

Soil phosphate chemistry and the P-sparing effect of previous phosphate applications

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Abstract Soil phosphate research has been hampered by the persistence of superseded ideas and language. Consequently few have recognised the two phosphate-sparing effects of previous phosphate fertilizer application: one caused by the decreased buffering capacity; the other caused by the eventual cessation of the diffusive movement of phosphate into the adsorbing particle. This is one cause of excessive phosphate applications and thence to contamination of water.

Keywords Phosphate sorption · Residual value · Phosphate-sparing · Hysteresis · Available P · Precipitation · Calcium phosphates

Introduction

In 1842, Laws and Gilbert patented superphosphate. This means there has been more than 17 decades of research into the phosphate chemistry of soil. Surely that is sufficient time for all of the problems to be solved. However, this considerable period is of itself part of the problem. Before we understood very much about the nature of soil phosphate, many terms and attitudes became part of the literature. Some examples follow.

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Inappropriate descriptions

The idea that a category of soil phosphorus that could be distinguished as “available” was first expressed by Dyer (1894). He distinguished this category using a 1 % solution of citric acid because he thought it reflected the mechanism by which plants took up nutrients. He wrote: “it approximates fairly well to the average strength of the natural solvent (root sap) used by the plant itself”. The existence of an available category was disputed by Hall and Plymen (1902) who wrote: “no sharp line of distinction can be drawn between “available” and non-available phosphoric acid and potash in the soil”. Today, we know that the mechanism by which plant roots take up phosphate is not the secretion of root sap. It starts with the removal of phosphate ions from the soil solution nearest the root. This initiates diffusion through the solution down the concentration gradient with the solution phosphate partially replaced by desorption from solid particles. There is no sharp end point to this process and therefore no discrete category that can be called “available”. Yet the term “available P” appears in many manuscripts: a remarkable persistence of 19th century thinking.

Often the term is used to indicate phosphorus extracted by a particular soil test. However, we should as a matter of principle, distinguish what we observed from our interpretation. That is why this journal advocates separation of Results and Discussion. The results obtained from a soil test should therefore be described in terms of the test used: as for example Olsen P or Bray P.

Many manuscripts submitted for publication contain a sentence which may be paraphrased as: “phosphate

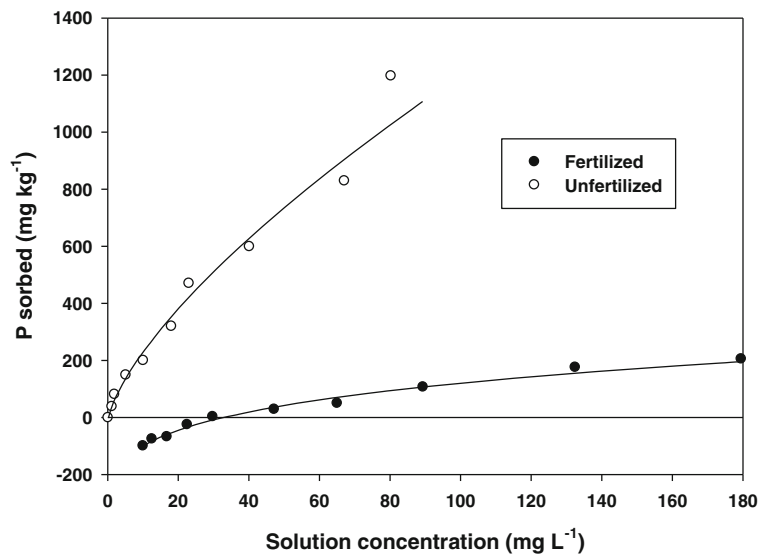


Fig. 1 Typical sorption curves of soils from Northern India. For the unfertilized soil, the phosphorus status is low and the curve can be taken as passing through the origin. The Freundlich equation ($y = a x^b$) may be used. For the fertilized soil, the curve does not pass through the origin. Desorption (that is, negative sorption) occurs and the Freundlich equation must be modified by adding an intercept q : ($y = a x^b - q$). Curves such as these reflect the buffering

capacity of the soils. To summarize this property using a single number, the instantaneous slope at some convenient concentration may be used. When the curves are described as here, this may be calculated by differentiating the equation: $dy/dx = a b x^{b-1}$. Note that the fertilized soil has a smaller buffering capacity than the unfertilized soil. Data from Barrow and Debnath (2014)

added to soil is rapidly precipitated as iron¹ and aluminium phosphates”. When phosphate fertilizers are applied, the concentrated, often-acid solutions formed near the fertilizer source dissolve some of the soil constituents and some of the added phosphate does indeed precipitate (Sample et al. 1980). However, these compounds are unstable and phosphate diffuses away from the site of application to react at lower concentrations. These initial precipitation reactions do not seem to be relevant to the matters to be considered here. Evidence for this is that the slow reactions that decrease the effectiveness of phosphate fertilizer appear to be similar whether the phosphate is supplied as superphosphate granules as in Barrow (1974b) or in dilute solutions mixed with the soil as in Barrow and Shaw (1975). Hence this article will concentrate on reactions with dilute solutions.

