

Phosphate Equilibria on Stream Sediment and Soil in a Watershed Draining an Agricultural Region

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A study was made of the availability of phosphate adsorbed on streambed sediment and soil surrounding the stream in a watershed draining an agricultural region. The equilibrium level of phosphate in the ambient solution supported by the sediment

when compared with soluble phosphate in stream water indicates that the phosphate moves from the water to the sediment. Thus the sediment in this watershed acts as a scavenger for soluble phosphate.

The objective of the work reported here was to compare phosphate concentrations in the water of a stream draining agricultural land and the concentrations that could be predicted from laboratory studies of the equilibrium levels of phosphate in the soils and sediments in the area. The stream chosen for examination was a tributary of Mahantango Creek, which flows into the Susquehanna River north of Harrisburg, Pa. The Mahantango watershed, which encompasses 162 square miles, is a research watershed under study by the Northeast Watershed Research Center of the Soil and Water Conservation Research Division, ARS, located at University Park, Pa.

Two mountains, the Mahantango and Bear, run northeast to southwest, separating the region into two valleys, drained by the main Mahantango stream and Pine Creek. Little Deep Creek, the stream selected for the study, enters the lower Mahantango from the south, draining an area of more uniform topography and soil type than exists on the rest of the valleys. The predominant soil series is the Schuylkill, which is a light-textured loamy soil, low in organic matter, low in base exchange capacity, and slightly acid, being derived from noncalcareous, iron-rich parent material.

MATERIALS AND METHODS

Soluble phosphate in stream water was determined following the method of Dickman and Bray (1940) by evaporating 100 ml of water naturally free of solids to dryness, then redissolving in 4.0 ml of 0.5 *N* HCl before making up to 50-ml volume along with 5 ml of ammonium molybdate solution [24 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ per liter in 6 *N* HCl]. Six drops of SnCl_2 (a 1:9 dilution of 10 g of $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ dissolved in 25 ml of concentrated HCl) was added rapidly and the sample was immediately shaken. Spectrophotometric readings were made against a water blank at 720 $m\mu$ within 15 min after adding SnCl_2 .

The equilibrium phosphate concentration (EPC), the concentration that is supported by the solid sample when in contact with an ambient solution such that no phosphate is either gained or lost by the solid, was determined by the method of White and Beckett (1964). Soil samples were obtained with an auger and sediment samples were obtained with a spade. All samples were air dried and stored at 25° C. In this procedure, 2.5 g of solid material were equilibrated for 60 min in 25 ml of 0.01 *M* CaCl_2 containing differing amounts

of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (0 to 0.62 ppm of P), with 10 sec stirring on a Vortex mixer at 15-min intervals. Equilibration times, concentration of phosphate, and solid to solution ratios were altered in certain studies to examine some secondary effects. The equilibrated samples were centrifuged at $612 \times g$ for 10 min. Then 20-ml aliquots were taken up to 25-ml volumes along with 1 ml of ammonium molybdate solution [25 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ plus 275 ml of concentrated H_2SO_4 brought up to 1 l.] for soluble P determination following the procedure of Jackson (1958). One drop of SnCl_2 reagent (25 g $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ plus 50 ml of concentrated HCl brought up to 500 ml) was added and the contents were thoroughly shaken. Percent transmittance readings were taken promptly 7 min after addition of SnCl_2 on a spectrophotometer at 660- $m\mu$ wavelength through a solution thickness of 22 mm. The relative concentration error for most of the samples is estimated at 2%. For the few samples near the detection limit of 0.002 ppm, the relative concentration error is estimated at 25%.

Figure 1 illustrates the method used for determining the equilibrium phosphate concentration. The amounts of phosphate adsorbed or desorbed from the soil (in ppm of P) on equilibration with solutions whose initial concentrations were P_1' , P_2' , P_3' are calculated and plotted as a function of the final concentrations P_1 , P_2 , P_3 . The resulting curve establishes the equilibrium phosphate concentration (EPC) which is defined as that concentration at which no net adsorption or desorption takes place. This equilibrium concentration is, in effect, an empirical reference point on the sorption curve permitting a direct estimate of the capacity of the soil or sediment to adsorb or release phosphate if the concentration is changed. As an example, the heights of the ordinates at P_2 and P_3 in Figure 1 will represent the amounts of phosphate (in ppm P) that must be taken up or released if the soil or sediment reequilibrates to these concentrations from the original EPC. The slope of the tangent to the sorption curve is mathematically related to the Q/I relation of White and Beckett (1964). This slope may be regarded as an index of the capacity of the soil or sediment for buffering the phosphate concentration in the solution.

