

PHOSPHORUS SORPTION FOR ON-SITE WASTEWATER ASSESSMENTS

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Abstract

Of all the likely sources of contamination from effluent application to land, whether from single on-site systems or from large urban sewage treatment works, phosphorus (P) is treated as the demon. Its reputation is associated with its high correlation with *cyanobacteria* (blue green algae) in water systems. In soil systems, mechanisms reduce the movement of phosphorus away from the disposal area, minimising losses through percolation or lateral flows and conserving a scarce resource.

The concentration of phosphorus in domestic effluent is highly variable and the various proportions of soluble inorganic and insoluble organic P vary both within and between wastewater systems. While average values of effluent P may be derived to use in nutrient balances, the variable P-sorption (adsorption) capacity of the soil is often incorrectly assessed from inappropriate analyses or misinterpretation of the impact that P-sorption may have on retaining a significant proportion of the P in the effluent. Even measuring P in the soil is open to significant differences between methods and across laboratories.

This paper examines the various laboratory methods available to the soil scientist to quantify the ability of a soil to immobilise P from effluent and how this component should be treated in subsequent nutrient balances.

Keywords

adsorption, immobilisation, nutrient balance, P-isotherm, P-sorption, phosphorus, wastewater,

1 Introduction

Many constituents of domestic wastewater, and the effluent from the various treatment devices employed to degrade raw wastewater, are potential pollutants of both on-site and off-site environments when the concentration exceeds the ability of the landscape to adequately capture and confine the chemical. Phosphorus is one such element which, when in water bodies (natural and artificial) may give rise to *cyanobacteria* (blue green algae) blooms, leading to significant loss of water quality.

Phosphorus in domestic wastewater results from the human diet and food preparation, and chemicals used for general cleaning (laundry detergents, cleaning agents). Typical household levels of total phosphorus (TP) in wastewater have been recorded locally by the author as 3-30 mg L⁻¹ (Patterson, 1994) and overseas by Crites & Tchobanoglous between 12-20 mg L⁻¹. Through wise choice of laundry products, up to 30% of the total P load from a dwelling can be prevented from entering the wastewater (Patterson, 2000).

Sources of P in the human diet are given in Table 1, indicating the high values from common foods. When the domestic wastewater system removes human excrement from the house, most of the components eventually end in the wastewater system, either as solids or liquids.

Table 1. Sources of Chemicals in General Foodstuffs

Food	Per 100 g edible portion				
	Protein g	Fat g	Calcium mg	Phosphorus mg	Sodium mg
whole milk	3.4	3.9	118	99	58
cheese, cheddar	26.1	33.2	860	506	610
broccoli, boiled	3.1	0.3	98	61	10
potatoes, baked	2.3	10.1	11	63	7
mushrooms, canned	1.5	0.2	7	110	400
peas, green, boiled	5.4	0.4	20	100	1
hamburger with onion	15.3	21.0	18	141	2040
steak, rump, medium	24.5	25.4	17	240	93
corned beef, boiled	20.9	28.4	13	193	1740

Source: Patterson, 1998

The phosphorus load from the human diet results in both inorganic and organic P compounds in the septic tank (or AWTS) effluent. The contribution by laundry products to the total P load is in the form of sodium tripolyphosphate, a form that can only be measured in the laboratory by determining total phosphorus after acid digestion. Laundry products contribute up to 50 mg L⁻¹ in the water discharged from a washing machine's full load (Patterson, 2000).

The behaviour of phosphorus in water is significantly different from its actions in soil. In water, the total phosphorus (TP) load is the sum of the inorganic P in its various dissolved forms, the insoluble organic P (living and detritus) and the inorganic P attached to colloidal matter. The latter may later flocculate and settle as sediment. Phosphorus in the water column is mostly in soluble form, with a small proportion as organic P. It is only the soluble inorganic P (as orthophosphate) that can be assimilated by the aquatic plants and animals. Some soluble P will combine with colloidal material in the water and settle to the bottom of the water body. Thus a measure of the inorganic P in the water column is a measure of the potential for plants and animals to uptake P for their own physiological purposes. The TP measurement allows the calculation of the organic fraction, that part of the total phosphorus load held in organic molecules not available for bio-assimilation, albeit a potential source of P, and any P adsorbed onto suspended matter. In wastewater and effluent, TP analysis also measures complex inorganic P such as tripolyphosphate from laundry detergents.

