

The Relationship between Phosphate Adsorption and Soil Organic Carbon from Organic Matter Addition

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ABSTRACT

The Relationship between Phosphate Adsorption and Soil Organic Carbon from Organic Matter Addition (FH Yusran): The application of organic matter (OM) can increase soil phosphorus (P) availability via soil mineralisation. In lateritic soils, however, soluble organic carbon (OC) from OM may also reduce phosphate adsorption capacity, a process that also releases P in soil solution. In these soils, competitive adsorption could be dominant compared to mineralisation. The main objectives of this study were to study phosphate adsorption in three lateritic soils which have been treated with different types and amounts of organic amendment, and had intrinsic OC removed by combustion. The adsorption isotherms showed that OM addition could reduce phosphate adsorption and that this reduction could last up to nine months after application. Lucerne hay was more effective than peat and wheat straw additions in reducing phosphate adsorption capacity. The bicarbonate phosphorus (BP) release through mineralisation occurred despite the increase of phosphate adsorption capacity due to the combustion of soil samples. Peat treatment was predicted to be more effective in creating organo-metal complexes with Al and Fe. Overall, mineralisation from added organic amendment was effective in minimising P adsorption in lateritic soil.

Keywords: Lateritic soils, phosphate adsorption, soil organic carbon

INTRODUCTION

The addition of OM to soils may increase phosphate availability by decomposition and mineralisation of organic-P (OP), or by abiotic processes such as ligand-exchange effects on phosphate adsorption. It is difficult to separate the effects of biotic and abiotic processes on the release of phosphate. This article describes experimental work which investigated the direct effect of OM addition on adsorption of phosphate in four types of lateritic soils.

The OM content of highly weathered soils has been shown to be negatively correlated with phosphate adsorption capacity. For example, Singh and Gilkes (1991) found a negative correlation between phosphate sorption by soil (quantified by the Freundlich K_F parameter) and soil OM (SOM) content for 97 mainly highly weathered soils of Western Australia. Based on Freundlich K_F values, Dubus and Bacquer (2001) also found a significant negative

correlation between phosphate sorption and SOM content.

Three abiotic mechanisms are proposed to explain the role of SOM increase P availability in soils (Iyamuremye and Dick 1996). First, soluble organic molecules may specifically adsorb to soil minerals by ligand exchange in competition with phosphate (Erich *et al.* 2002; Ohno and Crannel 1996; Singh and Jones 1976). Second, the soluble OM may react with bound Al^{3+} or Fe^{3+} at the surface of mineral phase to form soluble complexes of these elements and release phosphate which was previously sorbed or which was present as insoluble Al and Fe-phosphate (Haynes and Mokolobate 2001). Third, OM may be sorbed to soil particles at non-specific sorption sites, resulted in higher negative charge of the particles (Haynes and Naidu 1998; Naidu *et al.* 1997). This process reduces the electrostatic attraction of phosphate and decreases phosphate ions activity at the reactive surface. All three abiotic mechanisms may occur simultaneously, and in combination with biotic release of phosphate by mineralisation.

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Results from previous experiments (Yusran *et al.* 2005; Yusran 2008) showed that phosphate, extracted with 0.5 M NaHCO₃ pH 8.5 (BP), was significantly higher in soil amended with OM than in unamended soil, especially from green manure amendment (lucerne hay) followed by peat. The effect of soluble OM on phosphate release from Oxisols has been found to be transient (Afif *et al.* 1995). The findings in this work therefore lead to the question of whether peat (the passive pool) would have a longer abiotic effect due to its resistance to decomposition, and possible slow release of soluble organic ligands which can compete for adsorption sites with phosphate. This issue is poorly understood. The abiotic effects of OM additions could be determined by analysing phosphate adsorption isotherms for soil incubated with lucerne hay and peat for varying lengths of time up to one year. Organic matter addition also released P to the soil solution as a result of biotic mineralisation process (Cobo *et al.* 2002; Kwabiah *et al.* 2003; Lupwayi *et al.* 2003). These two mechanisms maybe particularly difficult to separate in soils with high sorbing capacity for phosphate, such as lateritic soils with high sesquioxide or 1:1 clay content. By (i) observing net release of extractable phosphate (Yusran 2008) and (ii) determining phosphate adsorption isotherm, the two processes (inorganic effects on adsorption, and mineralisation of OP) can be separated as being more and less important for releasing soluble phosphate into soils.

