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A Rapid Method of Estimating the Phosphorus Sorption Capacity of Soils

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ABSTRACT

Phosphate sorption capacities of soil samples representing the A, B, and C horizons of six soil types found in the Lake George (New York) drainage basin were determined. Sorption capacity was defined as the amount of P sorbed by a soil at equilibrium with a 2×10^{-4} M P solution after 72 hours of shaking in the laboratory. Capacities ranged from 6.3 to 69 mg P/100 g soil. Each soil's B horizon had a higher sorption capacity than its C horizon. Plots of $c/(x/m)$ vs c , where c = equilibrium P concentration and x/m = P sorbed, yielded slightly curved lines, indicating lack of adherence to the Langmuir equation. A square-root extension of the Langmuir equation fit the P sorption data better than the Langmuir equation and explained at least 99.6 percent of the variation in $c/(x/m)$ for each soil horizon. It was found that the amount of P sorbed from a solution containing 20 μ g P/ml during a 15-minute shaking period could be used to estimate P sorption capacity and the time required for P saturation of the soil in septic tank drainfields.

Additional index words: Regeneration of P sorption capacity, Langmuir equation, Lake George (New York), septic tank drainfields, P sorption maximum.

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A RAPID METHOD OF ESTIMATING THE PHOSPHORUS SORPTION CAPACITY OF SOILS

By G. F. Griffin

Phosphorus (P) contamination of lakes and reservoirs used for recreational purposes has been a major environmental concern for several years. In the drainage basins of such water bodies, residential septic systems are a source of P. The degree of P removal from the effluents of these systems depends to a large extent on the nature of the soil in the vicinity of the system. Near oligotrophic lakes many soils are shallow to bedrock, thereby providing relatively small volumes of soil to sorb P before it reaches lake water. In these situations, the P sorbing capacity of the soil should be considered in the design of the septic system. For example, if the P sorbing capacity of the soil is relatively low, it may be necessary to treat the septic tank effluent chemically to reduce its P concentration. In other cases, it may be essential to determine the volume of a particular soil needed to reduce P concentrations to a safe level. For these reasons, it is important and useful to have a means of measuring accurately and quickly the P sorption capacities of soils of lakeside residential sites.

Many P sorption studies have involved laboratory determination of P sorption maximum (P max) values which have been

used as indices of P sorption capacities of different soils (5, 10, 13, 14). Frequently, the Langmuir equation has been used to obtain P max values by calculating the reciprocal of the slope of the straight line obtained by plotting $c/(x/m)$ vs c , where c is the equilibrium P concentration and x/m is the amount of P sorbed by the soil.

Some workers have encountered difficulty obtaining P max values using the Langmuir equation because plots of $c/(x/m)$ vs c have not yielded straight lines. In some cases two or more straight lines have been obtained (8, 12), while other investigators have reported curvilinear relationships (3, 7). Gunary (7) found that phosphate adsorption by 24 British soils was best described by an extension of the Langmuir equation in which $c/(x/m)$ was related to both c and \sqrt{c} . Values for P max based on this equation were from 1.39 to 2.40 times those obtained by assuming linearity in the Langmuir plot.

Bache and Williams (2) used the slope of the isotherms of x/m vs $\log c$ measured at $c = 10^{-4}$ M P as a reference index of P sorption by 42 British soils. This index allows comparisons of soils having different amounts of sorbed P already present. Bache and Williams (2) obtained high correlations ($r = .932$ and $r = .976$) between their reference index and the sorption of P at equilibrium concentrations of 10^{-4} M and 10^{-3} M P, respectively. They also related their reference index to P sorption from additions of 20 and 50 $\mu\text{mol P/g}$ soil and obtained correlations of $r = .813$ and $.951$, respectively. More recently, Sawhney and Hill (11) used the sorption at $c = 2 \times 10^{-4}$ M P as a measure of the P sorption capacities of several Connecticut soils.

The objectives of this study were i) to develop a test to estimate rapidly and accurately the P sorption capacities

of soils found in the drainage basin of an oligotrophic lake; ii) to compare the P sorption capacities of the soils; iii) to examine the relationship between amounts of P sorbed by the soils and equilibrium P concentrations.