In soil, inorganic and organic P exist, but not simply as dissolved and organic components. The soil water solution is that small amount of water held around the soil particles in one of two forms – available water and unavailable water, depending upon the energy capacity of the plant to absorb that water. The chemical quality of these two forms of soil water (there will be no difference in quality between the two forms) will be related to the chemicals attached or trapped within the interstices of the soil matrix. A soil with low available P will have a low concentration of P in the soil water, thus limiting potential absorption by plants or loss in drainage water. As the plants take up P, more P will pass from the readily available adsorbed P into the soil water solution, reducing the reserve of P held in the soil.

The available P in the soil solution is inorganic P, usually orthophosphate. The reserve of inorganic P adsorbed to the soil minerals is referred to as sorbed P. Other reserves of P are held in organic molecules which must decompose to release inorganic P. Tisdale *et al.*, (1985) state that one half to two thirds of TP in soil is organic. They also suggest that if the carbon to inorganic P ratio is less than 200:1, then mineralisation of P occurs, while if the ratio is 300:1 immobilisation will occur. Such complex interactions in the soil create difficulties for simply measuring P and accounting for the P-sorption capacity. Measurements of P-sorption are made after equilibrating soil with inorganic P as orthophosphate. P-sorption measurements make no allowance for organic P in any form, nor assess the soil's ability to store organic P.

Barrow & Shaw (1979) suggest that solutions containing monovalent cations (Na^+ , K^+ , NH_4^+) desorb (release) more P than solutions containing divalent ions (Ca^{2+} , Mg^{2+}). The application of effluents high in monovalent cations may cause more P to move from the adsorption sites into the soil solution. This highlights potential difficulties with Na^+ in effluent.

Moody & Bolland (1999) state that soils with a high buffer capacity require more added P to attain a non-limiting soil solution P concentration than soils with a lower buffer capacity. It is important to understand the P-sorption capacity of the soil to estimate whether the soil solution will have sufficient P for normal plant functioning. Without adequate levels for plant uptake, loss by leaching will be insignificant.

This paper examines the P-sorption capacity and identifies inconsistencies between P-sorption tests by analysing 15 soils from different regions of NSW. It explains different methods of quantifying P-sorption, with particular reference to application of effluent to those soils. Methods in common use confuse the issue, rather than provide a simple quantification of a soil's ability to immobilise P.

2 Phosphorus Sorption

2.1 Tests and Indices

To date, quantification of P-sorption capacity has revolved around a need to assess and predict P in the soil solution for adequate plant growth in agriculture. The P-sorption methods outlined in Rayment & Higginson (1992) only evaluate P-sorption to levels of 150 mg kg^{-1} (Method 9I1) and 250 mg kg^{-1} (Method 9J1) – insignificant compared to the total P-sorption capacity of many soils. It is curious just how results from these methods can be used to predict P-sorption capacity to the 6000 mg kg^{-1} required for effluent application by the *Silver Book* (DLG, 1998). Since P-sorption only measures the orthophosphate uptake by soils when equilibrated at various solution strengths, the concentration of these solutions also impinges upon the amount of P sorbed or desorbed during the test.

In methods described in Rayment & Higginson (1992) and calculations provided in ANZECC & ARMCANZ (1999), the phosphorus buffer capacity (PBC) is determined by the slope of the line from a plot of P-sorbed against the \log_{10} of the concentration of the supernatant P solution. From this line, the P buffer capacity at $0.050 \text{ mg P L}^{-1}$ (identified as typical of soil solution P concentration) is determined. Levels of 0.050 mg L^{-1} are more closely identified with agricultural purposes than for effluent concentrations of 10 mg P L^{-1} applied to soil. An additional index, equilibrium P concentration (EPC) is derived from the point where the plotted line crosses the X-axis.

That P-sorption is being assessed for soil sorption at high concentrations from these indices poses the question as to the validity of the P-sorption capacity values used in predicting the potential long-term uptake of P and the protection against leaching P from the soil. While agricultural soils benefit from small applications of P to provide an adequate soil solution P concentration and need to determine P buffer capacity to allow such calculations, effluent application relies upon immobilising P in the soil to minimise leaching.

2.2 Phosphorus retention

The percentage of P retained when a sample of soil is shaken with 1000 mg P L^{-1} equilibrating solution (with other chemicals at pH 4.6) is determined according to Rayment & Higginson (1992) and reported on an air-dry basis. The soil/equilibrating solution ratio is 1:5. The method originated from the need to differentiate between soils exhibiting high and low P retention. Five classes are used: very low < 10%, low 10-30%, medium 30-60%, high 60-90% and very high >90%. This test is not a quantitative measure of P sorption.

