

DETERMINATION OF THE RATE OF TRIPOLY- AND PYRO-PHOSPHATE  
HYDROLYSIS IN SEDIMENTS

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## ABSTRACT

The rate of hydrolysis of tripolyphosphate (TPP) and pyrophosphate (PP) in sediments was determined. The sediments used were collected from Cape Fair, Thomas Hill Lake, Flat Branch Creek, and Maries River. The rate of hydrolysis of TPP and PP was similar to that predicted from first order kinetics. Half lives for the hydrolysis of TPP and PP were found to be 1.6 to 2.6 and 6.7 to 27.4 days, respectively. The influence of temperature, biological activity, and pH on the rate of TPP and PP hydrolysis was investigated using Flat Branch Creek sediment. The rate of TPP and PP hydrolysis increased with increasing temperature. The activation energy was 5415 cal/mole for TPP and 10,412 cal/mole for PP. TPP and PP were hydrolyzed faster in non-sterile sediment than in sediment which had been sterilized, possibly due to the destruction of phosphatase and pyrophosphatase enzyme systems during sterilization. The half life for TPP hydrolysis was 1.76 day at pH 5, 1.61 day at pH 7, and 2.16 day at pH 9. PP hydrolysis was increased as pH was increased from 5 to 7 to 9 as indicated by half lives of 13.7, 10.0, and 7.3 days, respectively. When TPP was added to the sediment as a  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  precipitate the rate of hydrolysis was slower ( $\frac{1}{2}$ life = 2.79 day) than when TPP was added as a solution ( $\frac{1}{2}$ life = 1.68 day).

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Keywords:

Phosphate, polyphosphate, pyrophosphate, tripolyphosphate

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## INTRODUCTION

Tripolyphosphate (TPP) or pyrophosphate (PP) may occur in sediment due to erosion of soils which were fertilized with long chain-, tripoly-, or pyro-phosphates. High analysis phosphate fertilizers containing PP, and TPP are manufactured either as liquid or solid fertilizers. Use of these materials has been steadily increasing. Detergents which contain TPP and PP are another source of phosphates in sediments. Aside from these sources, PP, TPP, and longer chain phosphates are synthesized in soils by microorganisms.

PP and TPP may be present in sediments. Phosphates added as fertilizers to soils may be transported by erosion to rivers, lakes, and streams. They could be added to sediment as effluents from sewage plants, septic tanks, and storm sewers. Feed additives used in feedlots also contain phosphates that could be washed off and added to sediments. No information is available on the rate at which PP and TPP are hydrolyzed to orthophosphate.

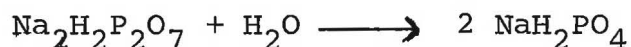
## STATEMENT OF THE PROBLEM AND OBJECTIVES

Control of levels of phosphates in rivers, lakes, streams, sewage systems, lagoons, and farm ponds depend on our knowledge of the nature, forms, and amount of phosphates present in these systems. A necessary part of this system is to know how long PP and TPP persist in sediments before they are hydrolyzed to orthophosphate.

Control of eutrophication where phosphorus is the limiting factor for algae growth is being studied by many researchers, some of these are concerned with the phosphorus chemistry of the sediment. Frink (1969a) conducted analysis and fractionation of orthophosphates in lake sediment. He also (1969b) made chemical and mineralogical characterizations of eutrophic lake sediments. If these sediments contain PP or TPP, it will be helpful to know the amounts present and rate with which they hydrolyze to orthophosphate. The study could add important information on the relationship between orthophosphate chemistry and the growth of aquatic plants. The rate of TPP and PP hydrolysis in sediments has not been measured.

Reaction of TPP with water results in the formation of one mole of PP and one mole of orthophosphate. One mole of PP can further hydrolyze to two moles of orthophosphate.

These reactions are shown below:



Van Wazer (1958) reported factors including temperature, pH, enzymes, colloidal gel, complexing cations, concentration, and ionic environment in the solution affect the hydrolysis of PP and TPP.

Van Wazer et al. (1952) and McCullough et al. (1956) have reported that the hydrolysis of large chain phosphates are pH dependent. The influence of pH on the hydrolysis of TPP has been reported by Blanchar and Hossner (1969a),



Growther and Westman (1954), and Huffman and Fleming (1960). PP hydrolysis as a function of pH has been reported by Crowther and Westman (1954), Gilliam and Sample (1968), Hossner and Melton (1970), and Sulton and Larsen (1964). Blanchar and Hossner (1969a) reported the maximum rate of TPP hydrolysis occurred near pH seven in soils. No measurements have been made on the rate of hydrolysis of TPP in sediments.

