

EFFECT OF STORAGE TIME ON THE SOLUBLE PHOSPHORUS CONCENTRATION OF UNFILTERED RUNOFF SAMPLES

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The change in soluble P concentration of unfiltered runoff samples with time following sample collection was investigated using simulated rainfall. No effect of storage time on soluble P concentration for 2 unfertilized soils was observed. With fertilized soils (50 kg P/ha) large increases (25%) in soluble P concentrations in runoff were observed when samples were stored for 24 hr at 4 C if the sediment content was 3500 mg/l or more. With a decrease in sediment content below 2000 mg/l, little change in soluble P concentration (<10%) was found in runoff from both fertilized and unfertilized soil. The results are discussed in terms of water quality monitoring for several other inorganic and organic pollutants.

INTRODUCTION

The importance of phosphorus (P) in runoff from agricultural land in controlling the growth of nuisance aquatic weeds and algae in lakes and rivers is well documented (1, 2, 3, 4). Due to the appreciably greater availability of soluble P than sediment P to aquatic organisms (5, 6), it is important to determine the relative amounts of the two forms of P transported in runoff. It is not always possible, however, to initiate sample analysis immediately following collection, as when large numbers of samples are produced during short time periods and remote watersheds are sampled. In such cases, samples may be stored for several days before filtration. As the release and uptake of P by sediment in runoff is rapid (7, 8), it is possible that transformations between soluble and sediment phases may occur, leading to erroneous values of the concentration of these nutrient forms upon analysis.

This paper reports an investigation of the extent to which storage time, temperature, and amounts of sediment in runoff affect the concentration of soluble P of unfiltered samples of runoff from simulated rainfall in the laboratory.

MATERIALS AND METHODS

The effect of (a) time interval between surface runoff collection and sample analysis and (b) storage temperatures on the soluble P concentration of samples was investigated for two soils using simulated rainfall. The soils used, Houston Black clay (Udic Pellustert, fine, montmorillonitic, thermic) and Ruston fine sandy loam (Typic Paleudult, fine-loamy, siliceous, thermic), were representative of two major soil types from watersheds in Oklahoma and Texas presently being monitored for water quality (8). The chemical and physical properties of the soils used are summarized in Table 1. Particle size distribution of the soils was determined by pipette analysis after dispersion with sodium hexametaphosphate (9). Soil pH was measured with a glass electrode using a

TABLE 1. *Physical and chemical properties of soils used.*

Soil	Particle size analysis			pH	Organic matter %	Total P $\mu\text{g/g}$	Water P ^a	
	Sand %	Silt %	Clay %				P applied (kg P/ha)	
							0 $\mu\text{g/g}$	50 $\mu\text{g/g}$
Houston Black	10.9	39.4	49.7	7.8	3.00	477	5.05	24.3
Ruston	73.5	18.3	8.2	6.5	1.86	241	6.71	36.7

^aWater-extractable P content (100:1 for 1 hr) of native and P-amended soil after the 3-day incubation

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1:2.5 soil:water ratio. Organic matter content was determined by loss in weight after ignition following acid treatment (10) and total P after perchloric acid digestion (11).

In each case, the top 10 cm of the soil profile was collected, air-dried and sieved (<4 mm) prior to being packed in perforated-bottom boxes 100 × 30 × 15 cm, facilitating free drainage. The slope of the soil surface was 4%. Two P treatments were evaluated by uniformly mixing $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with the top 4 cm of soil prior to packing, at rates equivalent to surface applications of 0 and 50 kg P/ha. The soil was packed to a bulk density similar to that of the field soil and slowly wetted by a drip system. Three days incubation was allowed before application of simulated rain.

Rainfall of 6 cm/hr intensity (approximate frequency of 2 years in Oklahoma and North Texas) was applied with a laboratory drip-tube type rain-simulator, 110 × 40 cm in dimension (12), for three 30-min periods at 2-hr intervals. Total runoff water was collected from each 30-min runoff event and 40 mg HgCl_2/l added to inhibit microbial activity (13). Subsamples (50-ml) were taken from the total runoff 1, 5, 15, 30, 60, 180 and 1440 min after runoff had ceased and centrifuged (15,000 rpm) to facilitate Millipore filtration (<0.45 μm). The concentration of soluble P of the sample collected 1 min after runoff cessation was taken as the initial P value prior to interaction with the suspended sediments.