In summary, it is expected that OM addition will reduce phosphate adsorption in soils, and this hypothesis will be addressed by determining phosphate adsorption at a range of OM application rates. This work will also test the novel hypotheses that: (i) any reduction in phosphate adsorption will be temporarily depending on the persistence of OM added (for example, peat is expected to reduce phosphate adsorption for longer than lucerne hay), and (ii) newly added OM will decrease phosphate adsorption, in the short-term, more than pre-existing SOM.

The objectives of this experiment were therefore: (i) to determine the effect of OM application rate on phosphate adsorption to soil, (ii) to determine the interactive effect of (a) application of different types of OM (varying in persistence following application) and (b) organic amendment–soil incubation time on phosphate adsorption to soil, (iii) to determine the effect of pre-existing SOM and newly added organic amendments on PO₄-P adsorption in soils, (iv) to study

the effect of phosphate adsorption and P mineralisation after OM addition on the process of bicarbonate-P release; and (v) to study the changes in dissolved organic-C (DOC) after OM treatment on closely related factors of phosphate adsorption in soil, *e.g.* Al, Fe, and pH.

MATERIALS AND METHODS

Design of the Experiment

Soil samples for the experiments were from four lateritic soils (two Oxisols, an Ultisol, and a deep regolith material or subsurface soil). The experiments were divided into three subsets which had been subjected to the following treatments: (i) soil incubation with peat, wheat straw, and lucerne hay treatment at 80 Mg ha⁻¹ for different times (3, 6, 9, and 12 months), (ii) different OM levels (40, 80, 120, and 160 Mg ha⁻¹) for peat, wheat straw, and lucerne hay, incubated with soil for six months, (iii) type of SOM (existing and new). The existing refers to inherent SOM plus additional fresh OM as of point 1. Whilst new refers to equal (in OC concentration) replacement of SOM plus additional fresh OM.

The first subset of this experiment was in a factorial design experiment with two factors: incubation time (3, 6, 9, and 12 months), and source of OM (nil (control), peat, wheat straw, and lucerne hay). The second subset was also factorial with two factors: source of OM (nil (control), peat, wheat straw, and lucerne hay), and OM levels (40, 80, 120, and 160 Mg ha⁻¹). The third subset was a factorial design with three factors: soils (an Ultisol, an Oxisol, and a subsurface soil), type of SOM (existing and new), and OM source (peat and lucerne hay).

The preparation for the first and the second subset of the experiment samplings and related data are described in Yusran (2008). Statistical analyses were performed either with GenStat (Payne *et al.* 1987) for analyses of variance, or SPSS (Coakes 2001) for regression analyses.

Phosphate adsorption isotherm was measured using methods of Morel *et al.* (1996) and Erich *et al.* (2002). Two common adsorption isotherm equations, Langmuir and Freundlich, were used to fit the phosphate adsorption data. The Langmuir equation, which is normally written as (Barrow 1978):

$$x = \frac{(K_L x_m c)}{(1 + K_L c)} \dots\dots\dots 1$$

becomes a linear equation when rearranged:

$$\frac{c}{x} = \frac{1}{K_L x_m} + \frac{1}{x_m} c \dots\dots\dots 2$$

where c = concentration of P in equilibrium solution (mg P mL⁻¹), x = amount of P sorbed (mg P g⁻¹ soil), x_m = sorption maximum (mg P g⁻¹ soil), and K_L = coefficient related to bonding energy. A plot of c/x versus c therefore has a slope of $1/x_m$ and intercept of $1/K_L x_m$.

The Freundlich equation, which is normally written as (Barrow 1978):

$$x = K_F c^b \dots\dots\dots 3$$

can be log-transformed to give simple linear equations:

$$\log x = \log K_F + b \log c \dots\dots\dots 4$$

where c = P concentration in equilibrium solution (g P mL⁻¹), x = amount of P sorbed (mg P g⁻¹ soil), K_F and b = constants with K_F being a a measure of adsorption surface and b relating to the energy of adsorption (Barrow 1978). A plot of $\log x$ versus $\log c$ has a slope b and intercept $\log K_F$.