Hydrolysis of TPP in aqueous solutions has been shown to be more rapid at higher temperatures, Huffman and Fleming (1960), Strauss and Treitler (1956), and Van Wazer et al. (1952, 1955). No reports on the effect of temperature variations on the rate of TPP hydrolysis in either soils or sediments have been reported.

PP was hydrolyzed at higher rates at higher temperatures. Hossner and Phillips (1971) showed activation energies of around 24,500 cal/mole in Texas soils for the hydrolysis of PP to orthophosphate. They concluded that an activation energy of this magnitude indicated that the reaction was biologically catalyzed. Many others have concluded that hydrolysis of PP in soils is biological, Gilliam (1970), Gilliam and Sample (1968), Ging and Sturtevant (1954), Hashimoto et al. (1969), Hughes and Hashimoto (1971), Juo and Maduakor (1973), Sutton et al. (1966), Sutton and Larsen (1964), and Racz and Savant (1972).

Hashimoto et al. (1969) found that in very dilute solutions, kaolinite, montmorillonite, and particularly goethite

showed some degree of catalytic activity for PP hydrolysis. However, Sutton and Larsen (1964) found no direct correlation between clay content of soil and hydrolysis rate of PP.

Do stable precipitates of TPP in sediments reduce the rate of hydrolysis? This question was partially answered by adding TPP to sediment as  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  and comparing its rate of hydrolysis of TPP added in solution. This technique is similar to that used in evaluating the effectiveness of various fertilizer reaction products as nutrient sources for plants used by Brown et al. (1963), Frazier et al. (1965), Getsinger et al. (1962), Giordano and Mortvedt (1969), Hossner and Blanchar (1968), and Terman and Engelstad (1966).

The specific objectives of our studies may be summarized as follows:

- 1) To measure the effect of differing sediments, pH, ~~temperature, biological c~~ temperature, biological activity, and method of addition on the rate of tripolyphosphate hydrolysis in sediments.
- 2) To measure the effect of differing sediments, pH, temperature, and biological activity on the rate of pyrophosphate hydrolysis in sediments.

#### METHOD OF INVESTIGATION

A method developed by Blanchar and Riego (1973) to separate and analyze ortho-, pyro-, and tripolyphosphate in sediments was used in this experiment. The sediment was extracted with 2% ethylenediaminetetraacetate plus 1N ammonium fluoride, pH 4.2. A second extract of 2% ethylenediaminete-

traacetate + 1N sodium hydroxide followed. Orthophosphate (OP), pyrophosphate (PP), and tripolyphosphate (TPP) were separated using anion-exchange chromatography.

#### REAGENTS

2% EDTA + 0.1N NH<sub>4</sub>F, pH 4.2: 20 g disodium ethylenediaminetetraacetate and 3.70 g NH<sub>4</sub>F were dissolved in distilled H<sub>2</sub>O and the pH adjusted to 4.2 by adding 6N HCl and the solution diluted to 1 liter.

2% EDTA + 1N NaOH: Dissolved 20 g disodium ethylenediaminetetraacetate and 40 g NaOH pellets in distilled water and diluted to 1 liter.

Dowex 50W-8 (20-50 mesh) cation exchange resin: Used resin from J. T. Baker Chemical Co. in the H<sup>+</sup> ionic form as supplied.

Anion Exchange Resin CGA-541: Used resin from J. T. Baker Chemical Co. in the Cl<sup>-</sup> form as supplied.

0.2M KCl + 0.025M CH<sub>3</sub>COOK, pH 4.5: Dissolved 14.9 g KCl and 2.45 g CH<sub>3</sub>COOK in distilled water, adjusted the pH to 4.5 by adding 6N HCl, and diluted to 1 liter.

1.5 KCl + 0.025M CH<sub>3</sub>COOK, pH 4.5: 111.8 g KCl and 2.45 g CH<sub>3</sub>COOK were dissolved in nearly a liter distilled water, the pH adjusted to 4.5 by adding 6N HCl, and solution diluted to 1 liter.

0.1N NaOH: Dissolved 4 g NaOH pellets in distilled water and diluted to 1 liter.

4.9N H<sub>2</sub>SO<sub>4</sub>: 136.1 ml concentrated H<sub>2</sub>SO<sub>4</sub> was diluted with distilled water to 1 liter.

