus buffering capacity decreased to the same extent (Fig. 1).

The amount of hysteresis also decreased from an initial value of 3.6. At the highest P level desorption curves approached the same slope as those for sorption curves and thus to a hysteresis value close to unity (Fig. 1). This indicates that the penetration of P into the reacting surfaces decreased to close to zero. The amount of phosphate in a similar status to that of the sorbed phosphate increased. This can be inferred extrapolating the sorption curves in Fig. 1f to the horizontal axis. These values are shown later (Fig. 4c) when comparisons are made with the plant growth experiment.

With increasing levels of legacy P, the slope of the plant response curves increased, indicating that the fertilizer had become more effective (Fig. 2). The increase in effectiveness was about four-fold (Fig. 3). This result is consistent with the decreased buffering capacity.

Fig. 2 Plant response to phosphate. Parts a to e shows the effects of period of incubation for each amount of legacy P as indicated. Part f shows the effect of level of legacy P at zero period of incubation. The equation fitted was: $Y = M_{ax} (1 - \exp(-\gamma(x+d)))$ (3), where Y indicates the weight of plants, x the level of phosphate applied, and the other terms are parameters that were fitted. The values of the parameter γ are used in Fig. 3 and those of d are used in Fig. 4



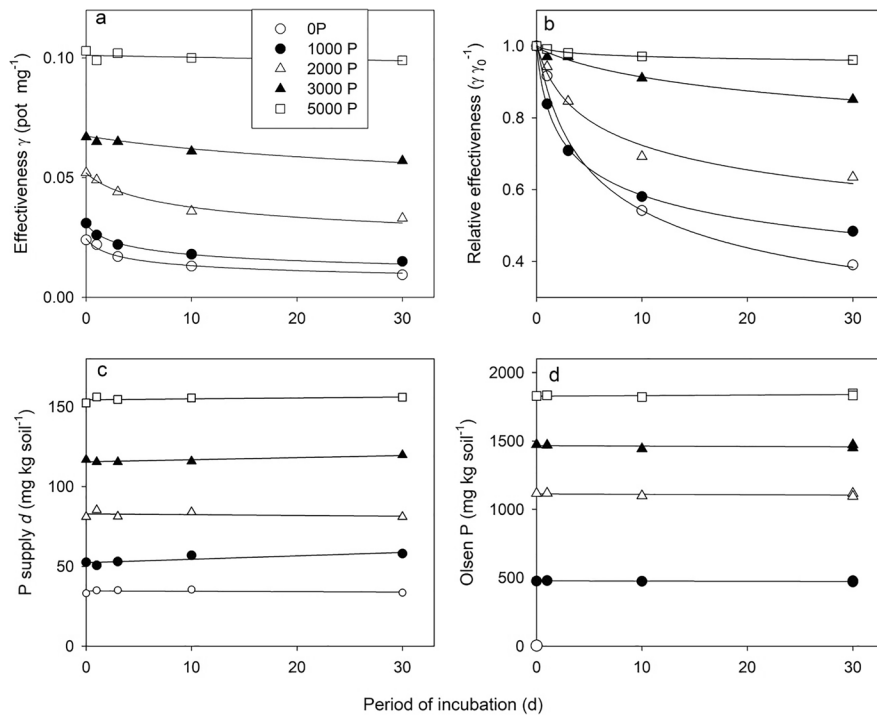


Fig. 3 Effect of amount of legacy P and period of second incubation on the values of the parameters that characterise plant response, and on Olsen P. Part a shows the values of γ . This parameter reflects the slope of the response curves in Fig. 2. The lines indicate the equation fitted: $\gamma = \gamma_0(1 + kt)^{-\beta}$ (6). Where γ_0 is the regression estimate of the value of γ at zero time, t is time in days. The parameter k reflects the rate of change, and the parameter β controls the curvature of the

plots. The least squares value of the parameter β was 0.22 when a common value was used for all treatments. Using a common value did not significantly increase the residual sums of squares. Part b shows the values of γ/γ_0 and therefore shows the change in effectiveness relative to its initial value. Part c shows the values of the parameter d . This reflects the extrapolation of the response curves in Fig. 2 to the horizontal axis. Part d shows the values for Olsen P

There was a large interaction between the levels of legacy P and the effects of period of second incubation on the response (Fig. 2a). When there was no legacy P, the effectiveness of the second dose of P decreased to about 40% of its original value with increasing time (Fig. 3b). As the amount of legacy P increased, this effect became smaller and almost disappeared at the highest value of legacy P (Fig. 3a, b). This is consistent with decreasing penetration of P into the reacting surfaces.

