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## SOIL AND WATER FACTORS AFFECTING EPC

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### INTRODUCTION

Equilibrium phosphate concentrations (EPC's) have been used extensively as a means of assessing the pollution potential of soils and sediments (Taylor and Kunishi 1971, McDowell and McGregor 1980). Several factors, including the period of equilibration, amount of P adsorbed, solution-to-soil ratio, vigor of mixing, microbial activity, type and amount of electrolyte in the equilibrating solution, and extent of particle aggregation, may influence P adsorption-desorption reactions and, thus, values of EPC obtained. Effects of these factors may be largely eliminated from relative comparisons by standardizing measurement conditions. However, if results of EPC determinations are to be used to predict behavior of P on sediments in runoff, effects of several of the above factors may need to be accounted for either by selecting measurement conditions expected to approximate those in runoff or, if factors vary widely in runoff, by adding additional model parameters to account for their effects. This report will briefly discuss the influence of each of the above factors.

### PERIOD OF EQUILIBRATION

The EPC has been shown to be relatively insensitive to the period of equilibration (Taylor and Kunishi 1971). However, slopes of isotherm segments, such as that illustrated in figure 1, tend to increase with equilibration time, pivoting approximately on the EPC as adsorption and desorption reactions continue (Taylor and Kunishi 1971). Hence, the slopes, termed "P buffer capacities," will depend on the equilibration time used.

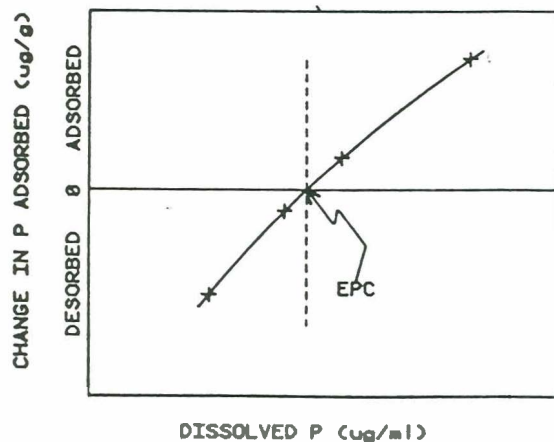


Figure 1.--Typical segment of P adsorption-desorption isotherm from which the EPC is estimated by extrapolation.

Rates of adsorption and desorption are initially rapid followed by a period of slower reaction rates. The more rapid reactions usually reach completeness within a few minutes or hours (Barrow and Shaw 1975a), but slower reactions may continue for days or months (Enfield and Bledsoe 1975). Most runoff events are expected to occur over a period of a few hours or less and, thus, the fast reactions will dominate P adsorption and desorption reactions on soil particles in runoff in most cases. Use of equilibration times of sufficient length to encompass the majority of fast reactions will provide estimates of the maximum expected P buffer capacity. Such estimates should be applicable to sediments in runoff as a steady state between dissolved and adsorbed P forms is approached. Although selection of an appropriate equilibration time may be somewhat arbitrary, buffer capacities consistent with observed amounts of P desorbed have been obtained using a 6-hr time period (Taylor and Kunishi 1971).

### TEMPERATURE

In describing effects of temperature on P reactions in soils, it is convenient to divide P into three forms (Barrow 1979)

dissolved P  $\rightarrow$  adsorbed P  $\rightarrow$  firmly held P  
+  $\quad$  +  $\quad$  +

Phosphate dissolved in solution is assumed to equilibrate with adsorbed P. Firmly held P is assumed to equilibrate with adsorbed P, but not directly with P in solution. The distribution of solid-phase P between adsorbed and firmly held forms is based primarily on kinetic considerations. Thus, quantities of P in the adsorbed and firmly held categories are somewhat analogous to quantities associated with fast and slow reactions, respectively.

Although varying temperature does not greatly affect the relative distribution of P between adsorbed and firmly held forms, increasing temperature causes a shift to dissolved forms (Barrow 1979), indicating that the adsorption process is exothermic. EPC determinations are usually made using short equilibration times; hence, dissolved and adsorbed P are the primary forms involved. Thus, increasing the temperature of measurement should increase the EPC and probably reduce the slope of the isotherm segment used for estimating buffer capacity. An approximately twofold increase in EPC determined at 25° C compared with that determined at 10° C has been observed (Barrow and Shaw 1975a). Similar effects would be expected with temperature variations in runoff. However, sufficient data are not available to estimate the magnitude of these effects over a variety of soil types.