MATERIALS AND METHODS

Soil samples representing the A, B and C horizons of six soil series in the drainage basin of Lake George (New York) were collected during July and August, 1974. Suborder classifications and selected physical and chemical properties of the soils are shown in Table 1. Lake George is a narrow, 51-kilometer long oligotrophic lake located near the eastern border of New York State about halfway between New York City and Montreal, Canada. Additional details about the lake's physical and chemical characteristics can be obtained from Ferris and Clesceri (6).

The samples were air-dried and passed through a 2 mm sieve. To determine P sorption capacities, duplicate 2.5 g samples of soil were shaken with 25 ml of 0.01 N NaCl containing varying amounts of inorganic P as KH_2PO_4 for 72 hours at $20^\circ \pm 1^\circ \text{C}$. Each sample was treated with at least ten different solutions which ranged in P content from 2 to 80 or from 2 to 120 $\mu\text{g P/ml}$, depending on the soil. Samples of the Charlton and Madalin B horizons received in addition a 200 $\mu\text{g P/ml}$ solution, while the Deerfield A and B horizons were also treated with 200 and 300 $\mu\text{g P/ml}$ solutions.

After the shaking period, the soil-solution suspensions were filtered through a glass fiber filter and an underlying millipore (0.45μ) filter. An automated procedure utilizing the method of Murphy and Riley (9) was used to measure the orthophosphate content of the filtrates. Phosphorus sorbed by the soil was calculated as the difference between the P

concentration of initial contacting solution and that of the filtrate.

In a procedure designed to measure P sorbed during a very short contact time, duplicate 2.5 g samples were shaken with 25 ml of 0.01 N NaCl containing 20 μ g P/ml for 15 minutes at $20^{\circ} \pm 1^{\circ}$ C. Filtrates were obtained and analyzed for P as described above.

Soil pH was determined on a 1:1 soil:water suspension using a pH meter. The hydrometer method was used to determine soil texture.

RESULTS AND DISCUSSION

P sorption capacities of soils

Sorption of P varied considerably with both soil type and soil horizon. The isotherms in Figure 1 illustrate marked differences in sorption by the Deerfield A horizon and the Oakville A, B and C horizons. The values of c identified on each of the isotherms are the equilibrium P concentrations resulting from contact between the soil and the solution initially containing 20 μ g P/ml. For example, when a 20 μ g P/ml solution was shaken with the Deerfield A samples, the P concentration of the solution was reduced to 0.14 μ g P/ml after 72 hours of shaking, compared to 12.7 μ g P/ml for the Oakville C samples. It can be seen that the Deerfield A samples removed much more P from solution than did any of the Oakville samples.

An appropriate reference index for P sorption by the soils used in this study is the sorption at an equilibrium concentration of 2×10^{-4} M P. This is the approximate con-

Table 1 - Classification, pH, textural class and percentage clay of soil samples used in study.

Soil series	Horizon	pH	Textural class	Clay	Classification
				- % -	
Madalin	A	7.2	sandy clay loam	33.0	Mollic Ochraqualf
	B	7.8	clay loam	36.2	
	C	7.6	silty clay loam	24.2	
Oakville	A	5.1	fine sandy loam	5.0	Typic Udipsamment
	B	5.6	loamy fine sand	4.2	
	C	6.0	fine sand	2.2	
Deerfield	A	6.2	fine sandy loam	8.4	Aquic Udipsamment
	B	6.6	fine sandy loam	10.2	
	C	6.4	fine sand	4.6	
Charlton	A	5.2	fine sandy loam	12.8	Typic Dystrochrept
	B	6.0	fine sandy loam	18.2	
	C	5.9	loamy sand	8.2	
Ridgebury	A	5.7	fine sandy loam	12.6	Aeric Fragiaquept
	B	6.1	sandy loam	8.2	
	C	6.5	sandy loam	8.8	
Windsor	A	5.4	loamy fine sand	5.5	Typic Udipsamment
	B	5.4	loamy fine sand	7.5	
	C	5.7	loamy fine sand	1.4	