1% ammonium molybdate: Dissolved 10 g  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in distilled water and diluted to 1 liter.

2% Ascorbic Acid: Dissolved 20 g L-ascorbic acid in distilled water and diluted to 1 liter.

Stannous chloride stock solution: Dissolved 25 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 50 ml concentrated HCl.

Dilute stannous chloride: Diluted 1 ml stock solution to 20 ml with distilled water (prepared daily).

Isobutanol: Analytic reagent grade isobutanol from Mallinckrodt Chemical Works was used as supplied.

Saturated Boric Acid: Boric acid was dissolved in distilled water until a saturated solution was obtained.

5N HCl: 416.7 ml concentrated HCl was diluted with distilled water to 1 liter.

6N HCl: 500 ml concentrated HCl was diluted with distilled water to 1 liter.

1N NaOH: Dissolved 40 g NaOH pellets in distilled water and diluted to 1 liter.

0.125M  $\text{Ca}(\text{NO}_3)_2$ : Dissolved 2.95 g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in distilled water and diluted to 100 ml.

#### Phosphorus Standards

Orthophosphate:  $\text{KH}_2\text{PO}_4$  was oven dried for 1 hour at 105C. 4.39 g was dissolved in distilled water and diluted to 1 liter to give a 1000 ug P/ml standard.

Pyrophosphate: Dissolved 7.20 g  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in one liter to give a 1000 ppm P as PP standard.

Tripolyphosphate: Weighed 5.17 g  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and 1 g

NaOH pellets into an evaporating dish and dissolved in about 5 ml distilled water. The thick paste was gently heated until dry. The mixture was transferred to a furnace preheated to 560C and heated for 1 hour, cooled, and then 10 ml of distilled water was added to dissolve the solid. The liquid was transferred into two 50 ml centrifuge tubes and 2.5 ml 95% ethyl alcohol added. After 30 minutes the mixture was centrifuged and the liquid poured off. 25 ml 1:4 ethanol:water was added to each tube and shaken for 15 minutes, centrifuged and the liquid decanted. Added another 25 ml 1:4 ethanol:water was added to the precipitate in each tube then shaken for 15 minutes and centrifuged. The clear solution was decanted. The precipitate was washed into a 100 ml volumetric flask, dissolved, and the volume adjusted to 100 ml with water. The phosphate content of the TPP standard and the percentage of the standard which was tripolyphosphate was determined. TPP prepared in this manner contained 4% OP, no detectable PP and 96% TPP as the total P fractions.

#### Sediment Samples

Sediment samples used in these experiments were collected from the following sites around the state of Missouri:

Cape Fair: From the James River arm of Table Rock Lake approximately 8 miles downstream from Galena on July 17, 1972. Sediments were collected at a depth of approximately 6 feet.

Thomas Hill: From the cold water arm of Thomas Hill Lake on July 13, 1972. Sediments were collected

at a depth of approximately 8 feet.

Flat Branch: Samples were taken at a distance of 100 feet from the outflow of the Columbia sewage plant NO. 1 on December 2, 1972. Samples were collected at a depth of approximately 1 foot.

Maries River: The sediment was collected at a point 15 miles east of Jefferson City, Missouri off Highway 54 on July 17, 1972. Samples were collected at a depth of approximately 4 feet.

Subsamples of the sediments collected were air-dried, ground, and passed through a 2-mm sieve. Some physical and chemical properties of the sediments were determined and the results shown in Table 1.

The  $pH_w$  of the sediments ranged from 6.0 for Thomas Hill Lake to 7.0 for Flat Branch Creek. Cape Fair showed the lowest organic matter content at 1.5%. The rest of the sediments contain more than 2% organic matter. Thomas Hill Lake sediment has the highest clay content at 28% and lowest sand content at 8%. There are no marked differences in the clay, silt, and sand content of the sediments collected from Cape Fair, Flat Branch Creek, and Maries River.

Samples of the sediments were extracted with 1N  $NH_4Ac$ , pH 7. Extracts were analyzed for Na, K, Ca, and Mg. Another extraction using 1N  $NH_4OH$ , pH 4.8 was made and Al, Fe, and Mn were determined. Na and K were determined using a Coleman flame photometer. Ca, Mg, Fe, and Mn were analyzed by atomic absorption while Al was analyzed by flame emission.