¹ It is probable that most of the reaction of phosphate is with iron oxides. However, some reaction with aluminium oxides may also occur. It is difficult to distinguish them; nor is it very useful as both oxides have similar variable charge properties. Further, “iron oxides” contain appreciable aluminium and vice versa. In the remainder of this manuscript “iron” should be read as “iron and perhaps aluminium”.

Precipitates of iron phosphates are unlikely when dilute phosphate solutions are considered. Iron does indeed have a high affinity for phosphate. Consequently there are several iron phosphate compounds of low solubility. For many decades, attempts were made to explain the presence of phosphate in soil in terms of such compounds. However iron itself has very low solubility; there is very little of it in the soil solution. That is why iron persists in soils and one of the reasons why soils have their characteristic colour. For precipitation to occur, the solubility product must be exceeded by the iron and phosphate ions in solution. This is very unlikely indeed. Rather, the strong affinity between iron and phosphate manifests itself as reaction between phosphate ions and the surface of iron oxides.

Similarly, many manuscripts contain sentences indicating that formation of calcium phosphates causes a serious decrease in effectiveness. When phosphate sorption is studied on a calcareous soil, the usual result is that, at first, the behaviour is not markedly different from that for a non-calcareous soil. Plots of sorption of phosphate versus concentration of phosphate in a solution in contact with the soil form a curve little different from that of a non-calcareous soil. With increasing period of reaction, the concentration drops for all levels

of addition but after a few hundred hours, the drop in concentration becomes most marked when the level of addition of phosphate is high. With a long period of contact between soil and phosphate solution, treatments with a high level of phosphate all tend to converge to a common concentration of phosphate in solution of 1–2 mg P l⁻¹. Thus calcium phosphates form slowly, and moderately high phosphate concentrations are needed to initiate their formation. A soil would have to have been fertilized with very heavy applications of phosphate before this process could be important. Further, calcium phosphates are in equilibrium with fairly high concentrations of phosphate in solution. They tend to be sources of phosphate rather than sinks.

The idea that calcium phosphates are important components of soil phosphate is given greater currency from fractionation schemes in which the phosphate extracted

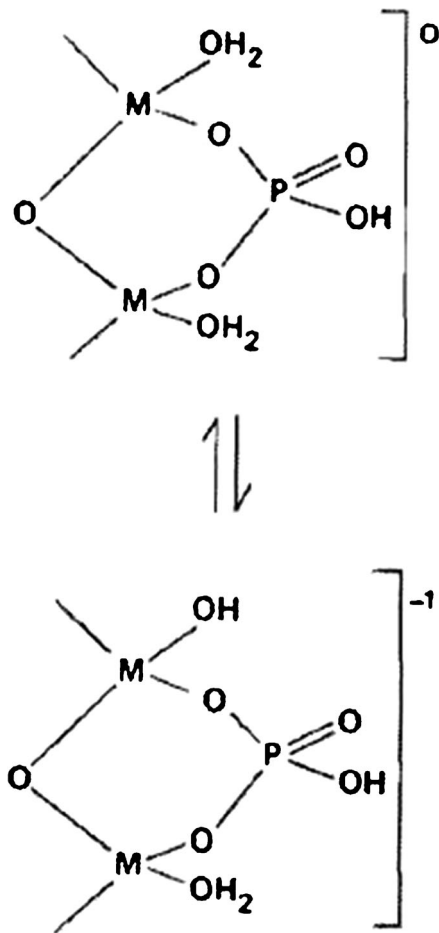


Fig. 2 Postulated bidentate bond between metal ions in a variable charge oxide and a phosphate ion shown at two values for surface charge. From Barrow (1980)

in a particular way is labelled as such. I have seen no evidence that the fractions so specified represent reality. They cannot be taken as indicating the amounts of calcium phosphate present or even that they are present at all. Direct evidence for the presence of calcium phosphates in soils is limited. Norrish and Rosser (1983) found that apatite grains could be observed in less weathered Australian soils but, even in these soils, they were only a small fraction of the total phosphate.