Due to their simplicity, *i.e.* only two adjustable parameters, the Langmuir and Freundlich equations do not always fit experimental data well. The Brunauer-Emmett-Teller (BET) equation was applied to take into account the plateaus, points of inflection, and maxima observed in some data (Giles *et al.* 1974; Hinz 2001). Unlike the Langmuir and Freundlich equations, which are classified as high affinity adsorption equations, the BET is an adsorption equation that can explain sigmoidal isotherms, as observed for some data from this experiment.

The equation is usually written (Burau and Zasoski 2002):

$$x = \frac{K_{BET} c x_m}{(c_s - c) \left(1 + (K_{BET} - 1) \left(\frac{c}{c_s} \right) \right)} \dots\dots\dots 5$$

Like the other two equations, the BET equation has a linear form after algebraic rearrangement:

$$\frac{c}{c_s - c} \cdot \frac{1}{x} = \frac{1}{K_{BET} x_m} + \left(\frac{K_{BET} - 1}{K_{BET} x_m} \right) \left(\frac{c}{c_s} \right) \dots\dots 6$$

where c = P concentration in equilibrium solution (g P mL⁻¹), c_s = the concentration of the solute (*i.e.* soil),

x_m = adsorption maximum (mg P g⁻¹ soil), and K_{BET} = a constant for energy of interaction with soil particles (Burau and Zasoski 2002). A plot of $c/(c_s - c)(1/x)$ versus $c/(c_s - c)$ therefore has a slope $(K_{BET} - 1)/(K_{BET} x_m)$ and intercept $1/(K_{BET} x_m)$.

Statistical Analysis

In order to determine the statistical significance of differences between treatments, linear regression analysis with grouped data was performed on data transformed to give linear Langmuir or Freundlich relationships, as described above. This procedure allowed statistical significance to be assessed without replication of points on adsorption isotherms.

RESULTS AND DISCUSSION

Based on the values of adsorption isotherm parameters for the Langmuir and Freundlich equations (Table 1 and Table 2), the data presented support the hypothesis that organic amendments decreased the soils' affinity (Langmuir K_L) and capacity (Freundlich K_F) for phosphate adsorption. These results are in agreement with Iyamuremye *et al.* (1996) and Hue *et al.* (1994) that addition of organic amendments can significantly decrease phosphate adsorption capacity of the soil.

Although wheat straw application reduced phosphate adsorption as also observed by Reddy *et al.* (2001), peat and lucerne hay applications reduced phosphate adsorption for longer (up to nine months after treatments). For peat and lucerne hay applications nine-month incubation was significantly greater ($p \leq 0.01$) than the three-month incubation.

Peat persisted longer than lucerne hay in soil (Yusran *et al.* 2002; Yusran, 2008), but lucerne hay produced more DOC than other sources (*i.e.* peat and wheat straw) which would be expected to decrease phosphate adsorption (Erich *et al.* 2002). In addition, the nature of soluble organic matter from peat is likely to be relatively recalcitrant and to have a more long-lasting effect in blocking phosphate adsorption sites, whilst the abundant simple organic acids originating from plant materials are easily degradable. It is therefore assumed that peat application decreased phosphate adsorption, at least partly, by mechanism other than competitive ligand exchange with DOC.

The reduction of phosphate adsorption by the organic amendments persisted for at least 12 months following application, shown by the continued difference between treatments and controls (*e.g.*

Table 1. The effect of organic matter sources (80 Mg ha⁻¹) and incubation time on phosphate adsorption parameters based on Langmuir and Freundlich equations.

Organic matter sources	Langmuir			Freundlich		
	K _L	x _m	R ²	b	K _F	R ²
Three months						
Control	0.7934	1094.1	0.997	0.41196	457.9	0.912
Peat	0.6068	1150.8	0.993	0.44838	424.4	0.949
Wheat straw	0.5894	1018.3	0.997	0.37781	387.2	0.967
Lucerne hay	0.4343	1065.0	0.996	0.42039	347.2	0.957
Six months						
Control	0.6869	1017.3	0.994	0.36010	414.7	0.985
Peat	0.6875	1021.5	0.996	0.36998	412.9	0.970
Wheat straw	0.4476	979.4	0.993	0.36612	342.1	0.990
Lucerne hay	0.4087	940.7	0.995	0.35026	325.5	0.991
Nine months						
Control	0.5981	1035.2	0.984	0.35554	406.5	0.912
Peat	0.4077	995.0	0.992	0.37298	338.5	0.952
Wheat straw	0.3761	1078.8	0.980	0.42485	331.3	0.974
Lucerne hay	0.2233	962.5	0.992	0.40546	246.4	0.975
Twelve months						
Control	0.6751	1074.1	0.995	0.40017	423.8	0.983
Peat	0.5086	1124.9	0.994	0.44033	385.7	0.986
Wheat straw	0.5359	1038.4	0.996	0.39345	376.3	0.976
Lucerne hay	0.4524	1012.2	0.993	0.38131	349.1	0.991