Chemical analysis of exchangeable cations in the sediments showed that Flat Branch Creek contained 138 ppm Na, 146 ppm K, 3225 ppm Ca, and 400 ppm Mg. These concentrations are high compared to 21 ppm Na, 59 ppm K, 495 ppm Ca, and 70 ppm Mg in the Cape Fair sediment. Thomas Hill Lake sediment contained 100 ppm Fe and 125 ppm Mn in exchangeable form. It contained 64 ppm Na, 145 ppm K, 2010 ppm Ca, and 433 ppm Mg. Cape Fair contained 88 ppm exchangeable Al while Al content of the rest of the sediments ranged from 19 ppm to 37 ppm.

#### Experimental treatments

Sediment samples were collected from James River (Cape Fair), Thomas Hill Lake, Flat Branch Creek, and Maries River. Several samples were randomly collected from each site. They were thoroughly mixed and a composite sample taken. The representative sediment samples were placed in 2-liter wide mouth plastic bottles and were transported to the laboratory in an ice chest. Excess water from each bottle was poured off and the sediments were stored in a refrigerator at 4C. Subsamples were removed and the percent solid was determined by weight loss after drying at 105C for 48 hours in an oven. Enough wet sediment was weighed into 50-ml centrifuge tubes to give 4 g of oven dry sediment.

The sediment sample collected from Flat Branch Creek was selected to be used to study the influence of pH, temperature, and biological activity on the rate of pyro- and tripolyphosphate hydrolysis. The untreated Flat Branch Creek

Table 1. Some physical and chemical properties of Cape Fair, Thomas Hill Lake, Flat Branch Creek, and Maries River sediment.

Sediment	pH <sub>w</sub>	O.M.	Clay	Silt	Sand	Exchangeable Cations						
						Al	Fe	Mn	Na	K	Ca	Mg
			----- % -----			----- ppm -----						
Cape Fair	6.9	1.5	12	59	29	88	74	113	21	59	495	70
Thomas Hill	6.0	2.4	28	64	8	37	100	125	64	145	2010	433
Flat Branch	7.0	2.1	19	54	27	24	59	59	138	146	3225	400
Maries River	6.9	2.6	16	55	29	19	71	102	18	99	1075	453



sediment has a pH of 7. Two subsamples of the Flat Branch sediment were removed from the refrigerator. The pH of one sample was adjusted to 5.0 by addition of 6N HCl. The pH of the other sample was adjusted to 9.0 by addition of 1N NaOH. Both sediment samples were equilibrated in a refrigerator at 4C overnight and the pH checked the following day and found to be as adjusted. Excess water was poured off the sediment. Percentage moisture was determined by oven drying subsamples for 48 hours at 105C. Enough sample was weighed into a 50-ml centrifuge tube to give 4 g of oven dry sediment.

Sterilized sediment samples were prepared to study the effect of biological activity on the rate of hydrolysis of PP and TPP. The tubes containing fresh sediment were covered with clinical cotton and sterilized in an autoclave at 248C and a pressure of 15 atm for 15 min.

Standard Addition: 1600 µg P as TPP standard solution was added to each sample in the centrifuge tube. Enough water collected from each respective sampling site was added to each tube to give a total volume of solution of 15 ml. Distilled water was added to the sterilized sediment.

To study the influence of temperature on the rate of hydrolysis of PP and TPP, enough tubes containing Flat Branch Creek sample treated with TPP standard were stored at 15C in a bath. Another batch of tubes containing samples treated with TPP were incubated at 35C in a water bath. All the other treatments were stored at room temperature which was held close to 25°C. All the tubes were equilibrated for 0,

1, 2, 4, 8, 16, and 32 days.

A precipitate of calcium tripolyphosphate,  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$ , was prepared as described by Bobtelsky and Kertes (1954). Five parts of 0.125M  $\text{Na}_3\text{P}_3\text{O}_{10}$  was mixed with 5 parts of 0.125M  $\text{Ca}(\text{NO})_2 \cdot 4\text{H}_2\text{O}$  and 15 parts distilled water. The solution was mixed thoroughly and the precipitate allowed to form. The white precipitate was allowed to settle, the excess water decanted, and pressure-filtered at 80 lbs/in<sup>2</sup> through 0.45M millipore filter paper. The solids were air-dried and ground. The  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  precipitate was added to Flat Branch sediment at the rate of 0.0061 g/4 g sediment. This amount was equivalent to 1600 ug P<sub>as</sub> as TPP added to 4 g sediments as standard solution.