The initial reaction

The initial reaction is reversible, specific adsorption, on variable charge surfaces. “Adsorption” because it is on the outside. “Reversible” because the reaction does not go to completion: some phosphate always remains in solution. Consequently plots of adsorption versus concentration can be drawn (Fig. 1). The legend to this figure explains how such curves may be used to obtain a measure of the buffering capacity. “Specific” because phosphate is greatly preferred in comparison to say chloride. “Specific” is a description not a mechanism.

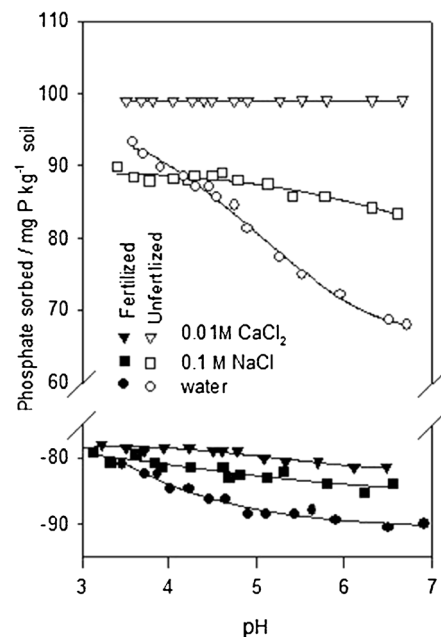


Fig. 3 Effect of salt concentration and of fertilization on phosphate sorbed by soils from northern India. For the unfertilized soil, the Point of Zero Salt effect is at about pH 4.2; for the fertilized soil it is at about pH 3.3. Negative values for the fertilized soil indicate that desorption has occurred. In all cases, more phosphate is sorbed when the background solution is calcium chloride than when it is sodium chloride. From Barrow and Debnath (2015)

The mechanism involved is formation of a bidentate link to two of the metal atoms in the surface (Fig. 2). This forms a strong bond because there is a strong affinity between the metal atoms of the oxide and the phosphate ions in solution, and because the ring structure is stable. Evidence that “charged surfaces” are involved comes from the observation that the amount of adsorption depends on the salt concentration (Fig. 3). Almost always the charge on the surfaces with which phosphate reacts is negative and therefore increasing salt (e.g., sodium chloride) concentration increases adsorption (mnemonic: increased concentration of the positive sodium ions facilitates adsorption of negative phosphate). “Variable charge” because if the pH is altered the magnitude of the salt effect changes. There is a pH at which the salt effect disappears (Fig. 3). This is the Point of Zero Salt Effect (PZSE). Below that pH, the surfaces with which phosphate reacts are net positive (mnemonic: increased chloride concentration decreases adsorption of phosphate). When the background solution is a calcium salt rather than a sodium salt, adsorption is greater at all pH values (Fig. 3). This is not because formation of calcium phosphates. It occurs firstly

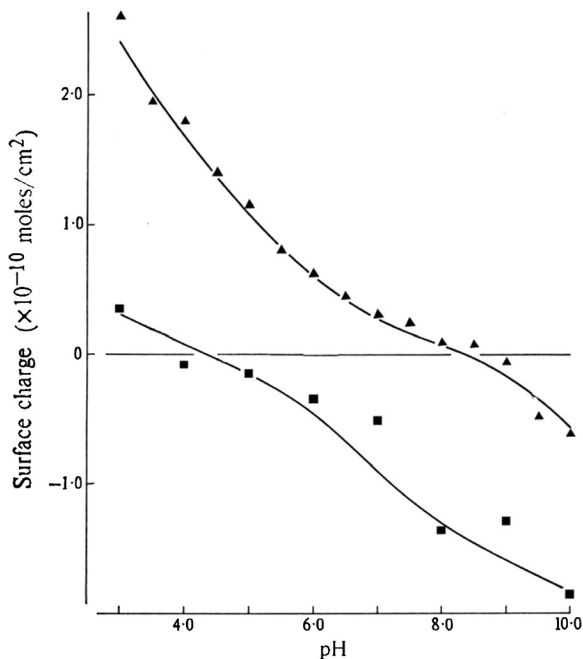


Fig. 4 Effect of reaction with phosphate on the net surface charge on goethite. *Lines* indicate values derived from a model, *points* indicate observations. *Triangles* are values in the absence of phosphate; *squares* indicate an initial concentration of 645 mM of phosphate. Redrawn from Bowden et al. (1980)