Prior to the first runoff event, the soil in the packed boxes was sampled to a 1-cm depth at 4 different locations, and analyzed for water-extractable inorganic P. The holes thus made were plugged with paraffin wax. Soil water-extractable P was determined by extraction of duplicate samples at a ratio of distilled water to soil of 100:1 for one hr, on an end-over-end shaker at 25 C. The water-extractable P content of air-dried suspended sediment from each runoff event was also determined at a water:sediment ratio of 100:1 after one hr shaking.

The effect of suspended sediment content of runoff samples on the change in soluble P concentration with time after collection was evaluated. The suspended sediment was concentrated to a slurry by settling and decantation. This was carried out by mixing different amounts of sediment from the first runoff event, as a concentrated slurry, with distilled water of soluble P concentration of 0.30 mg/l (added as KH_2PO_4). The mixture was kept at 4 C and the concentration of soluble P measured at intervals over a period of 24 hr. The concentrations of suspended sediment and soluble P used in the experiment are equivalent to those observed in both field and laboratory studies (8). The concentration of soluble P was determined on all filtered samples by the colorimetric molybdenum-blue method (14), with absorbance measured at 712 nm using 10- and 5-cm cells, allowing a detection limit of 0.004 and 0.008 mg/l, respectively. Sediment content was determined as the difference in the weights of 250-ml aliquots of unfiltered and filtered samples after evaporation to dryness.

RESULTS AND DISCUSSION

The reproducibility of the experimental techniques used to simulate runoff were investigated using four replicate treatments of Houston Black soil, amended with 0 and 50 kg P/ha. The variability of the mean soluble P concentration for the 30-min event was 2.4 and 6.1% of the average value for the four replicates (at the 5% confidence level), for amendments of 0 and 50 kg P/ha, respectively. A slightly greater variability of 8.0 and 6.6% was obtained for sediment content. It is apparent that the treatments gave fairly reproducible results and thus, no replication was used for further treatments.

The effect of storage time on the soluble P concentration of unfiltered runoff samples, from the first runoff event for Houston Black and Ruston soils, is presented in Fig. 1. For both unamended Houston Black and Ruston soils, the soluble P concentration of runoff kept at 4 C remained constant at values of 0.036 and 0.083 mg/l, respectively, during 24 hr following sample collection (Fig. 1). When the unfiltered samples were kept at 25 C, no significant difference in soluble P concentration was observed (Fig. 1). In the case of soil amended with 50 kg P/ha, an increase in soluble P concentration occurred with sample storage at 25 C compared to 4 C. Although similar trends were observed for successive runoff events, a decrease in soluble P con-

centration with increasing event number was evident. At corresponding events and P treatments, however, the concentration of soluble P of runoff from Houston Black soil was lower than that from Ruston soil (Fig. 1). This may be attributed to the lower water-extractable P content of Houston Black compared to Ruston soil for both native and P amended soil (Table 1).

The percent increase in soluble P concentration from the initial value, 1 min after collection for the first and third runoff events, as a function of time and incubation temperature, is given in Fig. 2. Sample incubation temperature had no effect on the increase in soluble P concentration during the initial 30-min after sample collection. Following this, however, the percent increase in concentration was greater at the warmer temperature. Twenty-four hours after sample collection the soluble P concentration had increased by 27 and 31% for the first runoff event from Houston Black soil, when kept at 4 and 25 C, respectively, and similarly 29 and 38% for Ruston soil. The increase was not as great for the third runoff event, where P concentrations in runoff from Houston Black and Ruston soil had increased by only 21 and 26%, respectively, when stored at 4 C for 24 hr (Fig. 2). The results indicate that if surface runoff from the amended soils is not filtered within 30 min of collection, soluble P concentration can increase by more than 10%.