This buffer capacity is not necessarily related to the total adsorbed phosphate or even the amount of biologically available phosphate. Owing to differences in texture and chemical composition, two soils may have curves of different slopes at the same EPC value. The values of the slopes of the two tangents will then represent the relative amounts of adsorbed phosphate that are in immediate exchange equilibrium with the particular concentration. If the amount of biologically available phosphate were defined as that which must be

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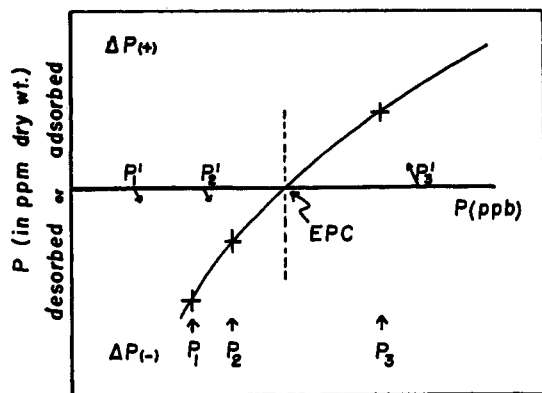


Figure 1. Estimation of the EPC by equilibration of a sample with different initial phosphorus concentrations, P_1' , P_2' , and P_3' . After equilibration, the intercept of the adsorption-desorption curve (through P_1 , P_2 , and P_3) yields the value of the equilibrium phosphorus concentration (the EPC) where phosphate is neither adsorbed nor desorbed

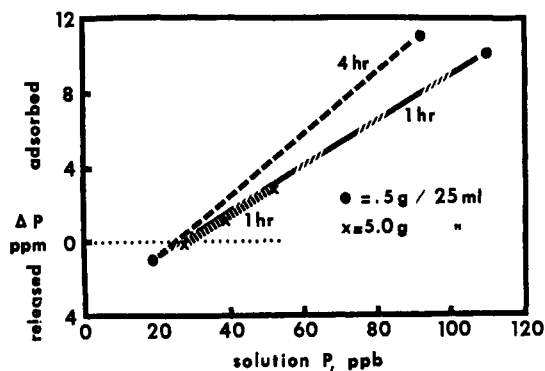


Figure 2. Phosphate sorption curves for a stream sediment sample measured with different sediment:solution ratios and equilibration time periods

removed to bring the sediment into equilibrium with an arbitrarily chosen concentration (say 5 ppb P), this could be estimated from the height of the ordinate at $[P] = 5$ ppb. Since the sorption curve is not always rectilinear, this value will usually be greater than an estimate obtained by extrapolation of the tangent to the curve at the EPC.

EXPERIMENTS AND RESULTS

Soil to Solution Ratio and Time of Equilibration. A sediment sample taken in the fall of 1969 from a tributary of the Little Deep Creek was used to determine a suitable soil to solution ratio and length of equilibration period.

Suspensions of the sample containing soil:solution ratios ranging from 0.5 to 5 g/25 ml equilibrated for 1 hr yielded EPC values that were nearly the same (Figure 2). For this and similar sediment samples yielding low EPC values, it appears that the choice of soil to solution ratio is not critical.

In another study with the same sample of sediment the equilibration period was extended to 4 hr. The results in Figure 2 show that where phosphate was not added to the equilibrating solution initially, the same amount of phosphate was released to the solution by the sediment with 1- and 4-hr equilibration periods. Where phosphate had been added to the equilibrating solution in excess of the EPC, more was taken up from solution by the sediment with increasing equilibration time. The difference in EPC between 1-hr and 4-hr equilibration periods was small, and the 1-hr period should provide a useful approximate value. Thus the

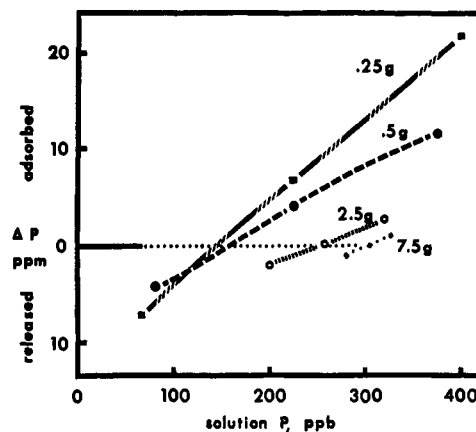


Figure 3. Phosphate sorption curves for a fertilized field soil sample at different soil:solution ratios. All equilibration times were 1 hr and all solution volumes were 25 ml