Table 2. The effect of organic matter sources and levels on phosphate adsorption parameters at six months incubations time based on Langmuir and Freundlich equations.

Organic matter sources	Langmuir			Freundlich		
	K _L	x _m	R ²	b	K _F	R ²
40 Mg ha⁻¹						
Control	0.9764	1005.2	0.989	0.33493	467.8	0.972
Peat	0.7811	1049.3	0.992	0.36795	445.9	0.990
Wheat straw	0.7513	1000.0	0.990	0.34062	426.8	0.989
Lucerne hay	0.6391	956.9	0.989	0.30622	402.5	0.991
80 Mg ha⁻¹						
Control	0.8797	1036.3	0.987	0.35414	462.9	0.975
Peat	0.8077	1009.1	0.991	0.34112	440.6	0.994
Wheat straw	0.5657	956.0	0.993	0.33173	375.9	0.995
Lucerne hay	0.4670	967.1	0.979	0.32035	365.5	0.959
120 Mg ha⁻¹						
Control	0.8029	1006.0	0.993	0.33969	439.0	0.969
Peat	0.7898	1008.1	0.991	0.34005	437.7	0.980
Wheat straw	0.5095	967.9	0.987	0.33328	364.4	0.988
Lucerne hay	0.4695	922.5	0.984	0.30698	355.6	0.984
160 Mg ha⁻¹						
Control	0.8603	1027.8	0.993	0.35592	454.0	0.973
Peat	0.7704	990.1	0.993	0.33136	428.5	0.990
Wheat straw	0.4651	956.9	0.986	0.34909	346.4	0.981
Lucerne hay	0.4023	925.1	0.979	0.30390	343.5	0.983