2.3 Phosphate Sorption Index

This test is described by Rayment and Higginson (1992) as being more closely related to soil P buffer capacity. The test requires that a soil sample is shaken with a solution of 7.5 mg P L⁻¹ at a soil solution ratio of 1:20. The strength and soil/solution ratio equates to a loading of 150 mg P kg⁻¹. From the results, a P sorption index is calculated:

$$\text{P-sorption index} = \frac{150 \text{ mg P L}^{-1} - \text{supernatant P conc (mg L}^{-1}\text{)}}{\log_{10} \text{ final supernatant concentration (}\mu\text{g P L}^{-1}\text{)}} \quad \text{Equation 1}$$

2.4 Phosphate Sorption Curve

At a soil/solution ratio of 1:10, five samples of soil are each equilibrated with increasing concentrations of P-equilibrating solutions within the range of 2.5 to 250 mg P kg⁻¹. The data are plotted with the P sorbed (in mg kg⁻¹) on the X-axis and the $\log_{10}C$ (concentration of final supernatant in $\mu\text{g P L}^{-1}$) on the Y-axis. The equilibrium P concentration is extrapolated to the point of zero sorption (X-axis intercept). The P buffer capacity (PBC) is the slope of the line.

2.5 Single Point Method

A calibration of various P-sorption tests with a single point test was made by Moody *et al.*, (2001) in a soil/solution ratio of 1:10 shaken with an equilibrating solution of 1000 mg P L⁻¹ and the P sorbed reported in mg P kg⁻¹. This method can determine up to 12 000 mg P kg⁻¹

2.6 Laboratory Dosing Trials

While the above tests can provide numerical values of P-sorption within 24 h, none indicates the level at which one can predict when leakage of the infiltrating P solution will commence. Laboratory trials, in which columns are equilibrated on a regular basis and the P in the leaching solution is determined, can be used to identify the P-sorption capacity to which strong bonding occurs and the capacity at which leaching commences. The major constraint to this type of analysis is the prolonged period over which the test must be conducted.

3 Methods and Results

3.1 Test Procedures

Fifteen soils from various regions of NSW were selected from samples held in the laboratory. Each soil had been air dried, crushed and sieved to < 2 mm. Each soil was measured for pH in water (pH_w) and electrical conductivity (EC), soil texture analysis and colour description. Three soil P-sorption tests were performed on each of the 15 samples. A comparison of the parameters set for each of the tests is given in Table 1.

Phosphate was determined using the ascorbic acid / molybdate colorimetric method. Other methods of P determination are available, however, one should be alert to the difference that may be obtained using different methods. Table 1 shows the comparative differences between the test and perhaps gives clues to the different results.

3.2 Results

The data collected from the three test procedures on 15 soils provided a range of P-sorption indices of various types shown in Table 2.

Column 1 identifies the soil Great Soil Group (Stace *et al.*, 1972) and the region from which the sample was obtained. Both surface and subsurface soils of alluvial sands to heavy clays are included. Column 2 indicates the pH in 1:5 soil/water solution. The soils cover the pH range of 3.78 to 8.91. The more acid soils (<5.5), with the exception of the Iluka sands, have retention values (Col.5) close to 100%. Values approaching neutral pH also have retention values around 100%. The two highly alkaline soils have retention values less than 60%. Such behaviour is consistent with the findings of Keeney & Wildung (1977) in that labile inorganic P is sorbed onto Fe and Al containing minerals in acid soils. They also concluded that as pH

increased only 22% was adsorbed at pH 7.6 compared to pH 4.1. In the tests performed for this paper, there was a 40-50% decrease as pH rose.

Table 1. Test Parameters for Methods of Determining P Sorption

Parameter	Single point – 25 P sorption index	Five Point - P Sorption Curve	Single Point -1000
Mass of sample	2.0 g	4.0 g	4.0 g
P concentration	25 mg P L ⁻¹	25, 50, 75, 100 and 150 mg P L ⁻¹	1000 mg P L ⁻¹
Original method [#]	7.5 mg P L ⁻¹	0.25 - 25 mg P L ⁻¹	1000 mg P L ⁻¹
Soil/solution ratio	1:20	1:10	1:10
Equilibrating solution	0.01M CaCl ₂	0.01M CaCl ₂	0.01M CaCl ₂
Modified equilibrating solution	no	no	no
Tumbling period	17 h at 25°C	17 h at 25°C	17 h at 25°C
Maximum range P sorption	500 mg P kg ⁻¹	1 500 mg P kg ⁻¹	10 000 mg P kg ⁻¹

original methods as outlined in Section 3.