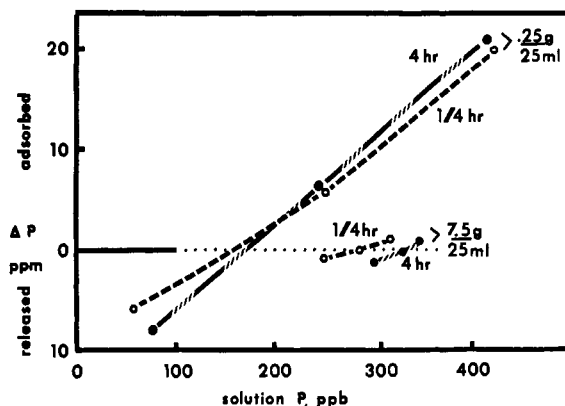


Figure 4. Phosphate sorption curves for a fertilized field soil sample with two soil:solution ratios and two equilibration times

1-hr equilibration period was chosen for most subsequent determinations. In this relatively short period of equilibration inorganic phosphate uptake by microorganisms was probably not significant.

A second sample used in this preliminary study was obtained from a field under continuous cropping that had been fertilized a few weeks before the sample was taken in the spring of 1969. Samples weighing between 7.5 and 0.25 g were equilibrated for up to 4 hr in 25-ml solutions containing 0.01 M CaCl_2 and different levels of phosphate.

In 1-hr equilibrations, the EPC increased as the amount of soil was increased, while the phosphate buffering capacity, as indicated by the slope of the curve, decreased (Figure 3). These differences observed with different soil:solution ratios indicated that the phosphate in the sample was not in an equilibrium condition, probably as a result of the recent addition of fertilizer phosphate. This interpretation rests in part on work reported by White (1966), who found that when nonequilibrium soils were stored under aerated, field-moist conditions, equilibrium was reached in about 100 days. The samples then showed no change in the phosphate sorption curve with change in soil:solution ratios.

The effect of nonequilibrium time on phosphate adsorption or release by the nonequilibrium soil varied with the soil:solution ratio and the direction of the reaction. Where phosphate was released, more desorbed as the equilibration time was increased regardless of the soil:solution ratio (Figure 4). Where phosphate was adsorbed by suspensions of lowest

soil:solution ratio (0.25 g/25 ml), adsorption continued for about 2 hr. In suspensions with greater amounts of soil (7.5 g/25 ml), the adsorption continued to increase with time up to 4 hr. The reason for these observations is not clear. Microbial uptake of inorganic phosphate does not appear to be significant for samples equilibrated up to 4 hr. The effect is more likely to be due to redistribution of unstable forms of phosphate as the suspension settles towards final equilibrium. If some slow dissolution of phosphate that has precipitated in the dry sample is taking place, the amount that has to re-equilibrate, and hence the time needed for completion of the reaction, will increase with the amount of soil present.

The selection of a single best soil:solution ratio and equilibration time is not possible. Where the original sample is close to equilibrium and has not been recently fertilized or cropped, the soil:solution ratio is not important.

Since the primary objective of the measurement is to determine the EPC, it is desirable that the amount of soil or sediment should be large enough to give accurately measurable changes in the solution phase during the equilibration. Thus, in Figure 1, the values of P_1 , P_2 , and P_3 should differ significantly from P_1' , P_2' , and P_3' . If very dilute suspensions are used, the amount of adsorbing or desorbing surface present may be too small to achieve this.

When the amount of phosphate released is very small, as may happen in a phosphate deficient sediment or a recent heavily cropped soil, a ratio of 1:10 may be required. For a recently fertilized, nonequilibrium sample, a soil:solution ratio of 1:100 may be justified since this reaches a state of slow change in an equilibration of 1 hr (White, 1966).