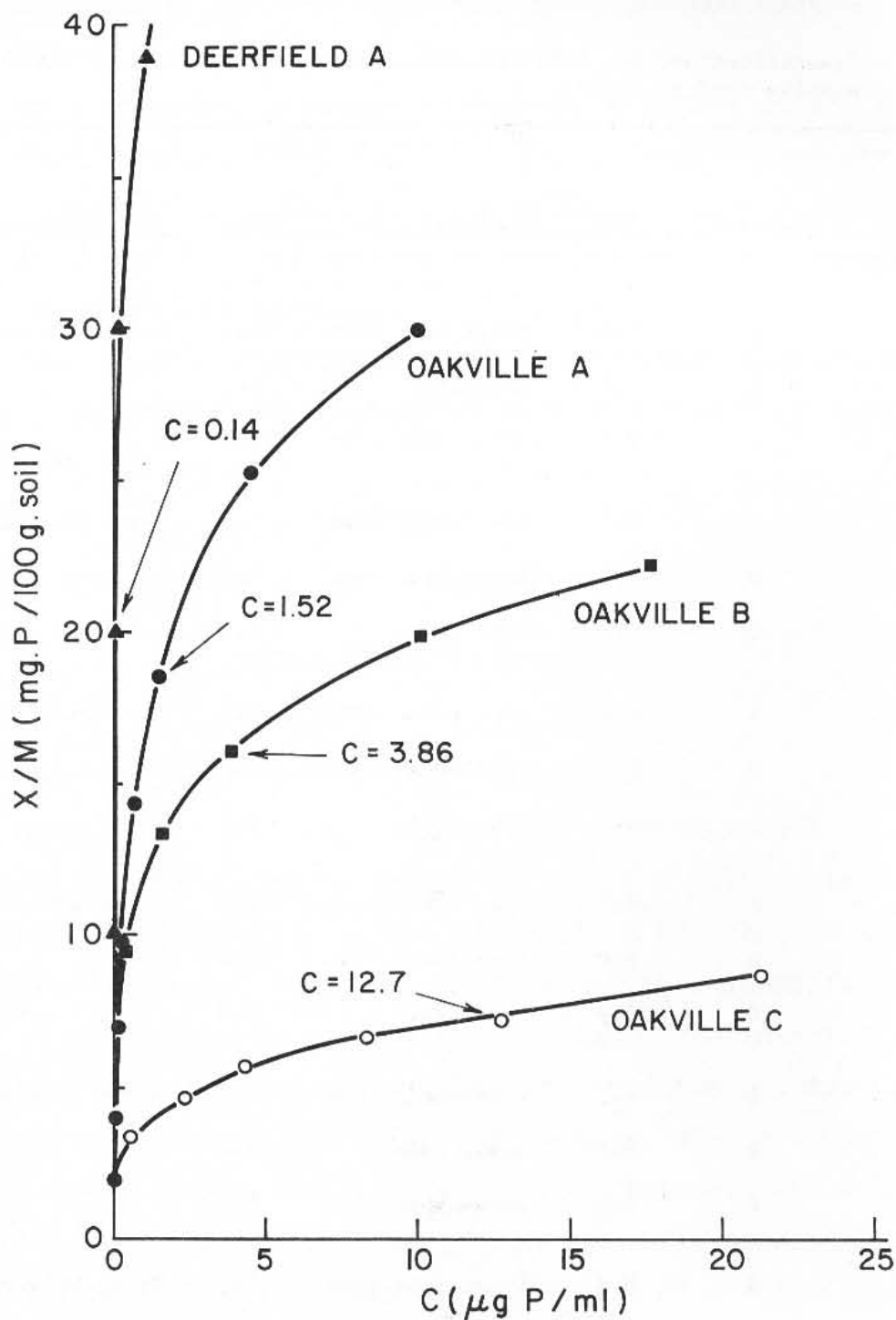


Figure 1. P sorption isotherms for soil samples of Oakville A, B and C horizons and Deerfield A horizon showing equilibrium P concentrations resulting from contact with solutions initially containing $20 \mu\text{g P/ml}$.

centration of soluble orthophosphate in waste waters. Table 2 shows the amounts of P sorbed by the soils at equilibrium P concentration of 2×10^{-4} M. The values were obtained from sorption isotherms like those in Figure 1 constructed for each soil. They further illustrate the differences among soils and soil horizons in their ability to remove P from solution. For example, samples of Deerfield B horizon sorbed over 10 times as much P as Oakville C samples at an equilibrium P concentration of 2×10^{-4} M. The B horizon of the Charlton fine sandy loam, probably the most commonly occurring of the six soils in the Lake George drainage basin, had a sorption capacity nearly twice that of the C horizon. Indeed, the B horizon of each soil had a higher sorbing capacity than the C horizon. Similar results were reported for Michigan soils by Ellis and Erickson (5), who pointed out that many tile drain fields are likely to be laid below the B horizon where the superior sorption capacities of this horizon cannot be fully utilized.