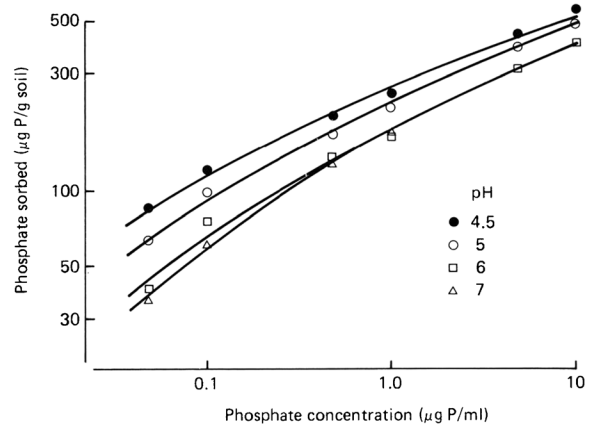


Fig. 5 Observed (*points*) and modelled (*lines*) effects of phosphate concentration and of pH on phosphate sorbed after 24 h at 25 °C. In the model, surfaces on to which phosphate is initially adsorbed are heterogeneous, with a normal distribution of affinities for phosphate, and there is a feedback effect of the increased negative charge on adsorption. From Barrow (1983)

because the calcium ion is divalent and has a greater effect at equal concentration and secondly because calcium ions have a smaller sheath of hydration.

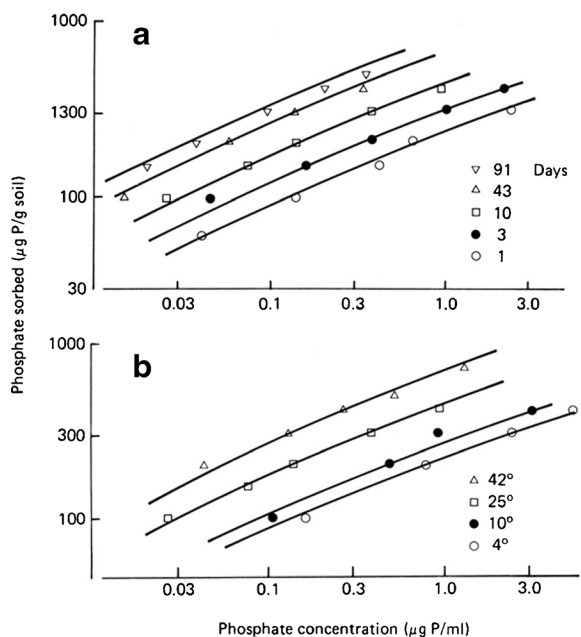


Fig. 6 Observed (*points*) and modelled (*lines*) effects of phosphate concentration time and temperature on phosphate sorbed. Part **a** effect of time at 25 °C; part **b** effect of the indicated temperatures for 10 days. In addition to the model assumptions indicated in Fig. 5, it is assumed that the initial adsorption is followed by a solid state diffusion into the adsorbing particle at a rate that depends on temperature. Redrawn from Barrow (1983)

Adsorption of phosphate ions always conveys some negative charge to the surface (Fig. 4). There is therefore a feed-back effect in which each extra moiety of phosphate reacts with a more-negative surface. This is contrary to the requirements for a Langmuir equation and is one reason why this equation is not appropriate for describing phosphate sorption by soils.

Over a limited range of concentrations, plots of sorption against concentration are fairly well described by the Freundlich equation. Plots on a double log scale are therefore approximately linear. However, if this relationship is explored over a much wider range of concentrations, the plots are gently curved rather than linear. Figure 5 shows that this shape can be reproduced by a model (Barrow 1983) in which the surfaces on to which phosphate is initially adsorbed are heterogeneous, with a normal distribution of affinities for phosphate, and there is a feedback effect of the increased negative charge on adsorption. I think this is why phosphate sorption curves have their typical shape. The heterogeneity is another reason why the Langmuir equation is inappropriate.

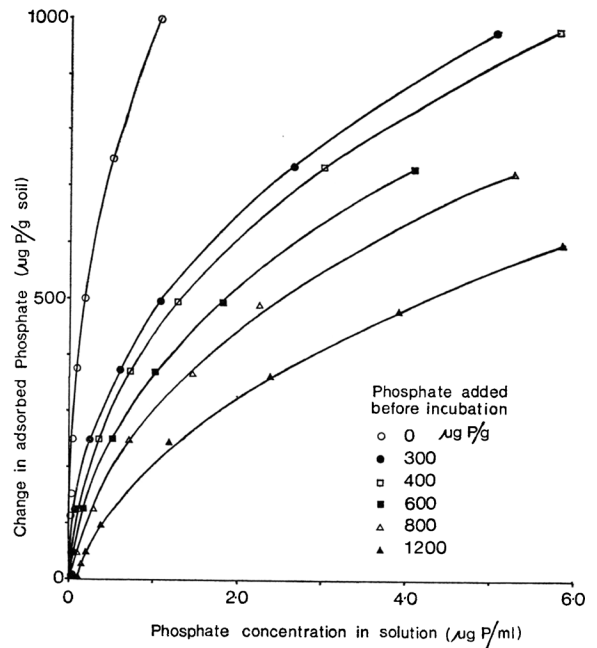


Fig. 8 Effect of incubating a soil for 12 months at 25 °C on the subsequent sorption of phosphate measured after 24 h mixing with phosphate solutions at 25 °C. From Barrow (1974a)