Multiple Equilibration Experiments. The usefulness of the slope of the tangent to the curve at the EPC as an aid to estimating the amount of phosphorus that would desorb from the soil was examined in another set of experiments. The nonequilibrium soil used in the time-of-equilibrium study was used in this work. This soil showed an EPC of 310 ppb. Three 2.5-g samples were equilibrated for 1 hr with solutions containing 620 ppb, 310 ppb, and zero phosphorus. The supernatant solution was then removed for analysis and replaced with fresh solution containing the same initial phosphate concentration. This procedure was repeated eight times. The changes in phosphate concentration in each solution were related to desorption or adsorption of soil phosphate in the normal way, and a selection of the resulting sorption curves is plotted in Figure 5.

The successive equilibrations at 310 ppb showed no change in the EPC, confirming the equilibrium condition. The equilibrations in the phosphate-free solution showed continuous desorption, although the amount released by the soil, and consequently the phosphate concentration established in the solution, decreased progressively with successive equilibrations. Adsorption from the 620-ppb solutions showed decreasing stepwise adsorption as the total retained by the soil increased. The amounts of phosphate released or adsorbed by the soil in each equilibration are plotted in Figure 6. Linear extrapolation of the curve through the "released" data suggests that ΔP will become very small after about 15 equilibrations. Summation of the total phosphate released yields a value of 12.7 ppm P. This value agrees well with the value of 12.5 estimated by extrapolation of the EPC tangent determined in a single 6-hr equilibration to the zero concentration axis (data not presented). A similar examination of the adsorption data suggests that again 15 equilibrations would bring the soil close to saturation at the 620-ppb concentration level with the total uptake of about 13 ppm P.

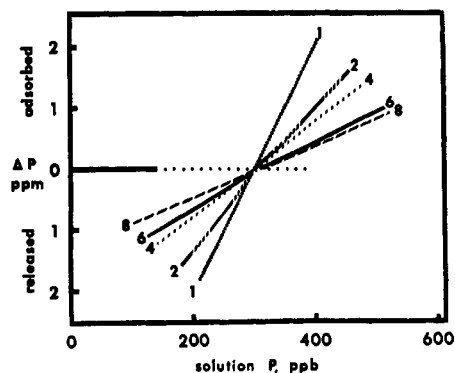


Figure 5. Changes in the sorption curves of a fertilized soil sample equilibrated eight successive times with solutions initially 620 ppb, 310 ppb, and zero P

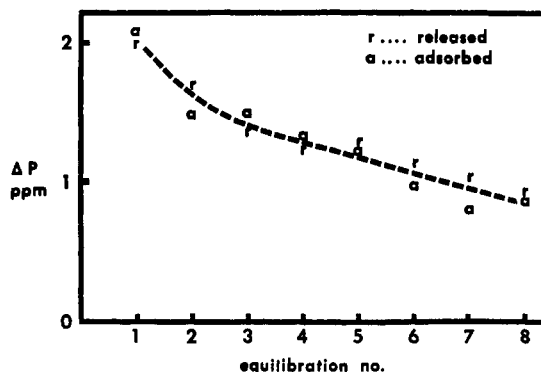


Figure 6. Adsorption and desorption of phosphate from a soil sample in successive equilibrations

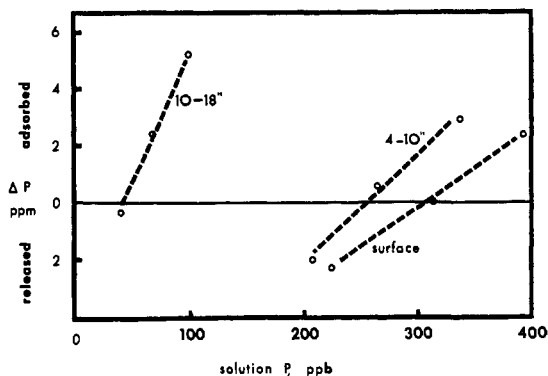


Figure 7. Differences in the sorption curves between soil samples taken at increasing depths at the same site

Even this high phosphate soil has a considerable capacity remaining for adsorption of phosphate from water containing levels of 600 ppb and above.

The multiple equilibration experiment confirms that a single 6-hr equilibration experiment yields good estimates of the EPC and the capacity of the soil or sediment to release or adsorb phosphate. In routine analyses this time may be inconveniently long and in some soils microbial effects may become significant (White, 1964). Where measurements are being made with samples from a restricted area that contain similar materials, single 1-hr equilibrations will give satisfactory EPC values, but the adsorption capacities may have to be estimated from the relation between EPC and capacity found in a limited number of 6-hr determinations on samples typical of the area being examined.