Columns 3, 4 and 5 relate to the P-sorption index determined using the method in Section 3.3, with the increase in P concentration from 7.5 mg L⁻¹ to 25 mg L⁻¹. The phosphate sorption index (PSI) was calculated using Equation 1. When compared with the P-sorb value, that is the amount of P sorbed by the soil as measured against a possible 500 mg kg⁻¹, the percentage sorbed (Col. 5) relates well to the categories of Moody & Bolland (1999).

The highest values are for the soils high in Fe and Al (gleyed podzolic, red podzolic and krasnozem) while the lowest was for alluvial sand. It is surprising that the heavy clays (black earths) with montmorillonite clays had only medium sorption.

Columns 6-10 report values for the five point sorption isotherm. The retention percent at the 25 mg P L⁻¹ solution strength (Col. 6) varies from the retention percentages (Col. 5). While both methods can be used to calculate the percentage retention at 25 mg P L⁻¹, the values for Col.5 are determined at soil/solution ratio of 1:20 while the values for Col.6 was made at the ratio of 1:10.

From the graphs prepared for each of the soils using the data for the P-sorption isotherm from Section 3.4, equivalent P concentration (EPC) and P buffer capacity (PBC) were derived.

A typical graph is shown in Figure 1 for the subsoil yellow podzolic (sample 1). EPC is determined by extrapolating the line of best fit to the X-axis. The PBC is the slope of the line.

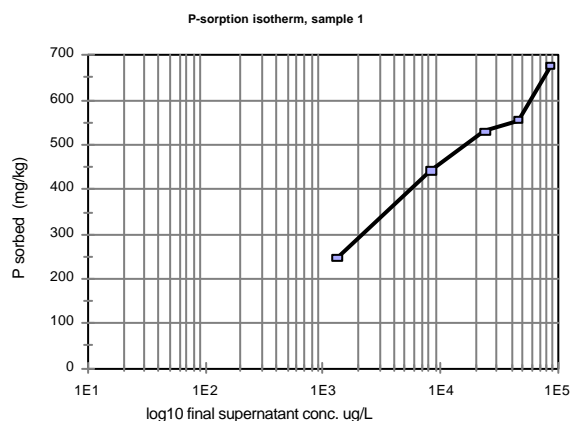


Figure 1. Plot of P sorb to Supernatant Concentration

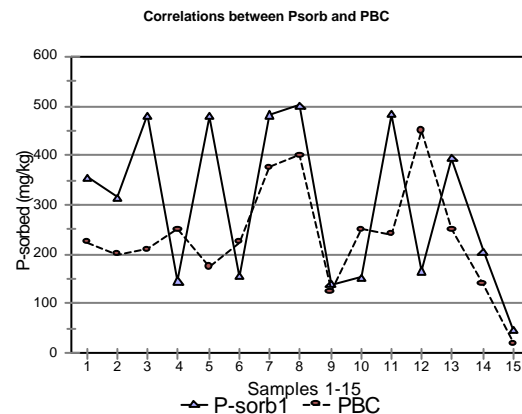


Figure 2. Correlation of Two Methods of Determining P Sorption

Table 2. Results of Three P-sorption Determinations on 15 Soils

1	2	3	4	5	6	7	8	9	10	11	12
Sample	pH _w	P-sorption index (25 mg L ⁻¹)			P-sorption isotherm (5 point equilibration)					P sorption (1000 mg P L ⁻¹)	
		PSI	Psorb	% S	% S	EPC mg/L	PBC ²	Dev ^a	Psorb	Psorb	% S
subsurface yellow podzolic	7.06	92	355	71.3	95.0	100	225	200	676	727	7.5
surface gleyed podzolic -T2	5.86	79	314	63.1	94.2	1150	200	200	628	1391	14.0
subsurface gleyed podzolic- B2	6.69	164	481	96.6	100	100	210	600	1087	1830	18.3
surface red podzolic - T3	5.94	34	146	29.4	54.5	1.5	250	< 200	359	1830	18.3
subsurface red podzolic -B3	6.45	161	479	96.2	100	1.5	175	550	1010	1629	16.3
subsurface yellow solodic	8.53	37	155	31.2	57.6	10	225	< 200	432	-677	-6.3
river alluvium - Newry Is.	3.78	166	482	96.8	100	4	375	800	1245	2544	25.3
subsurface Krasnozem-Dorrigo	4.67	332	501	100	100	8	400	1100	1402	2732	27.1
subsurface red brown earth – Dubbo	6.53	33	140	28.1	61.2	700	125	200	551	1228	12.4
surface red earth Hillston	8.91	36	153	30.7	56.9	1150	250	200	595	3020	30.0
subsurface red podzolic -Oberon	5.29	170	484	97.2	99.8	7.5	240	750	1084	1968	19.7
surface, chocolate – Armidale	7.15	39	166	33.4	60.9	1320	450	200	546	144	14.5
surface black earth –Armidale	6.25	106	395	79.4	96.6	100	250	400	858	2344	23.3
surface black earth Goondiwindi	7.73	49	205	41.3	69.4	1050	140	< 200	568	-25	0.1
sandy alluvium - Iluka	5.19	11	46	9.3	-16	12000	20	< 200	113	-476	-4.3

values in mg kg⁻¹ unless otherwise stated. a = point of deviation in mg kg⁻¹

The PBC correlates poorly ($r = 0.38$) with the P sorption value derived for Col. 4 in Figure 2.