The sorption data can also be examined in terms of the length of time required for a given volume of soil to reach an equilibrium P concentration of 2×10^{-4} M (saturation). Assuming a soil bulk density of 1.40 g/cc, a loading rate of 1.8 kg P/year of soluble inorganic P from a household of four and a soil volume of 1200 cubic feet surrounding the tile drain field, times needed for saturation of the soil with P can be calculated. Thus, 1.7 years would be required for the Oakville C horizon, 4.4 years for Charlton C, 7.7 years for Charlton B and 18.3 years for Deerfield B.

It should be emphasized that actual times under field conditions would change with the P concentration of the septic effluent, the volume of soil in the drain field, the soil's bulk density, the period of time the household is occupied each year, and most importantly, the regeneration

of P sorption capacity with time. Both Sawhney and Hill (11) and Ellis and Erickson (5) observed considerable regeneration with time and concluded that effective P sorption capacities of soils are much greater than values obtained from laboratory sorption studies.

Regeneration of sorption capacity would undoubtedly be of particular importance when residences are occupied only during summer months. This is the case with most residences in the Lake George Basin. Aulenbach and Clesceri (1) estimate that the total average summer population in the basin is 30,160 of which only 5575 persons are permanent, year round residents. Occupancy for two to three months would substantially lower the annual P loading rate and also allow for the regeneration of P sorption capacity during the periods between summers.

After evaluating a lakeside site's capacity for P removal from waste waters, consideration may need to be given in the future to reduction of the P concentration in septic tank effluent. On the basis of studies conducted by Clesceri (4), there exists the potential for over 90 percent removal of P from septic tank effluent through chemical treatment with alum. Theoretically, this reduction in P concentration could increase the time required for P saturation of the soil ten-fold. Thus, the Oakville C horizon would be saturated in 17 years rather than 1.7 years assuming the aforementioned conditions. Again, regeneration of P sorption capacity would further increase the soil's P sorption capacity and, therefore, the time required for saturation.

Sorption Isotherms

The P sorption data can be examined in many ways. As shown in Figure 1, the amount of P sorbed, x/m , can be plotted against c , the equilibrium P concentration. The resulting

Table 2 - P sorption capacities of soils as measured by amounts of P sorbed at equilibrium concentration of 2×10^{-4} M P and amounts of P sorbed by soils during 15-minute shaking period with one solution containing 20 μ g P/ml.

Soil series	Horizon	Sorption capacity	Sorption in 15 minutes from 20 μ g P/ml solution
- mg P/100 g soil -			
Madalin	A	22.3	10.5
	B	38.4	15.8
	C	23.8	12.0
Oakville	A	26.9	11.2
	B	17.7	9.9
	C	6.3	2.7
Deerfield	A	61.0	15.0
	B	69.0	15.1
	C	11.8	6.3
Charlton	A	15.6	8.7
	B	29.1	11.2
	C	15.9	8.6
Ridgebury	A	28.1	11.3
	B	11.8	6.3
	C	9.9	5.3
Windsor	A	23.6	9.4
	B	25.2	10.4
	C	12.2	7.5

isotherms show differences in P sorption and also illustrate differences in slopes at various c values. By plotting $c/(x/m)$ vs c , a straight line is obtained if the sorption data follow the Langmuir equation. In no case did plots of $c/(x/m)$ vs c yield straight lines for the data obtained in this study. Instead, all the plots, as shown by the examples in Figure 2, were curved. Similar results have been obtained by other workers (2, 3, 7). As pointed out by Bache and Williams (2), such curvature suggests that there is no well-defined P sorption maximum. On the basis of calculated linear correlation coefficients for $c/(x/m)$ vs c for the soils in Figure 2 ($r = .988$ for Charlton B, $r = .989$ for Windsor C, $r = .995$ for Windsor B), one might conclude excellent fits to the Langmuir equation. Yet, as seen in Figure 2, there is significant curvature in the plots. Extension of the Langmuir equation by introduction of a square root term, as described by Gunary (7), improved the fit. This equation can be written as follows:

$$c/(x/m) = a + b_1 c + b_2 \sqrt{c} \quad (1)$$

The improvement in fit is reflected in the R^2 values in Table 3, which are higher than the corresponding r^2 values for the Langmuir equation. Moreover, the coefficients of \sqrt{c} in equation (1) were all highly significant ($P < 0.01$). Thus, the square-root equation (equation 1) provided a better description of P sorption by the soils than the Langmuir equation. The excellent fit obtained by equation (1) suggests that the soil will sorb a small quantity of P tightly, a slightly greater quantity of P less tightly, and so forth until a P sorption maximum is reached. Theoretically, this maximum is equivalent to the reciprocal of b_1 in equation (1).