Characterization of Field Soils. The adsorption isotherms of six soil samples taken from the Little Deep Creek Watershed are presented in Figures 7 and 8. The samples fall into three

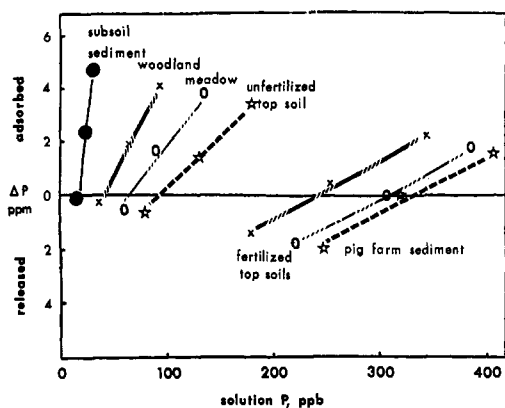


Figure 8. Phosphate sorption curves of samples of a range of soils and sediments from the Mahantango watershed

general groups. The first, with lowest phosphate status, includes subsoils and stream bank sediments with EPC values below about 50 ppb of P. The second group with EPC values between 50 to 100 ppb contains lightly fertilized fields, unfertilized meadows, and woodland soils. The third contains liberally fertilized topsoils and a sample of sediment taken from the bed of a small stream draining a farmyard containing a pig-rearing operation. The high level of this sample can be attributed to the cumulative effect of the animal waste. The range of EPC values of the surface soil samples gives some indication of the phosphate concentration to be expected in the water held by these soils or in runoff derived directly from them. Accurate predictions may be impossible because it is not possible to estimate how closely equilibrium conditions will be kept during the rapid fluctuations of flow during a runoff event.

The information on adsorptive capacity contained in the curves is of greater importance than a simple estimation of the EPC. The general increase in slope of the curves as the EPC values of the samples decrease shows that not only are the poorly fertilized materials lower in phosphate status but they have a greater capacity for removing phosphate from solutions brought into contact with them. The slopes of the curves in Figure 7 indicate that about 8 ppm of P must be desorbed from the surface soil to reduce its EPC to that of the sample from 10–18 in. in depth. At the same time the latter sample is capable of adsorbing much more phosphate than this when exposed to a solution containing 300 ppb of P. The larger bulk of material represented by the subsoil sample will amplify the effect of the higher adsorption capacity, making the downward movement of phosphate very slow and reducing the phosphate content of the subsoil water to not more than about 40 ppb of P.

The data in Figure 8 can be used to make similar predictions on the changes in phosphate concentration in runoff water as it is exposed to sediment. The curve for the subsoil and stream sediment in Figure 8 shows that this will take up 5 ppm of P as the concentration in the water is reduced from about 30 to 15 ppb. The amount that would be taken up from solutions containing 100 ppb or more is too large to estimate by extrapolation of the data presented. In contrast, the fertilized topsoil will desorb 0.3 ppm in response to a change of 15 ppb in the solution concentration. This implies that when runoff water comes in contact with phosphate-deficient sediments such as those derived from stream banks it will be exposed to a large adsorption sink that will remove considerable amounts from solution.

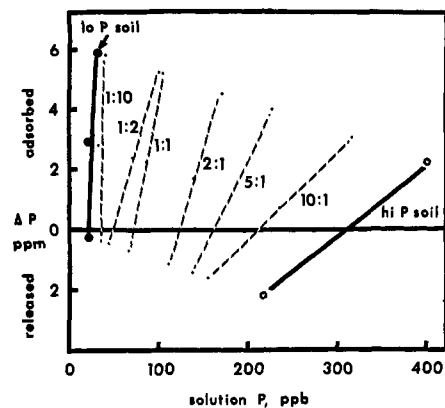


Figure 9. Phosphate sorption curves of mixtures of soil and subsoil

A parallel situation may arise during erosion when topsoil becomes mixed with sediments from stream banks, and the phosphate concentration in the solution will reflect the exchange between the two materials. In the experiment giving the data presented in Figure 9, 2.5-g samples were made by mixing fertilized topsoil and subsoil in different ratios and equilibrated for 1 hr with 25-ml volumes of solutions with different initial phosphate concentrations. The results show that the addition of 20% of the deficient material is sufficient to reduce the EPC by one-half, and equal amounts of the two soils produce an EPC about 70 ppb or about one-fifth of that in the fertile topsoil. The slopes of the sorption curves change uniformly with EPC, suggesting that the mechanism controlling the phosphate adsorption is essentially the same, changing only in degree as the sample becomes more deficient in phosphate.