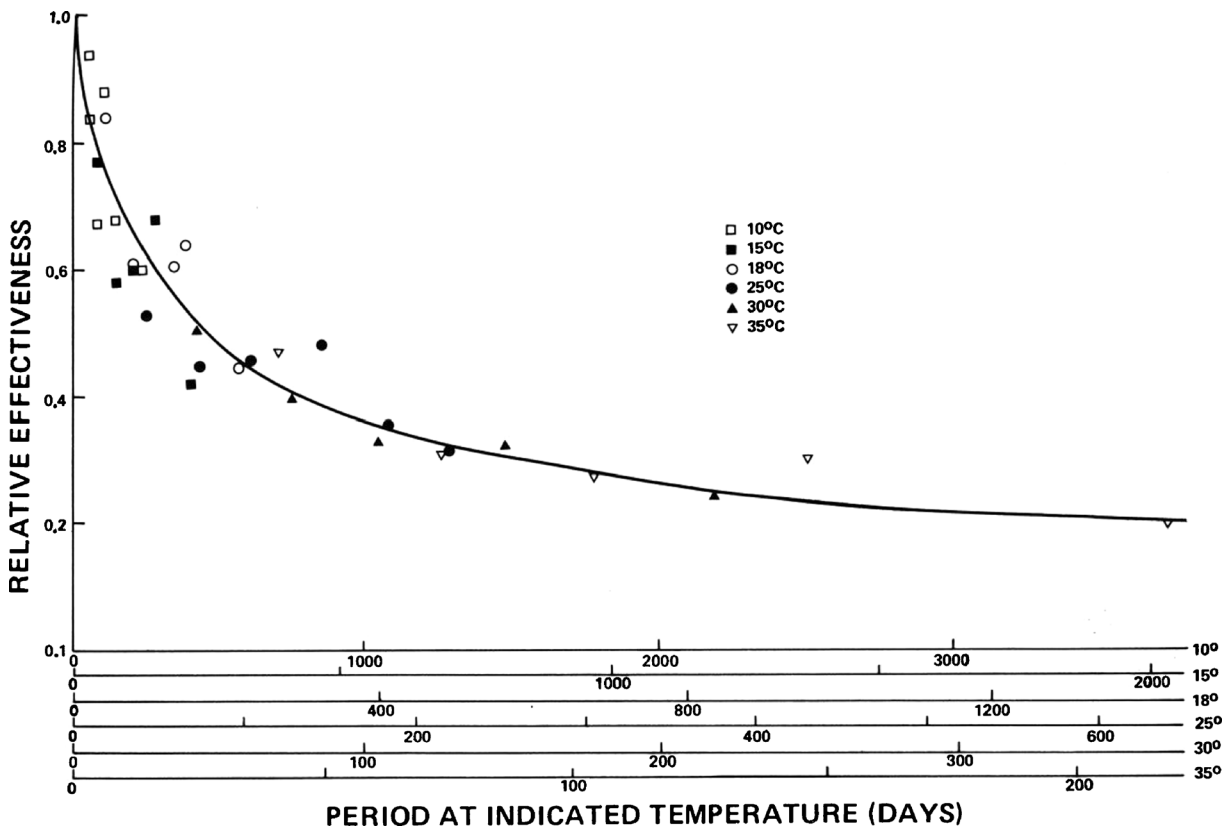


Fig. 7 Effect of time and temperature on the relative effectiveness of phosphate fertilizer for the growth of *Trifolium subterraneum* plants. From Barrow (1980)

The second reaction

When phosphate sorption is measured, authors seldom write that soil and phosphate solution were “mixed”: more commonly they write that soil was “equilibrated” with a phosphate solution. If they were indeed “equilibrated”, then it would follow that equilibrium has been reached, but this is not the case: soil and solution continue to react. Especially for a low-phosphorus soil, the solution concentration of phosphate declines at a rate that is proportional to a small fractional power of time (Barrow and Shaw 1975). There is also a substantial temperature effect, with the rate of decline increased by increasing temperatures (Fig. 6). These observations can be precisely reproduced by a model (Barrow 1983) in which the initial adsorption on heterogeneous surfaces is followed by solid-state diffusion into the adsorbing particles (Fig. 6). Strong support for the solid-state diffusion hypothesis is also provided by the observation that