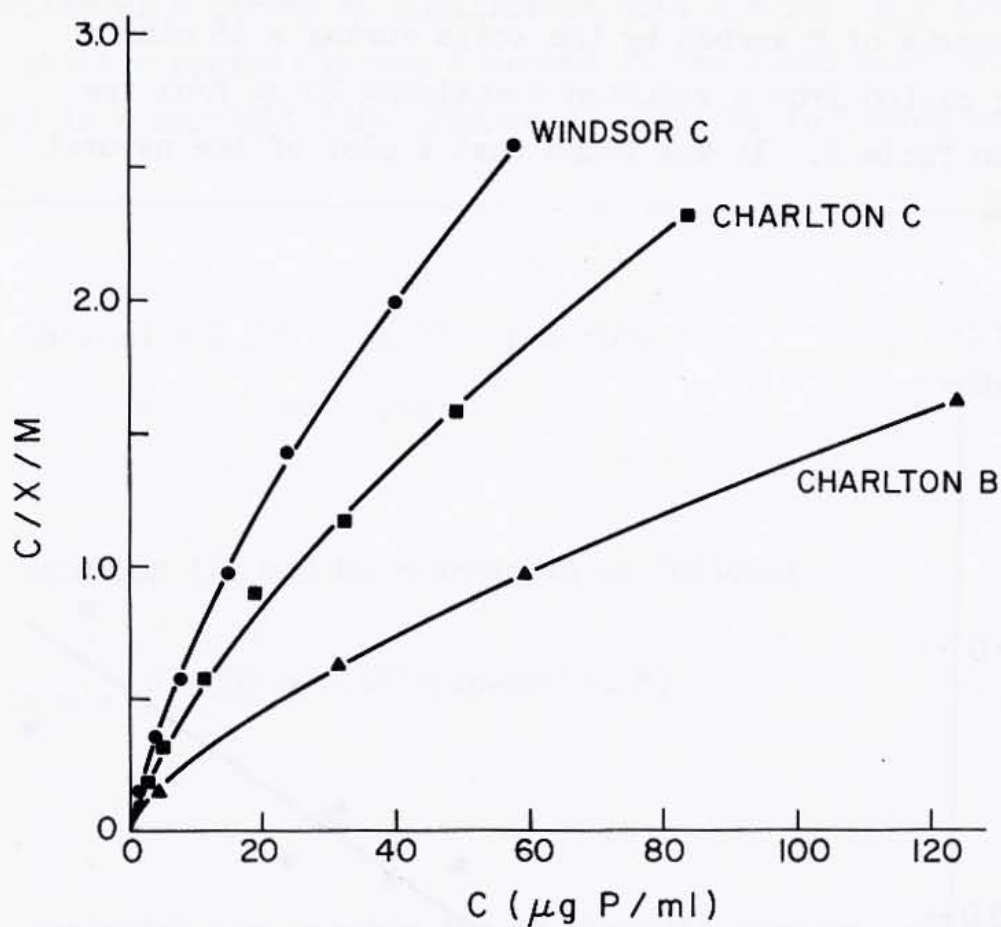


Figure 2. Plots of $c/(x/m)$ vs c for Charlton B and C horizons and for Windsor C horizon.