The amount of legacy P to which the plants had access is indicated by d from Eq. (3) of Fig. 2. It increased linearly with increasing level (Fig. 4c), but the slope of the line was equivalent to only 2.4%. In contrast to the changes in effectiveness with length of the second incubation, there were no discernible effects on P supply (Fig. 3c). This is

consistent with a similar lack of effect on the values for Olsen P (Fig. 3d).

Figure 4 shows the remarkable correspondence between effects measured by sorption/desorption with those of plant growth. In Fig. (4a), the measure of P effectiveness derived from the sorption measurements is the reciprocal of the buffering capacity. This reflects the portion of the phosphate in solution and is an important characteristic in determining the rate of diffusion.

The amount of phosphate that was extracted by three soil tests (Fig. 5) was correlated with but was larger than the amounts of legacy P to which the plants had access as indicated by the parameter d (Fig. 4c). The soil tests involve change in pH and also competition from anions; bicarbonate for the Olsen and Colwell tests, fluoride for the Bray and Kurtz

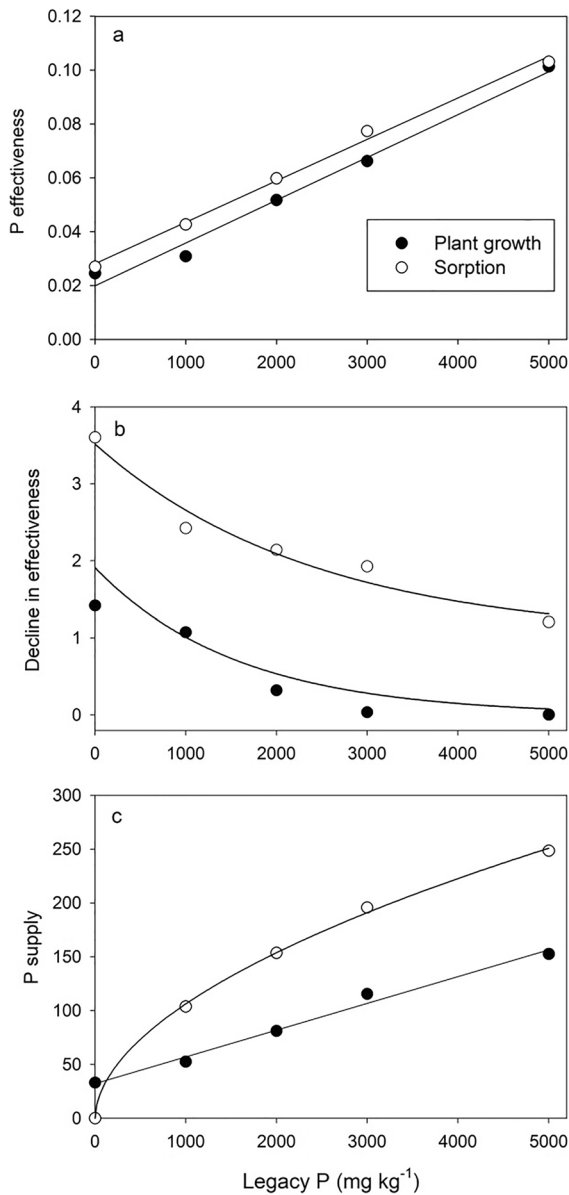


Fig. 4 Comparing the parameters fitted in the sorption/desorption experiment with those fitted in the plant growth experiment. For part a, the sorption characteristics are the values for $1/a_s$ from Eq. (1) of Fig. 1. This reflects the portion of the phosphate in solution and is an important characteristic in determining the rate of diffusion. The plant characteristics are values for γ from Eq. (3) of Fig. 2, representing the effectiveness of fertilizer for plant growth. For part b, the sorption characteristics are the values of a_d/a_s , the hysteresis for desorption from Eq. (1) of Fig. 1.; plant characteristics are the values for k from Eq. (4) of Fig. 3 and reflect the rate of decline in effectiveness. For part c, sorption characteristics are values of q_s from Eq. (1) of Fig. 1. They indicate the predicted value for the amount of P that would be desorbed if solution concentration were extrapolated to zero. Plant characteristics are values of d from Eq. (3) of Fig. 2. They indicate the predicted value if the response curves were extrapolated to the horizontal axis

tests. They therefore might be expected to be somewhat more effective at extracting P than are plants. For the Olsen and for the Bray and Kurtz tests there was a curved relationship. This is consistent with competition for sorption from the anions involved. For the Colwell test curvature could not be detected. This is consistent with the larger solution soil ratio and therefore larger supply of competing anion.