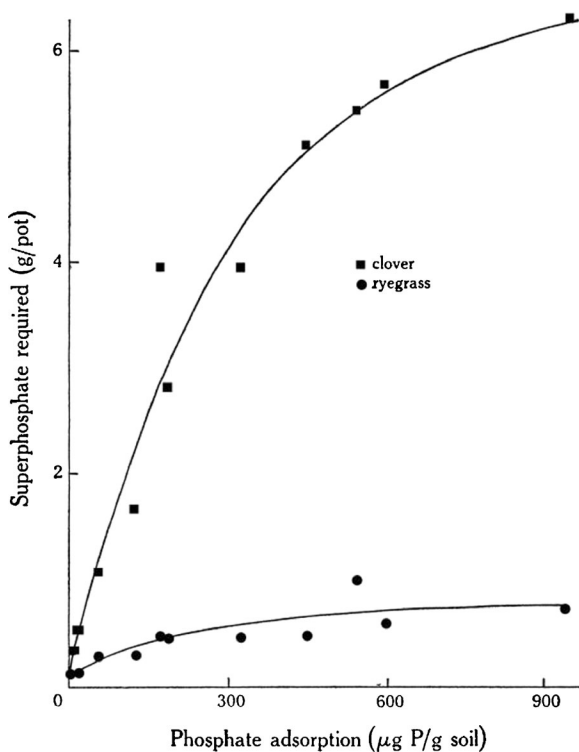


Fig. 9 Relationship between the phosphate required to give 90 % of the maximum yield (“Superphosphate required”) for subterranean clover and for ryegrass and the phosphate sorbed by 11 soils at a concentration of 0.2 mg P/l of solution. As the soils were all of very low phosphate status, the sorption curves passed through the origin and the amount sorbed at a given concentration is an indication of their relative buffering capacity. From Barrow (1975)

the activation energy for the forward reaction is similar to that for the back reaction (Barrow 1979). This is consistent with a diffusion reaction for which the energy barrier for the forward reaction would be the same as the energy barrier for the backward reaction but inconsistent with most chemical reactions.

It is not a coincidence that the effectiveness of phosphate fertilizer also decreases at a rate that is proportional to a small fractional power of time and that there is a similar substantial effect of temperature (Barrow (1974b) and Fig. 7). This decline in the effectiveness of phosphate fertilizer with time is caused by the diffusive penetration of phosphate ions into the adsorbing particles but is usually described by such imprecise terms as: fixed, occluded, or rendered unavailable. The use of such imprecise terms obscures important consequences: because phosphate *ions* penetrate the surface, the negative charge on the reacting surfaces increases. Evidence that this is the case is that the Point of Zero Salt Effect moves to a lower pH (Fig. 3). It is also why the slope of sorption curves decreases (Fig. 8 and Bolland and Allen (2003)). An index derived from the slope of such curves is usually taken to be a measure of the buffering capacity and decreased buffering capacity

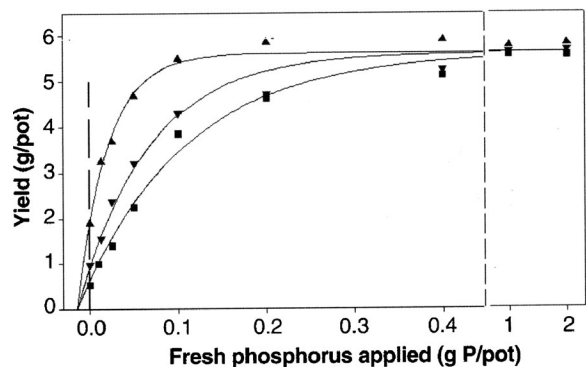


Fig. 10 Relationship between yield of dried wheat shoots and the amount of fresh phosphorus applied in 1996 to samples of soil collected from a field experiment to which different amounts of P were applied once only in May 1976 (squares: 0 kg P/ha; downward triangles: 86 kg P/ha; upward triangles: 599 kg P/ha). Lines are fits of a Mitscherlich equation of the form: $\text{Yield} = a(1 - \exp(-c_i(x + b)))$ where x is the amount of freshly-applied P. In this formulation, b is the P supplied from the soil and seed. The value was not significantly different amongst the residual fertilizer treatments. The relative effectiveness of the fresh fertilizer treatments is calculated from the ratio of the c_i coefficients for the 1976 P treatments. On the treatment that had received 599 kg P/ha, effectiveness of the fresh fertilizer was 3.5 times greater than that of the control. For treatments that had received 86 kg P/ha the value was 2.3. From Bolland et al. (2003), original in Bolland and Baker (1998)