#### Extraction of OP, PP, and TPP

At the end of each equilibration period, the mixture was mixed well and shaken for 15 minutes using a burrel wrist action shaker. The tubes were centrifuged for 10 minutes at 2000 rpm using a Sorvall angle centrifuge. The water extract was obtained by passing the solution through Whatman No. 42 filter paper and the solution saved. To the sediment left in the centrifuge tube, 20 ml of 2% EDTA + 0.1N  $\text{NH}_4\text{F}$ , pH 4.2 was pipetted. The mixture was shaken for 30 minutes, centrifuged for 10 minutes and then filtered. The solution was also saved. Twenty milliliters of 2% EDTA + 1N NaOH was added to the same sediment still left in the centrifuge tubes. The mixture was mixed well and shaken for 30 minutes centrifuged for 10 minutes, and then filtered. The extract

was again saved.

The extracts were collected and refrigerated and loaded onto an anion exchange resin for separation within one hour.

#### Preparation of the anion exchange column

A 10-cm column of anion exchange resin CGA-541 was made in a 10 ml Nalgene pipet shortened by cutting in half. Ten milliliters of 1N NaOH was passed through the column followed by 25 ml of 1.5M KCl + 0.025M  $\text{CH}_3\text{COOK}$ , pH 4.5, then washed with 5 ml of distilled water. The column was charged with 1 ml 0.1M NaOH and rinsed with 5 ml distilled water.

A 5-cm clear tygon tubing was attached to the top of the column. One cc of strongly acidic, cation exchange resin, Dowex 50W-X8, was placed in the tygon tubing using glass wool as support.

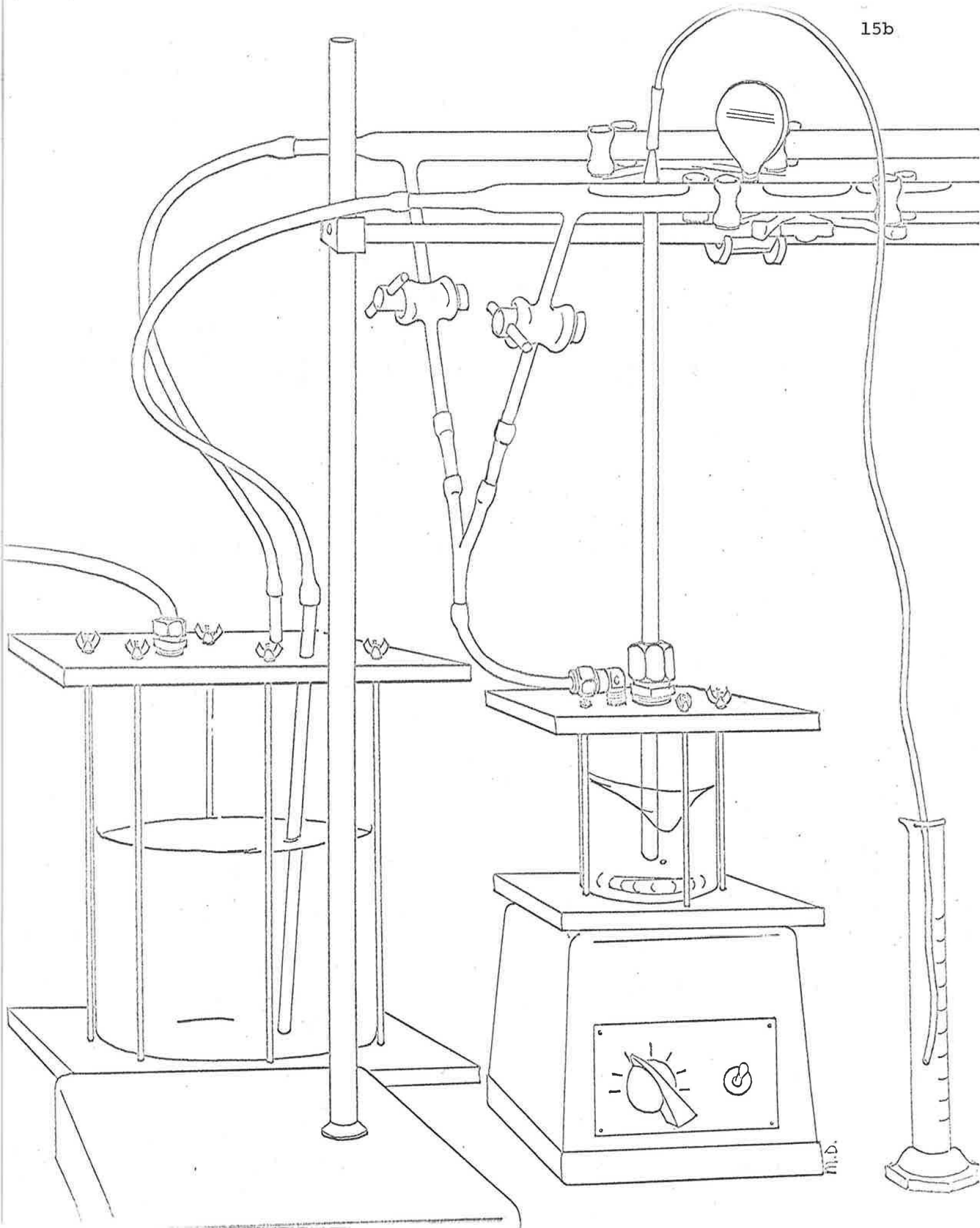
One half ml of the water extract was pipetted on top of the cation exchange resin and was allowed to fall to the anion exchange resin by gravity or use of slight water suction. One milliliter of the 2% EDTA + 0.1N  $\text{NH}_4\text{F}$ , pH 4.2 extract was added next, followed by one ml of 2% EDTA + 1N NaOH extract. The cation exchange resin was washed with five aliquots of distilled water to rinse all the samples into the anion exchange resin. The tygon tubing containing the cation exchange resin was then detached from the top of the column. The top of the anion exchange resin was covered with a piece of glass wool to prevent the resin from spilling out during the process of separation.