Rapid Test to Estimate P Sorption Capacities

Amounts of P sorbed by the soils during a 15 minute shaking period from a solution containing $20 \mu\text{g P/ml}$ are shown in Table 2. It was found that a plot of the natural

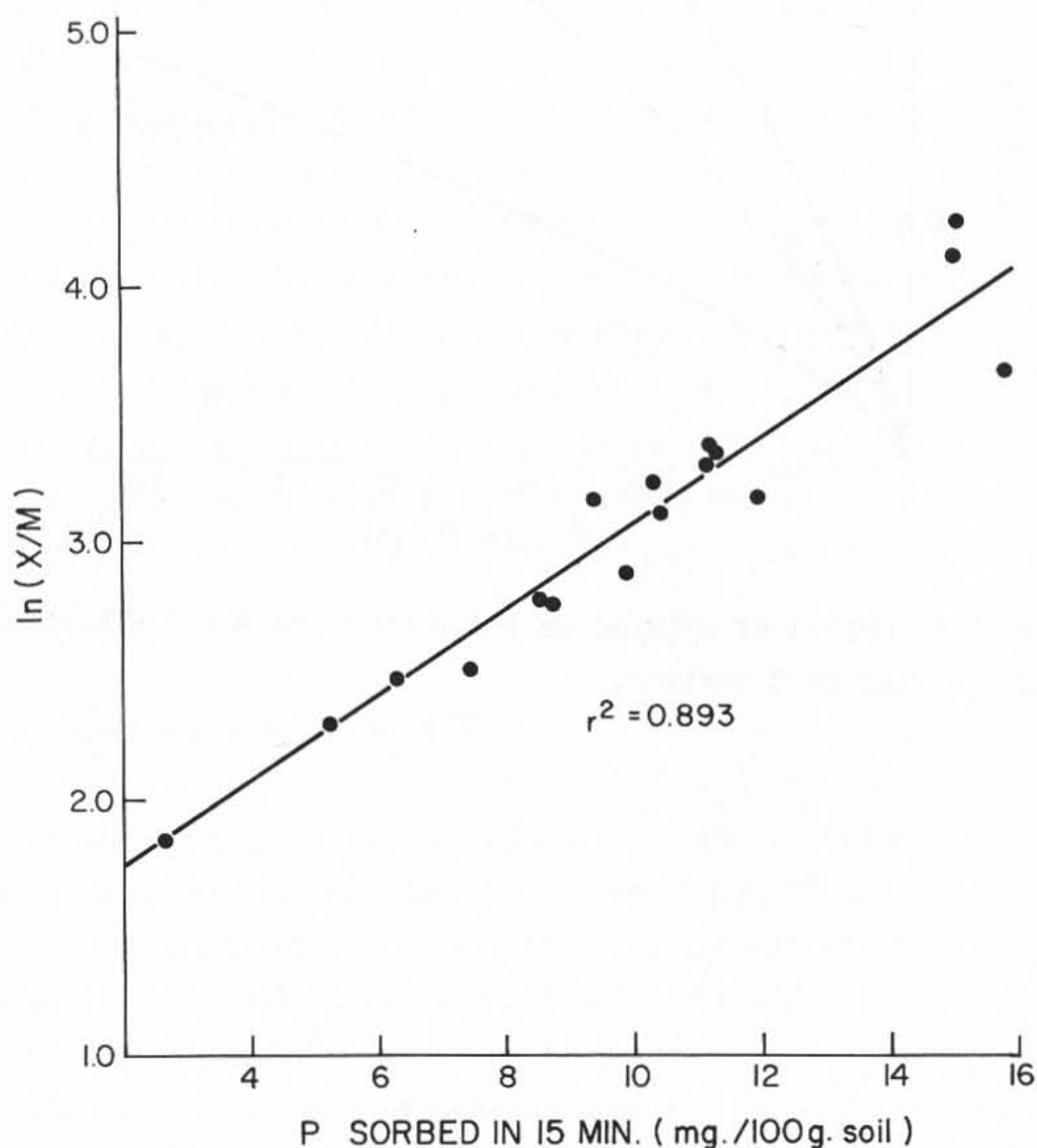


Figure 3. Plot of natural logarithm of P sorbed at equilibrium concentration of $2 \times 10^{-4} \text{ M P}$ vs P sorbed in 15 minutes from solution containing $20 \mu\text{g P/ml}$.

logarithm of P sorbed at equilibrium with 2×10^{-4} M P (72-hour shaking period) versus P sorbed in the rapid test resulted in a straight line (Figure 3) with the following equation:

$$\ln(x/m) = 1.396 + 0.167 \cdot \text{rap-sorbed P} \quad (2)$$

$$r^2 = .893$$

Equation (2) can be rearranged as follows:

$$x/m = e^{(1.396 + 0.167 \cdot \text{rap-sorbed P})} \quad (3)$$

Excluding the results for the Madalin samples, which are higher in clay content and pH than any of the other samples, increases r^2 to .932.