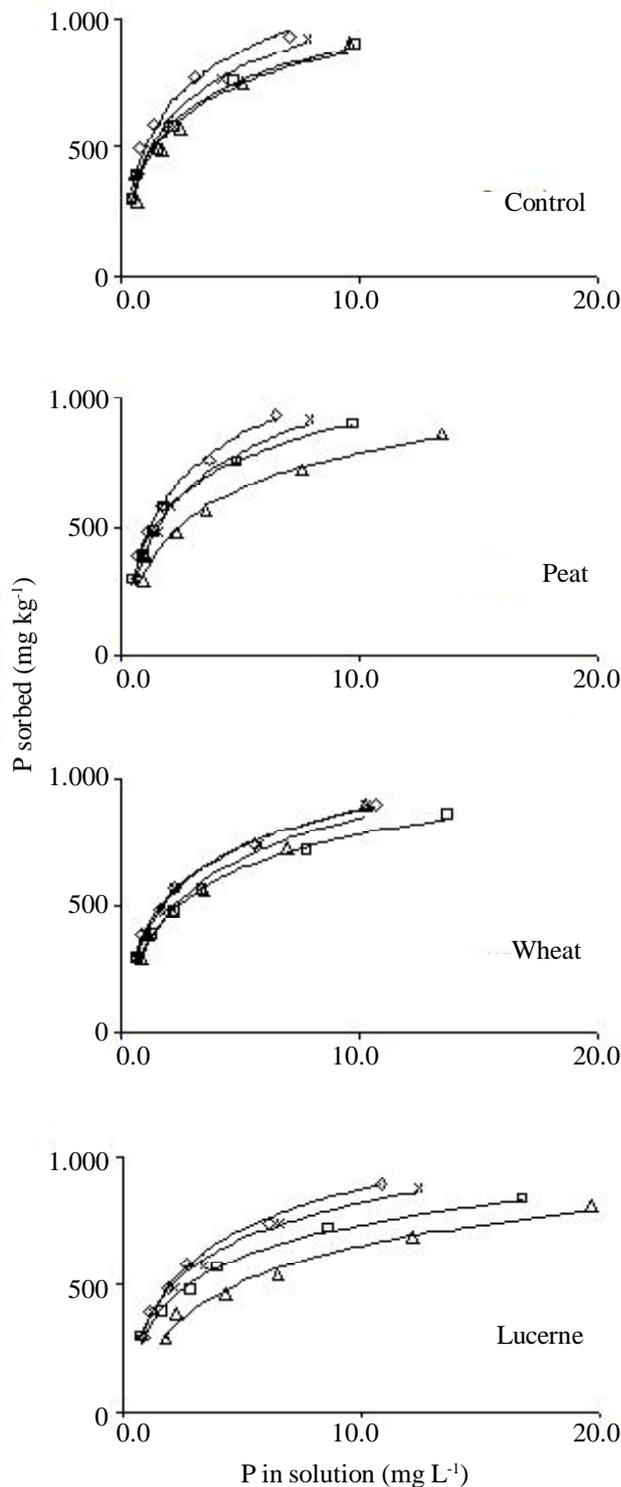


Figure 1. The effect of incubation time and organic matter sources on phosphate adsorption at 80 Mg ha⁻¹ organic matter in ‘Balkuling’ Oxisol. \diamond = three months, \square = six months, \triangle = nine months, and \times = twelve months incubation. Lines are a logarithmic trend of observations and a visual guide only.

Figure 1). This effect was observed despite the organic amendments becoming less effective at reducing phosphate adsorption with increasing time of incubation in soil. These conclusions are supported by the magnitude of the x_m parameter of the Langmuir equation and K_F of the Freundlich equation for every organic matter source throughout the incubation time (Table 1). The x_m parameter was decreasing in value across incubations and increased again after nine month incubation.

The hypothesis that newly added OM would decrease phosphate adsorption, in the short-term, more than pre-existing SOM was not supported by the data in this experiment. A number of factors interacted to affect phosphate adsorption by soils in this highly complex the experiment, with no clear effect of OM addition, as described below.

Contradictory results were obtained on the effect of new SOM compared with existing SOM. Instead of dissolved phosphate concentrations increasing due to addition of new soil organic matter as predicted; these concentrations decreased indicating an increase in phosphate adsorption (Figure 3). The Langmuir equation, which fit the adsorption data from the first two subsets of data, was not suitable. A more complex equation (the BET isotherm equation) was needed in order to explain the sigmoidal curvature observed in phosphate adsorption for soil subjected to the treatments in this experimental subset (Hinz 2001).

Combustion of soil samples prior to new SOM application might have altered some physical and chemical characteristics of the soils which affect adsorption of phosphate. Even though Kang and Sajjapongse (1980) and Giovannini *et al.* (1988) found that a 450°C temperature had a minimal effect on other physical and chemical properties of soils such as porosity, textural class, and soil acidity, however, a temperature up to 160°C will almost certainly change the microbial community structure (Pietikainen *et al.* 2000). Moreover, heating up soil to around 300°C will reduce the amount of SOM, as well as CEC and exchangeable bivalent cations like Ca and Mg (Badia and Marti 2003; Brais *et al.* 2000; Forgeard and Frenot 1996). High temperature can change physical and chemical properties of the clays and oxides. According to Kang and Sajjapongse (1980), high temperature up to 500°C altered some soil chemical and physical properties. Giovannini *et al.* (1988) found, however, that temperatures of 460°C or more need to be attained to change the physical properties of the soil such as particle size distribution, plasticity,