### Separation of OP, PP, and TPP

The apparatus used to elute OP, PP, and TPP from an anion exchange resin is shown in Figure 1. The apparatus was constructed from plexiglass. The storage cylinder on the left was constructed from a 15 cm diameter plexiglass tube fitted in both ends with O rings. One cm thick plexiglass plates are drawn tight to the cylinder on each end with 6 bolts. The solution in this cylinder is 1.5M KCl and 0.025M  $\text{CH}_3\text{COOK}$ , pH 4.5. Nitrogen gas pressure enters the storage cylinder from the pressure line on the left. The mixing cell on the magnetic stirrer was constructed from a plexiglass cylinder 1 cm long with an inside diameter of 5 cm and fitted with O rings on either end. The 1 cm plexiglass plates on each end are held in place by 4 bolts. The mixing cell is pressurized with air by opening the left stopcock is then closed and the right opened, under these conditions solution from the storage tank flows into the mixing chamber at the same rate that it flows out of the column. The anion exchange resin column containing the sample is fastened to the mixing cell by fitting a rubber gasket on the column and then bolting the column into the fitting at the center of the mixing chamber. Solution flows up through the inverted column which eliminates accumulating of air in the column.

The mixing cell contained 150 ml 0.2M KCl + 0.025M  $\text{CH}_3\text{COOK}$ , pH 4.5. Eluting solution was initially forced through the anion exchange resin by a gas pressure of 12 lbs/in<sup>2</sup>. After 5 minutes, the gas stopcock was closed and the

Figure 1. Apparatus used to elute OP, PP, and TPP from an anion exchange resin, showing the storage cell containing 1.5M KCl + 0.025M CH<sub>3</sub>COOK, pH 4.5 and the mixing cell containing 0.2M KCl + 0.025M CH<sub>3</sub>COOK, pH 4.5.



stopcock regulating the 1.5M KCl + 0.025M KCl, pH 4.5, opened. The flow of concentrated KCl from the storage cell into the mixing cell containing the dilute KCl was 2.9 ml/minute and was equal to the flow of eluent out of the anion exchange resin column. After fitting the column into the mixing cell, the exposed tip of the anion exchange resin column containing the sample is connected to the sample line of the autoanalyzer set-up. A good, continuous flow of the eluent from the column was obtained by placing a buret containing water between the column tip and the sample line of the autoanalyzer using a T-tube. Positive pressure was attained by adjusting the pressure coming from the gas tank.