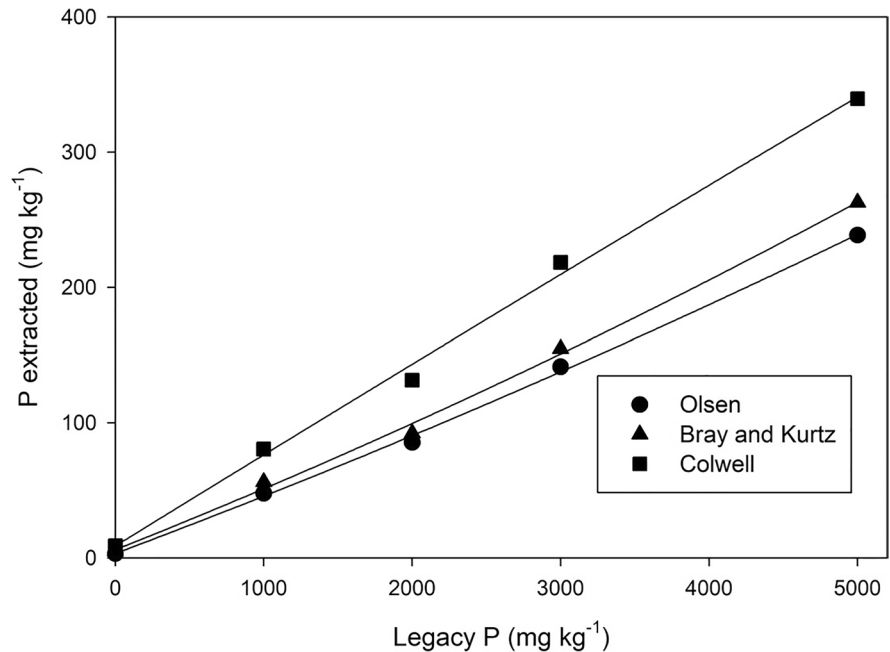
Discussion

This work emphasises the three components involved in the evaluation of legacy P. It shows that laboratory measurements of the components correspond remarkably closely with components of the response to P by plants.

Management of fertilizer programs places great emphasis on soil tests. We show that these correspond to just one component: that represented in Fig. 4c. This contention is strengthened by our observation that the Olsen soil test mirrored the lack of effect of the second incubation on the supply of P as measured by the parameter d . This result shows that after the initial incubation at 70 °C for 30 days, further reaction had practically stopped.

A point to be debated is whether soil tests also take into account the decrease in buffering capacity brought about by the increase in the negative charge on the reacting surfaces. When differences in buffering capacity are caused by differences in the amount and nature of the reacting surface in soils, soil tests such as the Olsen test extract a larger proportion of added phosphate as the buffering capacity decreases (Barrow and Shaw 1976). They would therefore reflect the greater effectiveness of fertilizers. However, when decreases in buffering capacity are caused by increasing negative charge, it is debatable whether this would also be reflected by the Olsen test. This test brings the soils to a common pH of 8.5. We suggest that the changes in negative charge brought about by this change in pH would swamp differences in charge brought about by phosphate treatment. We think a similar argument would apply to other soil tests, all of which involve changes in pH. Reliance on soil tests alone would therefore underestimate the effectiveness of further fertilizers. These are hypotheses; they need testing.

Fig. 5 P extraction from the legacy P treatments by the indicated soil tests



Especially in Australia, the importance of buffering capacity has been recognised since the early work of Ozanne and Shaw (1967) and soil tests are adjusted using a measure of phosphate buffering capacity (Moody and Bolland 1999). Single-point estimates of buffering capacity have been developed and the method of Burkitt et al. (2002) is widely used. This is designated as “PBI”. It is obtained by mixing a sample of soil with a phosphate solution which has a phosphate concentration sufficient to give phosphate sorption of 1000 mg kg^{-1} . It is calculated as: phosphate sorbed, divided by solution concentration raised to the power 0.41. Figure 6 shows that PBI calculated from the present data indicates the effects of legacy P on buffering capacity in a very similar way to that of the slope term (a) obtained using all the data. This correspondence is obtained without adjusting the total sorption using the amount extracted by the three indicated reagents. This is consistent with the recommendations of Burkitt et al. (2008). Use of this, or similar measures, should enable the effects of previous phosphate application of buffering capacity to be taken into account. However, there is at present, no simple way to assess whether the diffusive penetration is still important.