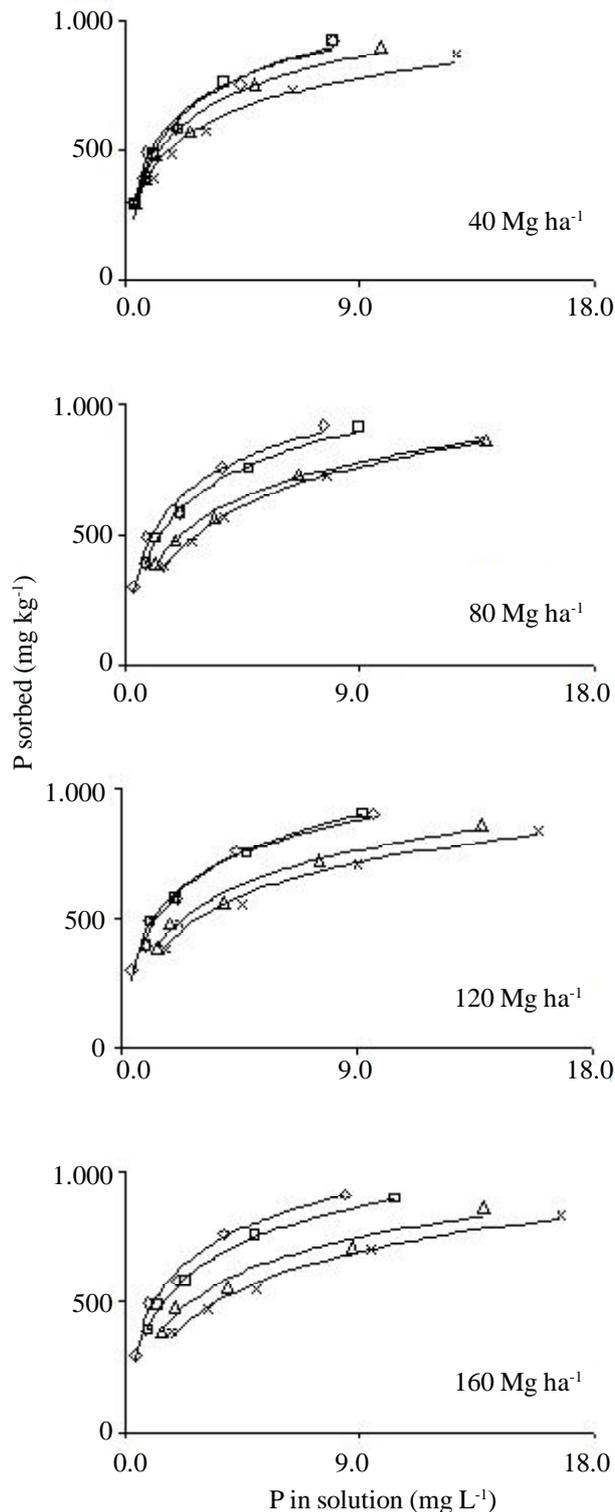


Figure 2. The effect of organic matter sources and their levels on phosphate adsorption at six-month incubation time in ‘Balkuling’ Oxisol. \diamond = control, \square = peat, \triangle = wheat straw, and \times = lucerne hay. Lines are a logarithmic trend of observations and are a visual guide only.

and aggregate stability. In this experiment, heating soil to 450°C changed some parameters related to phosphate adsorption such as oxalate extractable-Al and Fe contents.

Subsurface (regolith) soil and the Ultisol appeared to change phosphate adsorption capacity more than the Oxisol (Figure 2). This may be because the increases in extractable-Al and Fe due to soil combustion were more pronounced in the subsurface soil (Al_{ox} increased $\sim 10\times$, Fe_{ox} increased $\sim 2.5\times$) and the Ultisol (Al_{ox} and Fe_{ox} increased $\sim 2.5\times$) than in the Oxisol (Al_{ox} increased $\sim 4\times$, Fe_{ox} did not increase) due to dehydration and dehydroxylation. This phenomenon was also observed by Gao *et al.* (2002) as they partially removed SOM from paddy soils. In line with these results, Su *et al.* (2001) and Singh and Gilkes (1991) also found a significant positive correlation between amorphous Fe-oxides and phosphate adsorption in soils. In soils with 1:1 lattice clays, phosphate adsorption is mainly attributed to the hydrous oxides of Al and Fe, as well as occurring on the clay itself (Dubus and Becquer 2001; Sanyal *et al.* 1993).

The BET equation could explain the sigmoidal adsorption isotherms due to the above combustion. However, adsorption parameters in the original curvatures of adsorption (the Langmuir and Freundlich equation) appeared in negative slopes in the BET equation (Figure 2) to make numerical comparison impossible. Nevertheless, the decreasing trends of adsorption can be seen in Figure 3.