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## AMOUNT OF P ADSORBED

Adsorption isotherms relating the change in P adsorbed per unit mass of solid to dissolved P levels in solution may be approximately linear over short segments such as those used for determining EPC (Taylor and Kunishi 1971). Over wide ranges of dissolved and adsorbed P, however, adsorption isotherms are typically curved, having positive slopes that decrease with increasing amounts of P adsorbed. Hence, slopes of isotherm segments are expected to decrease with increasing EPC for a given soil (fig. 2). As a result, the usefulness of buffer capacity estimates for predicting the distribution of P between dissolved and adsorbed forms may diminish as dissolved P concentrations exceed the range used for EPC measurement.

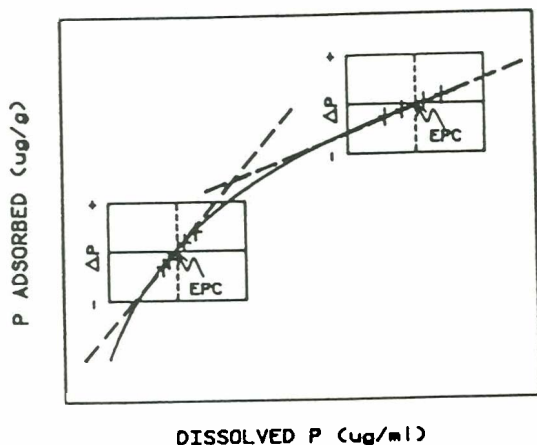


Figure 2.--P adsorption isotherm illustrating changes in P buffer capacity with EPC.

Errors resulting from extrapolations outside the range of measurement may be partially overcome by using nonlinear adsorption models to describe the relationship between dissolved and adsorbed P forms. However, this would increase the number of parameters needed to describe P adsorption, some of which would not be easily obtained. Moreover, the nonlinear adsorption models may also fail to fully describe P adsorption over wide concentration ranges (Barrow 1978). Thus, some extrapolation error would still be expected. However, these errors, although substantial, may be relatively small compared to those introduced in the hydrologic and sediment transport models or by assumptions on spatial variability.

## HYSTERESIS

Phosphate adsorption isotherms have often been observed to exhibit hysteresis in which less P is desorbed for equivalent changes in dissolved P than is adsorbed (fig. 3) (Barrow and Shaw 1975b, Fox and Kamprath 1970). Hysteresis is thought to be caused by the continued slow conversion of adsorbed P to more firmly held forms. When

sufficient time for P desorption is allowed (Madrid and Posner 1979) or when equilibration times are sufficiently short for slow reactions to be negligible (White and Taylor 1977), P adsorption reactions appear to be essentially reversible. EPC measurements primarily involve the fast reactions and, in the case of runoff, are applied to a system in which slow reactions are expected to have a minor effect. Hence, for this application, the assumption of isotherm reversibility should not result in major errors. However, an exception may be when major disequilibrium conditions exist (within sample heterogeneity with respect to P) in soil due to recent fertilizer P additions or severe depletion of P from localized areas by plant roots.

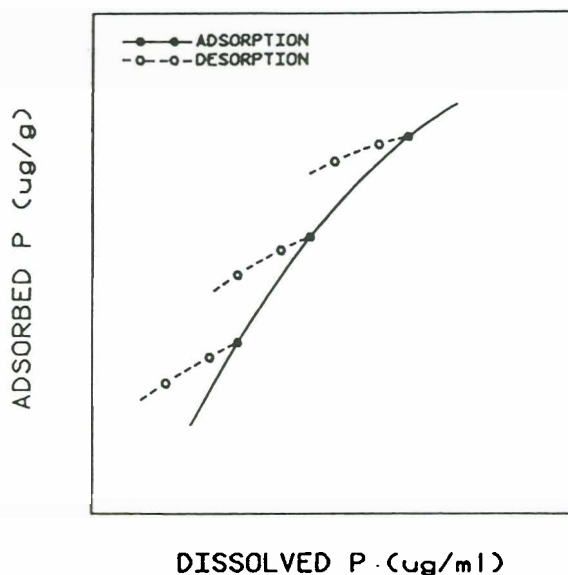


Figure 3.—P adsorption isotherm showing hysteresis frequently observed with subsequent P desorption.