The autoanalyzer set-up was composed of a technician proportioning pump, heating bath, magnetic stirrer, a Bausch and Lomb Spectronic 20 spectrophotometer, a Perkin-Elmer recorder, Figure 2. Using appropriate pump tubes in the proportioning pump, 2.90 ml/min sample from the anion exchange resin column, 0.32 ml/min of 4.9N  $H_2SO_4$ , and 2.00 ml/min air were pumped into the heating bath. Hydrolysis was attained at 90C in the heating bath. The sample was passed through a water bath to cool and then back to the proportioning pump and debubbled into a waste line. 2.5 ml/min of the sample, 0.32 ml/min of 1% ammonium molybdate, and 2.00 ml/min of air were pumped through a delay coil, then mixed with 0.16 ml/min dilute  $SnCl_2$  to develop the color. The solution was passed through another mixing coil, debubbled, and pumped through the spectrophotometer. The optical density was continuously

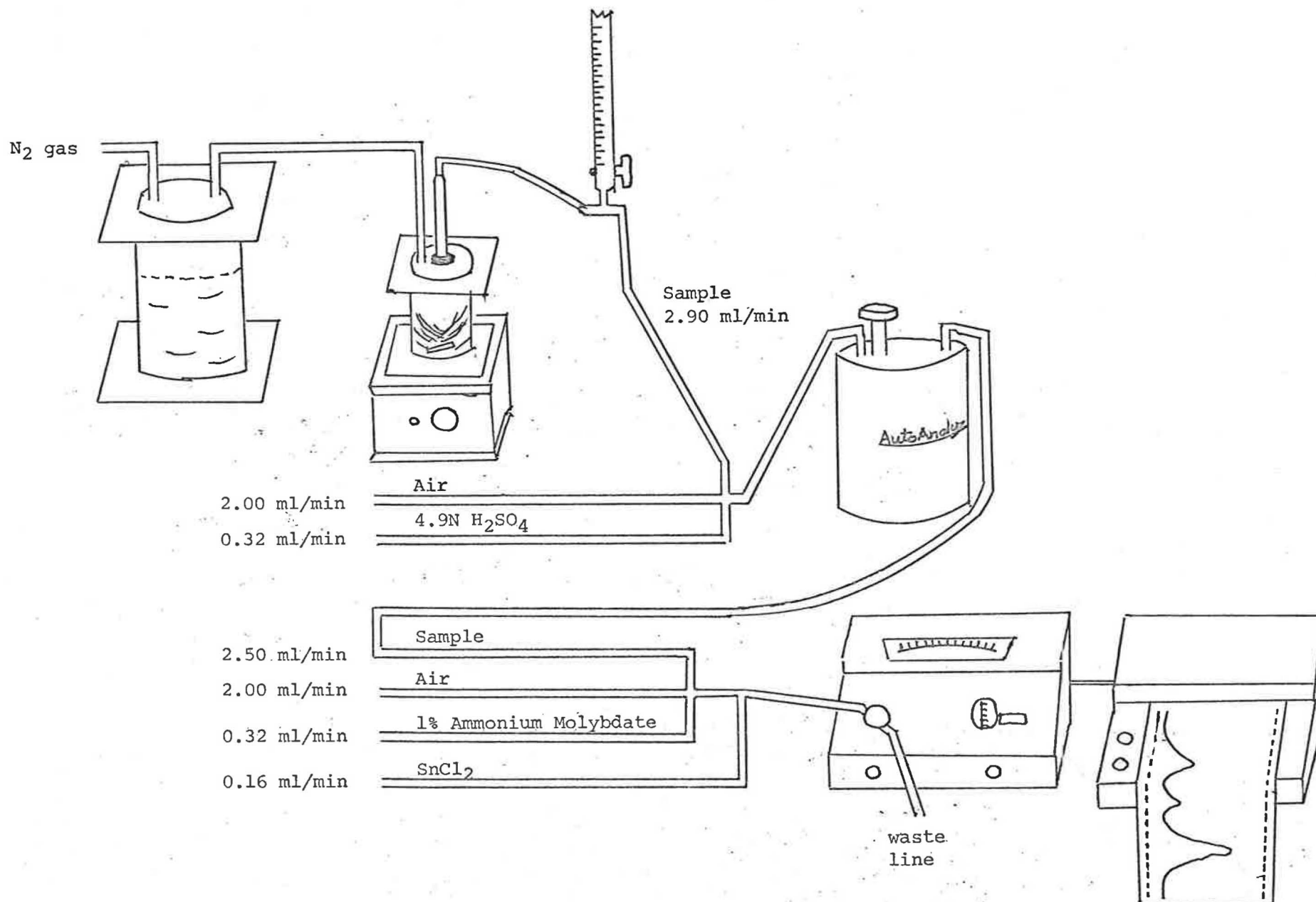


Figure 2. Autoanalyzer system for the analysis of solution from the anion exchange column.



recorded at a wavelength of 690 mu.

The concentration of PP and TPP for each separation was estimated by calculating the area under each curve in the chromatograph, Lundgren and Loeb (1961).