The concentration of sediment and soluble P of runoff 1 min after collection from Houston Black and Ruston soils, at both P amendments, is given in Table 2. A decrease in soluble P concentration was coincident with a decrease in sediment content of successive runoff events (Table 2). Consequently, the ability of sediments from successive events to change the soluble P concentration cannot be compared. The release of P from the sediment trans-

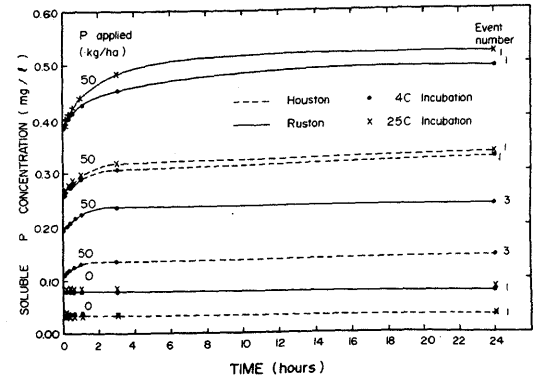


FIGURE 1. Soluble P concentration of unfiltered runoff from Houston Black and Ruston soils amended with 0 and 50 kg P/ha, as a function of time after collection with storage at 4 and 25 C, for events 1 and 3.

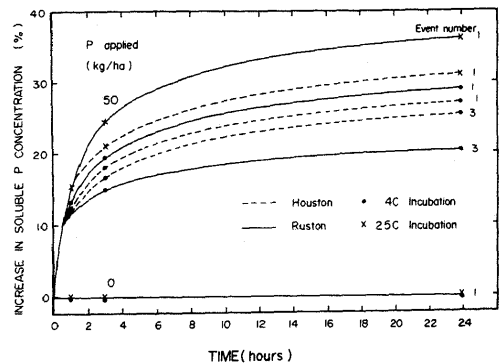


FIGURE 2. Percent increase in the soluble P concentration of runoff 1 min after collection for Houston Black and Ruston soils amended with 0 and 50 kg P/ha, as a function of time after collection with storage at 4 and 25 C.

TABLE 2. Concentration of sediment and soluble P of runoff 1 min after collection, for Houston Black and Ruston soils amended with 0 and 50 kg P/ha.

Soil	Event number	Sediment concentration (mg/l)		Initial soluble P concentration (mg/l)	
		0	50	0	50
Houston Black	1	2887	3320	0.036	0.257
	2	2683	2567	0.030	0.154
	3	—	2236	—	0.112
Ruston	1	4727	4950	0.083	0.382
	2	3927	3640	0.048	0.257
	3	—	3010	—	0.198

ported in runoff events during sample storage is thus represented on a unit weight basis (Fig. 3). It is evident from the data presented in Fig. 3 that the release of P from sediment decreases with increasing event number. This is consistent with a decrease in amount of water-extractable P in sediment transported in runoff from successive events (Table 3). As no P was added to the soil between events and the short time interval between events (2 hr) did not allow organic P to be mineralized, the source of inorganic P to runoff in the soil is depleted during runoff.

Because of the differing abilities of sediments to change the soluble P concentration of runoff with successive events, the effect of sediment content cannot be evaluated. In addition, sediment content of runoff from cropped and grassed watershed is not as high as measured in runoff from bare soil under simulated rainfall (8). Consequently, varying amounts of sediment from the first rainfall event were mixed with distilled water made to contain 0.30 mg/l soluble P (added as KH_2PO_4), and the mixture kept for 24 hr at 4 C. The percent increase in soluble P concentration as a function of sediment content, from Houston Black and Ruston soils amended with 50 kg P/ha, is presented in Fig. 4. A linear relationship between soluble P increase and sediment content was obtained for both soils over the range of sediment concentrations used. It is apparent that sediment contents in excess of approximately 2000 mg/l will increase the soluble P concentration of stored runoff above the initial value of 0.30 mg/l, by more than 10%.