Stream Water Composition. The phosphate concentrations in Little Deep Creek lie in the same range as those indicated by the subsoil data. Clarified samples obtained by centrifuging stream water taken during high spring flow contained 15 to 20 ppb of P. During low flow in quiet conditions in the fall the dissolved phosphate concentrations were in the range of 40 to 60 ppb of P, which is close to the level expected from water released from the subsoil. These concentrations are similar to others found in permanent streams draining agricultural land in the Appalachian region by Taylor *et al.* (1971). The seasonal variations may reflect temperature variations or be the result of the release of phosphate by decaying vegetation in the stream channel which is being reabsorbed from the flowing water. The process of adsorption may be expected to be least efficient under conditions of low water flow when there is least mixing with the water. Several samples taken from the main Mahantango Stream into which Little Deep Creek flows showed very low soluble phosphate levels of about 6 ppb P under similar quiet fall conditions.

The course of the adsorption process is illustrated by the data in Figure 10, in which phosphate concentrations in the stream water are compared with the EPC values of sediment samples taken from the stream bed at the same time and place. Except for the sample taken from close to the pig farm, all the EPC values lie between 10 and 30 ppb. Except in the immediate neighborhood of the pig farm, which represents a source of high phosphate water, all the stream concentrations are in the range between 30 and 60 ppb. Comparison of the concentrations and EPC values at the sampling sites reveals a tendency for the difference between them to

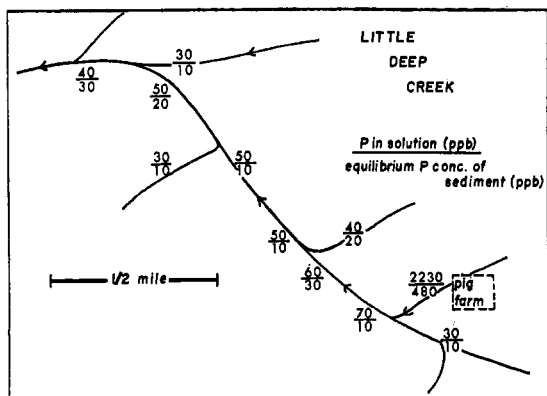


Figure 10. Phosphate concentration in stream water and EPC values of sediments taken together at points along the course of the stream under quiet conditions of low flow

decrease downstream as phosphate is taken up by the sediment. The effect is also very marked close to the pig farm itself where the concentration in the main stream decreases from 70 to 50 ppb within a half mile distance. The difference between the concentration in the pig farm tributary and the stream itself may be due in large part to dilution.

The lack of complete equilibrium between sediment and stream water may be due to several causes. Kinetic factors such as flow rate and the amount of mixing due to turbulence in the moving water will govern the fraction of the water that is actually exposed to the sediments. Under very high flow conditions where the sediments are disturbed and carried in the water, the equilibrium is likely to be reached more rapidly than in quiet conditions where there is little mixing. The samples described in Figure 10 were obtained under quiet conditions in the fall, when conditions were least favorable for complete equilibrium.

CONCLUSION

The data obtained show that in the Mahantango watershed the contribution made to the phosphate burden of the stream by sediments, stream banks, and field soils is small. The base material of subsoils and stream banks has a very large capacity to adsorb phosphate and acts as a strong buffer to reduce the phosphate level of the stream. Meadow soils, stream banks, and sediments all tend to adsorb the phosphate that may leave the more highly fertilized areas by runoff or erosion.

The largest source of phosphate input to the stream was from a small tributary draining a pig farm. The EPC value of the sediment in this tributary was higher than that in the most heavily fertilized field soil samples. Although the effect of this particular source of phosphate was not detectable in the sediment a short distance downstream from the confluence, the amount of phosphate in solution was raised significantly for about 1 mile downstream under the flow conditions prevailing at the time of sampling.

ACKNOWLEDGMENT

The authors wish to acknowledge the contribution of the staff of the Northeast Watershed Research Center at University Park in planning this study and for assistance in obtaining the samples examined.

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Received for review February 4, 1971. Accepted April 14, 1971. This work is part of a cooperative study between the Northeast Watershed Research Center at University Park, Pa., and the U.S. Soils Laboratory, both of the Northeast Branch of Soil and Water Conservation Research Division.