The hysteresis ratio as used here is an effective measure of this property with ratios approaching unity indicating that little diffusive penetration is occurring. We wondered whether a single-point

measure could be found using a process analogous to that for PBI. That is, we used the values of PBI for the sorption step; we then did a similar calculation for the desorption step; we tested whether the ratio PBI desorption/ PBI sorption would serve as a simple measure. We did a similar calculation on the

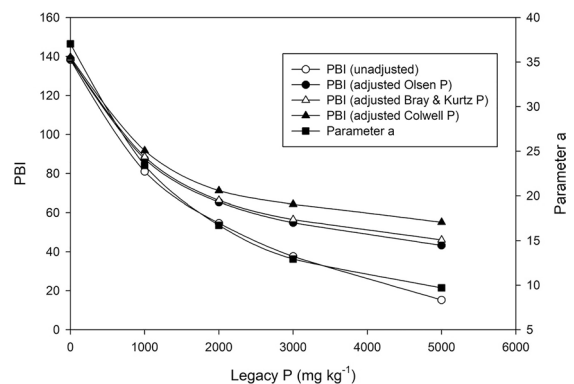


Fig. 6 Comparison of the effects of legacy P on the parameter a_s , the measure of buffering capacity used in this work, with the effects on PBI (Burkitt et al. 2002). This is a single-point measure of buffering capacity calculated from the treatment with an initial phosphate concentration of 100 mg L^{-1} , (solution:soil ratio was 10:1). It is calculated as P sorbed divided by the final solution concentration raised to the power 0.41. For the plots labelled “adjusted” the sorbed P has been adjusted by adding the P extracted by the indicated soil tests (Fig. 5)

much larger dataset of Barrow and Debnath (2014). Figure 7 shows that when the hysteresis ratio is large, the single-point measure does not reflect the value very well. However this is not a serious disadvantage; all we need to know for such soils is that it is large; the exact value is unimportant. The single-point measure does detect soils for which the hysteresis ratio is low. We suggest this would be a useful addition to soil testing services.

The levels of P applied here as pre-treatments were not unrealistically high. Consider the response shown in Fig. 2a for the treatment that had not been incubated with P. The P needed for nearmaximum yield was about 100 mg pot^{-1} . This large amount was needed because the soil has a high buffering capacity. This P was applied to 200 g of soil: thus the concentration in that soil was 500 mg kg^{-1} . Reapplication at that level for 10 years would reach a total application equal to that of the highest legacy P. In practice, there would be removal of phosphate in produce, and levels of application might be decreased, but nevertheless such a level would be achieved over a period much shorter than that pertaining to P application on much land in the developed world. That is why similar declines in the hysteresis with P application have been observed in soils collected from tea plantations

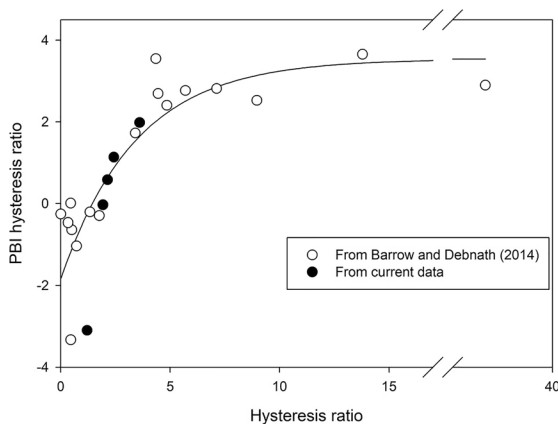


Fig. 7 Testing the possibility of using a single-point estimate of the hysteresis ratio. The horizontal axis indicates the hysteresis ratio derived from all of the data using the ratio of the parameters a_d/a_s . The vertical axis indicates a single-point value derived from the treatment with an initial phosphate concentration of 100 mg L^{-1} , as P remaining as sorbed after the desorption step divided by its solution concentration raised to the power 0.41 all divided by the P sorbed after the sorption step divided by its solution concentration raised to the power 0.41

in northern India (Barrow and Debnath 2014). We make two further points about this aspect. The first is that the numbers used here apply to a soil of high buffering capacity. For soils of lower buffering capacity, the numbers would be smaller. The second is that in many agricultural applications P is applied to the surface soil. It therefore mixes with a fairly small proportion of the soil and so high concentrations would be reached quickly.

Conclusions

Our work suggests that a phosphate fertilizer strategy, based on soil tests alone would underestimate the phosphate status of previously fertilized soils and lead to overapplication of phosphate fertilizers. Fertilizer strategies would be greatly improved by taking into account the decrease in buffering capacity and the decrease in the continuing reaction; both can be assessed by single-point methods.

Author contributions AD designed the experiment, supervised the work, helped analyse the data and wrote parts of the manuscript. DR carried out the experiment. NJB completed the data analysis and wrote most of the paper.

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Data availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests We have no relevant financial or non-financial interests to disclose.

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