A method of determining the potential for the soil to adsorb P from effluent applications is to plot the P sorbed against the concentration of the five equilibrating solutions. Where the curve deviates from the line of the equilibrating solutions marks the point at which P sorption ceases to be a total sorption function and only portion of the P is sorbed. The portion sorbed can be calculated by the rate of deviation from the line. Figure 3 is for the Krasnozem and the point of deviation is quantified in Col.9 while the total P sorbed for the test at solution 5 is given as Psorb (Col.10).

While a single point test using the 1000 mg P L⁻¹ solution outlined in Section 3.5 also allows for determination of Psorb and percentage sorption, the high strength equilibrating solutions cause P previously absorbed by the soil to be displaced (Col.11 and 12) – shown by the negative values.

Comparison of the retention percentage with either Col. 5 or Col. 6 shows that at the high concentration, only a small percent of the P in the equilibrating solution was adsorbed. There is no correlation ($r=0.4$) between the values derived using 1000 mg P L^{-1} and that at 25 mg P L^{-1} for the same (1:10) soil/solution ratio.

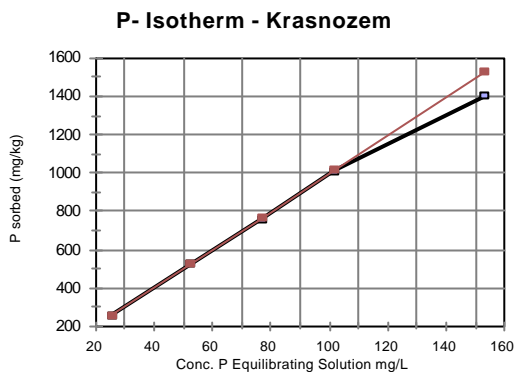


Figure 3. Plot of P sorbed against Equilibrating Solution Concentration

Due to time constraints, these soils were not subjected to laboratory leaching trials to determine the potential sorption under slow dosing regimes or the point at which leakage of the P from the soil commences and the rate of continued leaching. In recent leaching tests, the author conducted such tests that after 180 days of leaching, leakage rates could not yet be determined.

4 Conclusions

The methods for determining the soil phosphorus sorption capacity and the various indices to report those values are causes for confusion in interpreting the derived values. While methods have been documented, the variation between methods is shown here to make comparison difficult and so prevent useful predictions. In all the methods, P sorption only accounts for the addition of labile inorganic P being added and measured at specified pH for a particular period. The tests do not account for the pH of the effluent added or the other elemental constituents of the effluent, in particular the proportion of monovalent and divalent cations.

The addition of organic P components will have no immediate impact on determination of P sorption, yet substantial masses of organic P can be stored in the soil without loss by leaching.

The purpose of determining P sorption is to predict the capacity of the soil to bind, and reduce the potential for effluent-applied inorganic P leaching from the soil and entering surface or groundwater. The results of this testing program do not support the general discount factor of 70% from measured P sorption to that actually adsorbed. Since part of the P in effluent is in organic form, a soil's capacity to adsorb P is greater than determined for inorganic P sorption.

Since most of the work on P sorption has been done to satisfy the agricultural requirements for maintaining a soil solution concentration of $0.050 \text{ mg P kg}^{-1}$, extrapolating these methods with the same low concentrations of the equilibrating solutions to predicting soil solution P levels under effluent irrigation are seriously flawed.

One valid method of determining the potential leakage of P from added inorganic P is to firstly determine the deviation of the P-sorption isotherm from the concentration gradient as shown in Figure 3. Up to that point the P sorption mechanism is strong, then it slowly deteriorates.

At high equilibrating solution concentrations, retention percentages are low, mostly because the concentration saturates the adsorption site rapidly. At low solution concentration, there is insufficient P to meet the sorption capacity and high uptake rates were typical of all except the sandy soils and those with an alkaline pH.

There is an urgent need to identify and calibrate a suitable P-sorption test for determining long term protection of effluent application areas while maintaining suitable plant nutrient availability.

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