## SOLUTION-TO-SOIL RATIO

Experimentally determined phosphate adsorption isotherms have been shown to vary with the ratio of water to soil or sediment, often termed the "solution-to-soil ratio" (Barrow and Shaw 1979, Hope and Syers 1976). Hence, relationships between concentrations of dissolved and adsorbed P determined at standard solution-to-soil ratios may often be in error when applied to sediments in runoff over a range of sediment concentrations. The influence of the solution-to-soil ratio on P adsorption is thought to be due to breakup of aggregated soil particles during shaking (Barrow and Shaw 1979). At lower solution-to-soil ratios, aggregates are postulated to break up more rapidly. This exposes additional sites for P adsorption, resulting in greater amounts of P adsorbed. The magnitude of the effect varies with vigor of shaking and soil type, presumably due to differences in aggregate stability among soils.

For application of results of adsorption studies to field soils, Barrow and Shaw (1979) have recommended that equilibration procedures which minimize particle breakdown be used for soils with aggregates of low stability. Soil particles in runoff, however, have experienced some dispersive forces during detachment and entrainment. Thus, special precautions to minimize breakdown during equilibration may not be appropriate. But because the magnitude of dispersive forces is expected to vary with event, it is not possible to recommend a single solution-to-soil ratio or method of agitation that would be directly applicable in all cases.

#### MICROBIAL ACTIVITY

Little effect of microbial activity on soil P is expected over equilibration times of a few hours or less. Thus, EPC determinations using such equilibration times should not be greatly influenced by microbial activity.

#### TYPE AND AMOUNT OF ELECTROLYTE

Increasing the concentration of neutral salt in aqueous, supporting solutions shifts the distribution of dissolved and adsorbed P in favor of the latter (Barrow 1972, Clark and Peach 1960). Thus, the choice of the amount and type of electrolyte in equilibrating solutions will influence the results of EPC determinations. Many studies of P adsorption on soil have been performed using an equilibrating solution of 0.01 M  $\text{CaCl}_2$ . Calcium is the predominant cation in many agricultural soils; and, for many soils, this solution is a reasonable approximation of the Ca concentration in soil solution (Olsen and Khasawneh 1980). Thus, it may be useful when P concentrations in equilibrating solutions are to be used for estimating dissolved P levels in soil solution or for comparing intrinsic differences among soil and sediment samples. However, lower Ca concentrations are expected in runoff water due to dilution. Moss (1963) observed Ca concentrations in soil water to decrease rapidly with dilution up to solution-to-soil ratios of approximately 1 to 1 and to decline less rapidly with further dilution. At solution-to-soil ratios of 100 to 1, Ca concentrations were about one-twentieth that at 0.4 to 1. Thus, for direct application of results to runoff, a dilute electrolyte solution such as 0.01 M  $\text{CaCl}_2$  will probably be excessive in most instances. Equilibrations in water at sufficiently wide solution-to-soil ratios to avoid the region where Ca concentrations change rapidly with dilution may be more appropriate.

#### DISCRETE PARTICLE SIZE AND AGGREGATION

Because of greater surface area per unit mass, smaller-sized, discrete soil particles should contain greater quantities of adsorbed P and sites for P adsorption. Hence, their mass should contribute disproportionately more to the

solution P buffer capacity than that of larger particles. However, aggregation of smaller, discrete particles may influence amounts of adsorbed P and the P buffer capacity by reducing reaction rates with internal particles (Evans and Syers 1971, Alberts et al. 1983).

Because smaller-sized particles tend to be eroded preferentially (Stoltenberg and White 1953) and exhibit greater concentrations of adsorbed P, the size distributions of aggregated and dispersed particles in soil and suspended sediment loads are important considerations for predicting P movement in runoff. Preferential removal of small particles results in sediments having both greater adsorbed P concentrations at equivalent dissolved P levels and greater P buffer capacities than those indicated from EPC determinations on the source soil. It may be possible to obtain appropriate correction factors, termed "enrichment ratios," from relatively simple functions of sediment concentration as is done for total P (Menzel 1980). However, because much sediment in runoff may be in the form of water stable aggregates (Alberts and Moldenhauer 1981), predicted enrichment based on changes in the proportion of discrete particles may result in overestimation where aggregation significantly restricts reaction rates on some particles.

#### OVERVIEW

If EPC determinations are used for making comparisons of P status among samples or as input to empirical predictive models, the above factors should not be critical. For the former application, standardizing the data collection procedures for all samples will eliminate most effects. For the latter, on-site calibration of the model can compensate for these differences. If the user's objective is to describe P reactions in runoff, the conditions of measurement affecting P reactions should approximate those expected in runoff as closely as possible. Although many of these conditions may be roughly approximated, unaccounted for variations in each in runoff are likely to contribute to prediction errors.

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