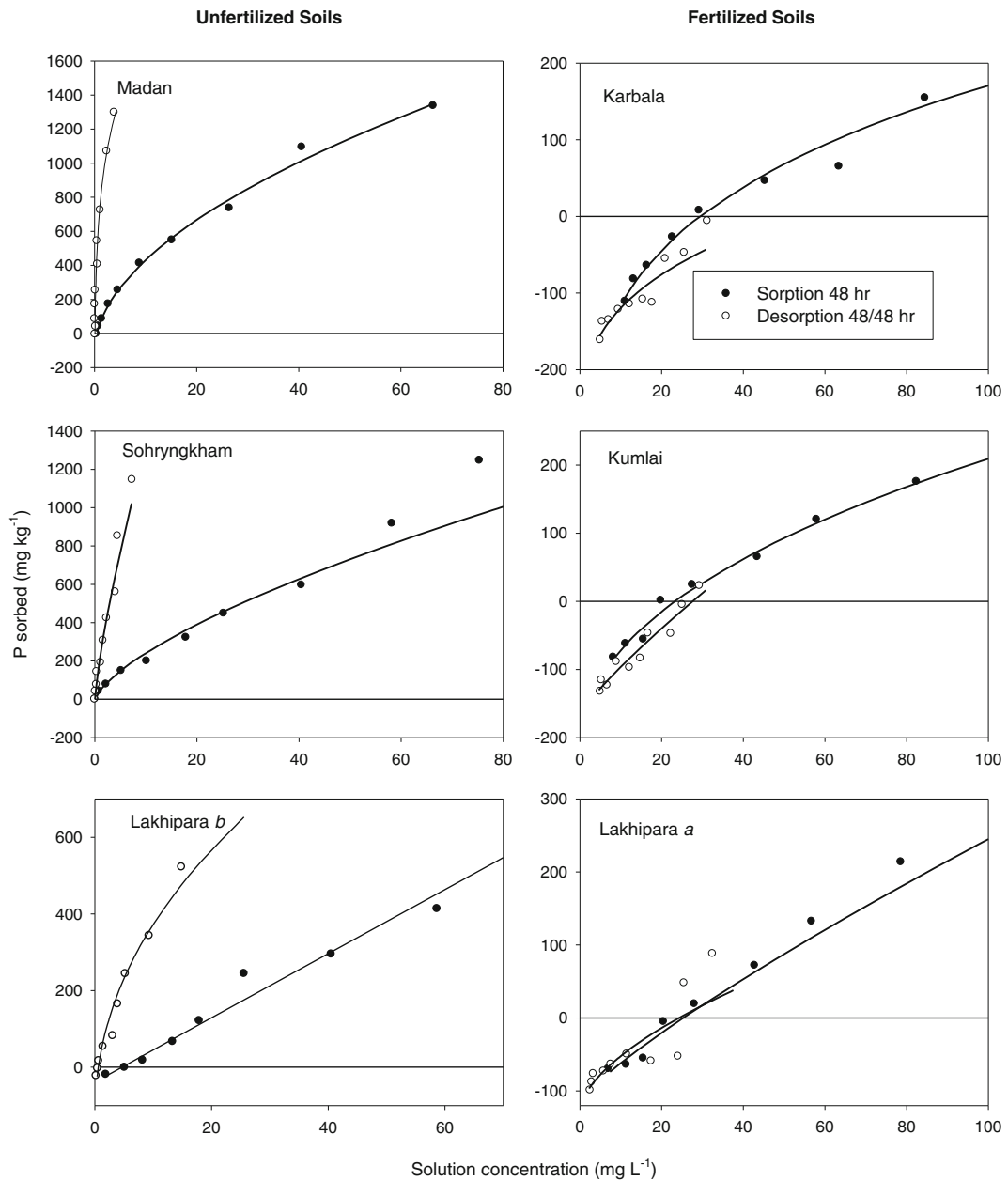


Fig. 11 Comparison of the sorption and desorption behaviour for three previously unfertilized soils (*left*) with that for three previously fertilized soils (*right*). The fertilized soils were collected from tea estates and had been fertilized for about a century.