It is well known that the application of manure and organic materials reduces phosphate adsorption capacity in soils (Berton and Pratt 1997; Hundal *et al.* 1988). In order to see the importance of phosphate adsorption in releasing IP into soil solution we reviewed some BP data from the previous experiment (Yusran 2008). New SOM increased BP content, especially peat and lucerne hay in the Ultisol and the Oxisol (Yusran, 2008), despite increasing phosphate adsorption capacity due to the combustion of the soils (Figure 3) as also indicated by the increase of K_{BET} in Table 3. In other words, changes in phosphate adsorption appear to be less important as a BP release mechanism when soils are treated with OM. According to Osiname *et al.* (2000) a sizable proportion of P released from OP mineralisation might be used to satisfy phosphate adsorption capacity of the soils. In applied practices, however, P mineralisation from OM should be accounted for when the adsorption isotherm technique is applied to

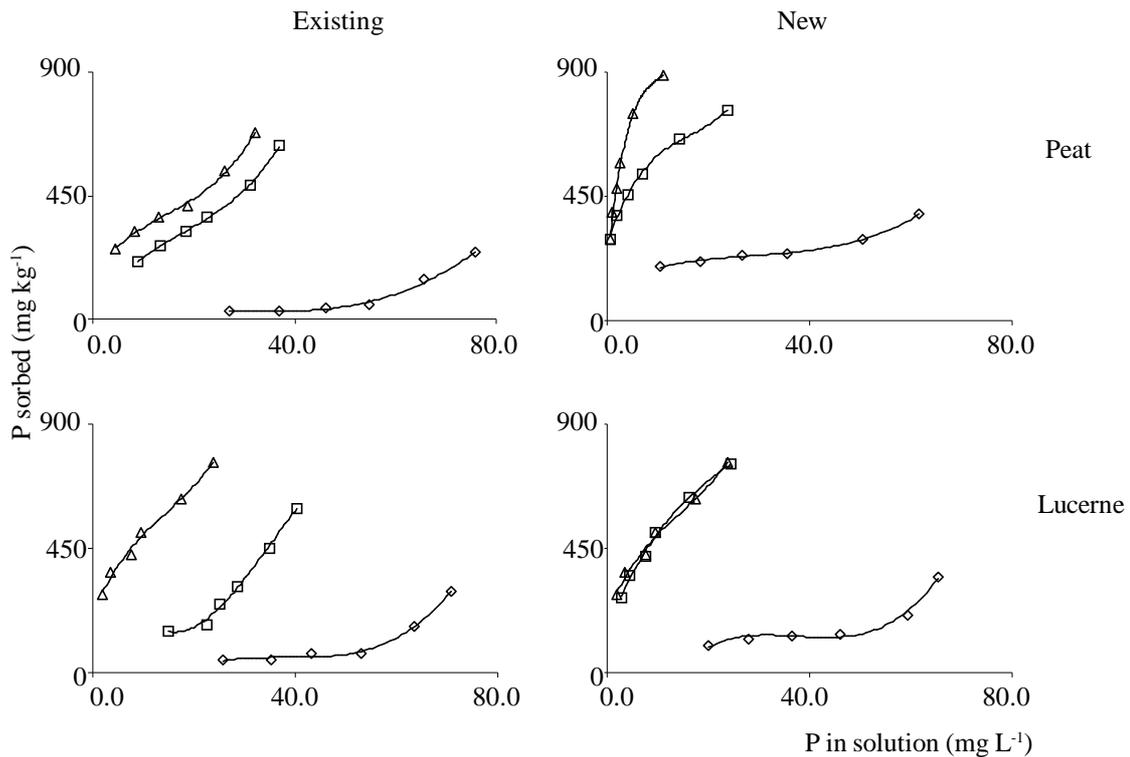


Figure 3. The effect of soils, existing and new soil organic matter on phosphate adsorption in peat and lucerne hay treatments at Mg ha⁻¹ and six-month incubation time. \diamond = subsurface soil, \square = Ultisol, and \triangle = Oxisol. Lines are polynomial trend for observations and are a visual guide only.

soils that have been amended with organic materials (Berton and Pratt 1997). In this experiment, although combustion plus treatment of soils with new SOM increased phosphate adsorption capacity, the BP release to soil solution showed no sign of decreasing. Contributions from incomplete oxidation of organic-P during combustion and the changes in acid solubility of soil inorganic-P (Anderson 1960; Condron *et al.* 1990; Williams *et al.* 1970) as a result of combustion might also have occurred in soil samples.