Equation (3) can be interpreted to mean that samples with low P sorption capacities sorbed relatively more P in 15 minutes than would be expected on the basis of the relative P sorption capacities of the soils. For example, a "rapidly-sorbed P" value of 5 mg P/100 g soil in equation (3) gives a sorption capacity (x/m at 2×10^{-4} M P) of 9.31, while a "rapidly-sorbed P" value of 15 yields a sorption capacity of 49.5. This relationship was probably due to the rapid decrease in the equilibrium P concentration by soils of high sorption capacities during the short shaking period.

Equation (3) could be used to estimate rapidly and accurately the P sorption capacities of soils like those used in this study. This information could then be utilized in

obtaining estimates of the time required for P saturation of the soil in septic tank drainfields by using one of the following equations:

$$T = \frac{0.000283 \cdot V \cdot D_b \cdot e^{(1.396 + 0.167 \cdot \text{rap-sorbed P})}}{\text{LRKG}} \quad (4)$$

$$T = \frac{0.000624 \cdot V \cdot D_b \cdot e^{(1.396 + 0.167 \cdot \text{rap-sorbed P})}}{\text{LRLB}} \quad (5)$$

Where T = time in years for soil to reach an equilibrium
P concentration of 2×10^{-4} M;

V = volume of soil surrounding tile drain field system
in ft^3 ;

D_b = bulk density of soil in g/cc;

LRKG = loading rate of soluble inorganic P in kg P/year;

LRLB = loading rate of soluble inorganic P in lbs P/year.

As an example, consider the C horizon of the Charlton. This soil and the closely related Canton series are found not only in New York but also extensively throughout southern New England. Using the rapidly-sorbed P value of 8.6 mg P/100 g soil and assuming a V of 1200 ft^3 , a D_b of 1.40 g/cc and a LRKG of 1.8 kg P/year, the time to reach saturation from equation (4) is 4.5 years. If the loading rate was decreased to .45 kg P/year due to residence only during summer months, the time for saturation would increase to 18 years.

Table 3 - Values of r^2 for $c/(x/m)$ vs c and R^2 for $c/(x/m)$ vs c and \sqrt{c} .

Soil series	Horizon	$c/(x/m)$ vs c r^2	$c/(x/m)$ vs c and \sqrt{c} R^2
Charlton	A	0.9817	0.9986
	B	0.9771	0.9997
	C	0.9705	0.9984
Oakville	A	0.9809	0.9989
	B	0.9783	0.9984
	C	0.9596	0.9969
Madalin	A	0.9569	0.9990
	B	0.9827	0.9997
	C	0.9757	0.9984
Windsor	A	0.9795	0.9979
	B	0.9892	0.9996
	C	0.9775	0.9984
Deerfield	A	0.9880	0.9998
	B	0.9860	0.9993
	C	0.9775	0.9977
Ridgebury	A	0.9837	0.9996
	B	0.9781	0.9991
	C	0.9791	0.9978

Under field conditions the times required for saturation would likely be longer than those estimated above because of the regeneration of sorption sites with time. Thus, the values obtained from equations (4) and (5) would be conservative.

CONCLUSIONS

The P sorption capacities of soil samples representing the A, B and C horizons of six soil types found in the Lake George (New York) drainage basin varied from 6.3 to 69 mg P/100 g soil. On each soil the B horizon had a higher sorption capacity than the C horizon. The equation, $c/(x/m) = a + b_1c + b_2\sqrt{c}$, where c = equilibrium P concentration and x/m = amount of P sorbed, fit the P sorption data better than the Langmuir equation ($c/(x/m) = a + b_1c$) and explained at least 99.6 percent of the variance in $c/(x/m)$ for each soil horizon. In no case did a plot of $c/(x/m)$ vs c result in a straight line. Amounts of P sorbed by the soils during a 15-minute shaking period from a single 20 μ g P/ml solution were related to P sorption capacities of the soils as follows:

$$x/m = e^{(1.396 + 0.167 \cdot \text{rap-sorbed P})}$$

$$r^2 = .893$$

Laboratory values for P sorption capacities can be used to obtain estimates of the relative times required for P saturation of soils associated with septic tank drainfields. These estimates are conservative due to the regeneration of P sorption capacity with time, as reported by other workers. In the case of soils with very low P sorption capacities, some form of chemical pretreatment of septic effluent to reduce its P concentration may be necessary.

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