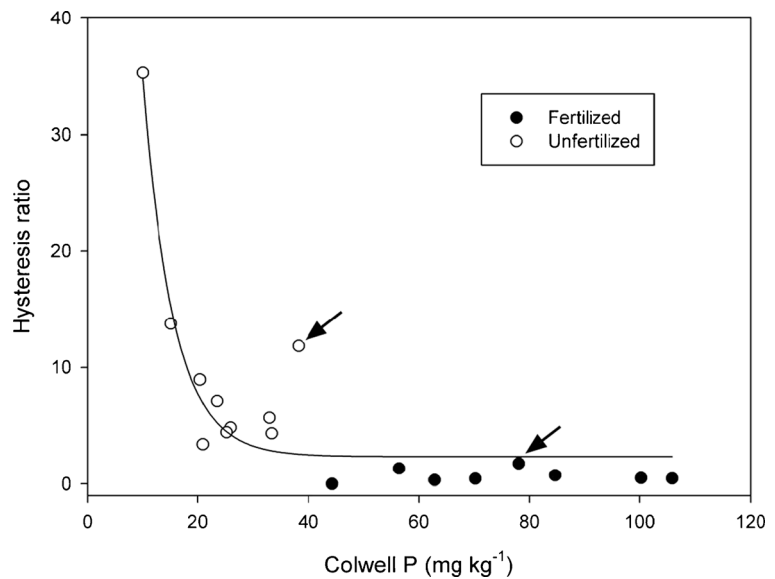
Desorption was measured at 48 h after 48 h sorption. The Lakhipara *b* soils was collected from a roadside in the tea estate where Lakhipara *a* was collected. From Barrow and Debnath (2014)

produces increased effectiveness of phosphate (Fig. 9). Thus, while penetration of phosphate ions decreases the effectiveness of the initial application, it should increase the effectiveness of subsequent applications. This hypothesis, which I think should be called the first phosphate-sparing effect of phosphate fertilisation has,

to my knowledge, only been tested once and is strongly supported (Fig. 10).

In a typical sorption/desorption experiment, phosphate solutions are mixed with a sample of soil for a specified period. After centrifuging, the supernatant may be removed and replaced with a zero phosphate solution

Fig. 12 Relationship between the hysteresis ratio and the phosphate P extracted by the Colwell reagent. The hysteresis ratio is an indication of the extent to which the desorption curves follow the sorption curves. A value of unity would indicate coincidence of the two curves. Values for the Lakhipara *a* soil (fertilized) and Lakhipara *b* soil (unfertilized) (see Fig. 11) are indicated by arrows. From Barrow and Debnath (2014)



and mixing is continued for an equal period. Plots of solution concentration against the amounts of phosphate remaining sorbed may not coincide. At first, such observations were described as “irreversible adsorption”, but, as is argued above, such terminology is an oxymoron. A more appropriate term is “hysteresis”. When hysteresis occurs, it is a consequence of the diffusive penetration of phosphate into the particle (Barrow 1983). The amount of hysteresis is therefore a convenient way of measuring the amount of diffusive penetration. The hysteresis index used by Barrow and Debnath (2014) is the ratio of slopes of the desorption and sorption curves: a large value means that there was much hysteresis; a value of unity means that there was no hysteresis. The left-hand side of Fig. 11 demonstrates typical observations for low-phosphate soils: there is appreciable hysteresis. However, the right-hand side of Fig. 11 shows that on fertilized soils there was little hysteresis. Furthermore, over the range of soils tested, the lower the phosphate status the greater the hysteresis (Fig. 12).

Diffusive penetration does not continue forever. It should be expected that it would eventually stop and that the decrease in effectiveness with time would also stop. There should then be no need to supply any more phosphate in a given year that was removed in the previous year. This is the second phosphate-sparing effect of phosphate fertilization. As far as I am aware, this prediction has not yet been tested.

Conclusions

The decline in the effectiveness of phosphate fertilizer with time is almost always viewed in negative terms as phosphate “fixation” and as a “problem” to be prevented, or circumvented, but without a great deal of success. However this decline is caused by penetration of phosphate *ions* into the soil particles. Because they are ions, the negative charge on the soil particles increases and the buffering capacity decreases. Consequently a greater proportion of soil phosphate is in the solution phase; diffusion to plant roots is faster; fertilizers are therefore more effective. This is the first phosphate-sparing effect of phosphate fertilization.

The second phosphate-sparing effect occurs because soil particles are not infinite sinks. Penetration has an end point. In this respect, accumulation of negative charge may be a more important limitation to the process rather than ‘saturation’ of a particle (Barrow 1983). Once a soil has reached the stage in which penetration is no longer important, there should be no need to supply any more phosphate than was removed in the previous year.

The best solution to the supposed phosphate problem is to apply phosphate rationally taking due regard of the phosphate-sparing effect of previous applications.

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