Increasing the level of OM in all treatments (*i.e.* peat, wheat straw, and lucerne hay) did not show the same trend in phosphate adsorption for all OM sources. Wheat straw and lucerne hay, according to their values of K_L in Table 2, consistently decreased phosphate sorption as the level of their applications increased. Peat, however, showed almost similar K_L values as the level of application increased. In other words, increasing level up to 180 Mg ha⁻¹ was ineffective for the purpose of decreasing phosphate adsorption in an Oxisol, when peat was applied.

Decreasing phosphate adsorption due to the increasing level of organic matter addition may also be

explained as a consequence of P content in their biomass. When phosphate is released during decomposition of organic matter, it is then rapidly adsorbed onto sorption sites. Therefore, more adsorbed P is present before the equilibration by CaCl₂ solution (Haynes and Mokolobate 2001; Iyamuremye and Dick 1996; Li *et al.* 1990). As a result, there is less phosphate adsorption capacity of the soil with respect to subsequently added phosphate.

Different types of OM had different effects on phosphate adsorption. Lucerne hay decreased phosphate adsorption more than wheat straw and wheat straw decreased phosphate adsorption more than peat (Table 1). Comparable values in Table 1 (row six months) and Table 2 (row 80 Mg ha⁻¹) appeared to be slightly different due to different sub samplings. However, declining trends in parameter K_L , x_m , b and K_F were similar to the effect of different OM sources. At the same time, increasing the amount of OM application also reduced phosphate adsorption more, indicating similar trend of declining phosphate adsorption capacity. Even at 180 Mg ha⁻¹, the order of effect was peat < wheat straw < lucerne hay. The

Table 3. The effect of soil organic matter type (existing and new) and soil types (subsurface soil, Ultisol, and Oxisol) on phosphate adsorption parameters based on fitting data to the Brunauer-Emmett-Teller equation.

Organic matter source	Soil organic matter					
	Existing			New		
	x_m	K_{BET}	R^2	x_m	K_{BET}	R^2
Subsurface soil						
Peat	-70	-8.4	0.543	408	49.0	0.885
Lucerne hay	-132	-7.6	0.467	1111	4.5	0.047
Ultisol						
Peat	1351	18.5	0.666	767	34.3	0.986
Lucerne hay	-625	-16.0	0.524	991	12.1	0.983
Oxisol						
Peat	820	61.0	0.858	998	501.0	0.995
Lucerne hay	893	56.0	0.739	903	158.1	0.959

Table 4. Correlation between inorganic phosphorus, dissolved organic carbon, extractable aluminium, and extractable iron in uncombusted soils treated with peat and lucerne hay treatments. Only significant correlations are presented.

	Existing SOM + peat			Existing SOM + lucerne hay		
	BP	DOC	Al	BP	DOC	Al
DOC				0.63**		
Al	-0.83**			-0.72**	-0.69**	
Fe	-0.64**	-0.44*	0.44*	-0.61**	-0.82**	0.56**

SOM = soil organic matter, DOC = dissolved organic-C, BP = bicarbonate-P. * represents a significant ($p \leq 0.05$) and ** a highly significant ($p \leq 0.01$) correlation.

fact that peat increased BP content in soils (Yusran *et al.* 2002; Yusran 2008) higher than wheat straw application again suggests that phosphate adsorption was not the dominant factor affecting BP release after peat addition. Though peat has lower P content than wheat straw (Yusran 2008), it could provide more BP if it is applied to soil. Peat probably could facilitate OP transformation to IP better than wheat straw by other mechanisms, except decreasing phosphate adsorption.

CONCLUSIONS

Organic matter addition could reduce phosphate adsorption and the effect could last up to nine months after application. Lucerne hay was more effective than peat and wheat straw addition in reducing

phosphate adsorption capacity. Langmuir equation fitted better than Freundlich in describing phosphate adsorption in this experiment.

Soil combustion in new SOM addition treatments increased phosphate adsorption capacity, especially in the Oxisol and Ultisol. At the same time, only the BET equation could describe the sigmoidal effect of treatments on phosphate adsorption. Consequently, comparing the effect of existing and new SOM treatment by comparing equation parameters was impossible.

The new SOM addition released more BP into soil solution. The experiment revealed the reduction of phosphate adsorption occurred during the first year of OM applications and long term release of BP in soil contributed to mineralisation, P hydrolysis, or P transformation.

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