In a similar study, Nelson and Romkens found that freezing runoff samples following collection resulted in a reduction in soluble P concentration compared to samples analyzed immediately following collection (15). This decrease was attributed to an increased P sorption due to soil freezing and frost heaving processes, concentrating P and increasing amounts of soil colloids suspended in the liquid phase.

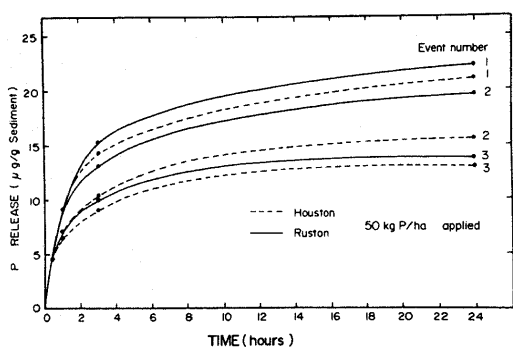


FIGURE 3. Release of P from sediment in unfiltered runoff from Houston Black and Ruston soils amended with 50 kg P/ha, as a function of time after collection with storage at 4 C.

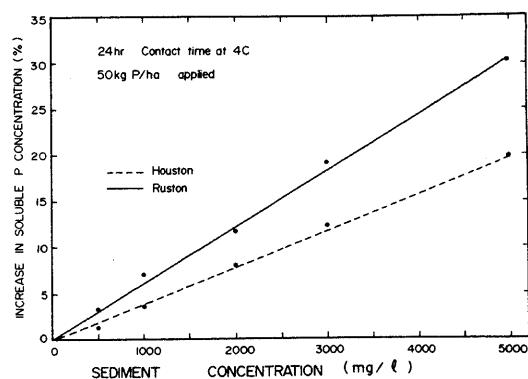


FIGURE 4. Percent increase in soluble P concentration from an initial value of 0.30 mg/l, as a function of sediment concentration, for Houston Black and Ruston soils previously amended with 50 kg P/ha after 24 hr contact with storage at 4 C.

TABLE 3. Water-extractable P content of sediment transported in 3 successive runoff events from Houston Black and Ruston soils amended with 0 and 50 kg P/ha.

Soil	Event number	Water extractable P ^a ($\mu\text{g/g}$)	
		0	50
Houston Black	1	7.4	20.9
	2	6.9	18.2
	3	—	15.8
Ruston	1	36.0	105.5
	2	31.2	77.7
	3	—	70.7

^aAmount of P extracted in one hr at a water:sediment ratio of 100:1.

CONCLUSION

It is apparent from the results presented that there was no effect of storage time on the soluble P concentration of unfiltered runoff samples for both unfertilized soils under simulated rainfall. With the addition of fertilizer P to the soil, however, unacceptably high changes in soluble P concentration (25% increase) were obtained for runoff samples with a sediment content of 3500 mg/l and initial soluble P concentration of approximately 0.30 mg/l, that were kept for 24 hr at 4 C. If the unfiltered samples were not cooled but kept at 25 C, the changes in P concentration were even greater (35% increase over 24 hr). With successive runoff events a decrease in the water-extractable P content of sediment transported in runoff was observed, which corresponded to a decrease in the ability of sediment to change soluble P concentrations of runoff with successive events.

The concentrations of sediment in runoff from the bare soils under simulated rainfall are higher than those usually observed in runoff from grassed and cropped watersheds, where the vegetative cover reduces the energy of rainfall impact and subsequently soil detachment and erosion. If the sediment content of runoff falls below approximately 1000 mg/l, then little change in soluble P concentration with sample storage, even for fertilized soils, can be expected.

The results obtained on the transformations of P between solid and liquid forms during sample storage can be extrapolated to other chemicals, such as pesticides, herbicides, and organic wastes, which may be sorbed by soil. The extent to which the soluble forms of these chemicals will change will be related to the soil's capacity to sorb the chemical. Although this capacity varies with soil type, it is expected that the degree of change in form of a chemical will increase as its capacity to be sorbed increases.

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