The orthophosphate content of the sediment samples were obtained by subtracting the concentration of PP and TPP from the total phosphate concentration.

In some samples, a major portion of the TPP added appeared hydrolyzed after 16 days of equilibration. No distinctive TPP peak showed in the chromatograph. To estimate the amount of TPP left unhydrolyzed, the TPP fraction was collected as is left the last mixing coil. A total volume of 25 ml was collected in a graduate cylinder.

The fractions collected were added into 5 ml isobutanol in a 125-ml separatory funnel. The mixture was shaken vigorously for 30 seconds and the phases allowed to separate for 15 minutes. The lower aqueous phase was drained off and discarded. The isobutanol solution was drained into spectrophotometer tubes. The tubes were lightly centrifuged to removed water mist from the isobutanol layer. The blue color density was read at a wavelength of 690 mu using a red filter in a Bausch and Lomb spectrophotometer. Standards containing 0 to 6 ug P were prepared. The color was developed in a similar manner as that of the sample. The standards were extracted into isobutanol in the same manner as the fractions collected. The readings were used as the standard curve for the TPP fractions.

### Analysis of Extracts for Total P

Into a 50-ml digestion tube, 0.75 ml of the water extract, 1.00 ml of 2% EDTA + 0.1N  $\text{NH}_4\text{F}$ , pH 4.2 extract, and 1.00 ml of 2% EDTA + 1N NaOH extract were pipetted. Five milliliters of 5N HCl was added and the solution mixed. The solution was heated for 1 hour at 90C in aluminum digestion blocks, Blanchard et al. (1965). The solution was collected and 5 ml saturated boric acid solution was added. The final volume was adjusted to 50 ml with distilled water. Total P was analyzed by pumping 3.4 ml/min of the sample, 0.42 ml/min 1% ammonium molybdate, 0.42 ml/min 2% L-ascorbic acid, and 2.00 ml/min air into a delay coil, and the color developed with 0.16 ml/min diluted  $\text{SnCl}_2$ . The solution was mixed in a mixing coil and passed into the spectrophotometer. The absorbance was read at a wavelength of 690 mu.

### RESULTS AND DISCUSSION

The results of these experiments showed that the rate of the hydrolysis reaction was proportional to the concentration of TPP not hydrolyzed. The first-order rate equation is:  $-\frac{da}{dt} = k(A)$  or  $-\frac{d(A)}{(A)} = kdt$  where (A) represents the concentration of the reactant k is the rate constant of the reaction,  $k(A)$  is the change in (A), and dt represents a change in time, t. The above equation can be integrated within limits to give the first-order rate equation:

$$\ln \frac{(A_0)}{(A)} = kt$$

This equation is convenient to define the quantity  $t_{\frac{1}{2}}$

called half-life. Half-life represents the time needed for a given reaction to be 50% completed. This quantity is very useful to characterize the speed of a reaction.

If  $t_{1/2}$  represent the time necessary for the reaction to be half-completed, (A) will be equal to  $\frac{1}{2}(A_0)$ . Therefore:

$$\log \frac{(A_0)}{\frac{1}{2}(A_0)} = \frac{kt_{1/2}}{2.303} = 0.301$$

$$t_{1/2} = \frac{0.693}{k}$$

If  $\log \frac{(A_0)}{A}$  is plotted versus time t, the slope of the line will be equal to  $-\frac{k}{2.303}$ . Since k equals  $2.303 \times (-\text{slope})$  then  $t_{1/2} = \frac{0.301}{\text{slope}}$ .

TPP and PP Hydrolysis in Cape Fair, Thomas Hill Lake, Flat Branch Creek, and Maries River Sediment.

There were differences in the rate of hydrolysis of TPP added to Cape Fair, Thomas Hill Lake, Flat Branch Creek, and Maries River sediment, Figure 3. Hydrolysis of TPP was slowest in Cape Fair sediment. At the end of 4 days, 54% of the TPP added still remained unhydrolyzed in Cape Fair sediment compared to 26% and 18% still left in Maries River and Flat Branch Creek sediment, respectively. The data also showed that a rapid hydrolysis of TPP in the sediment occur in the initial stages, usually up to 4 to 8 days. At 16 days the rate of hydrolysis tends to be slower than predicted by first order kinetics, Figure 4. For this reason, 2 regression lines were calculated to obtain an estimate of the half-life of TPP hydrolysis. One line was calculated based on hydrolysis rate between 0 and 8 days (A) and a second line calculated based on hydrolysis rate between 0 and 4 days (B).

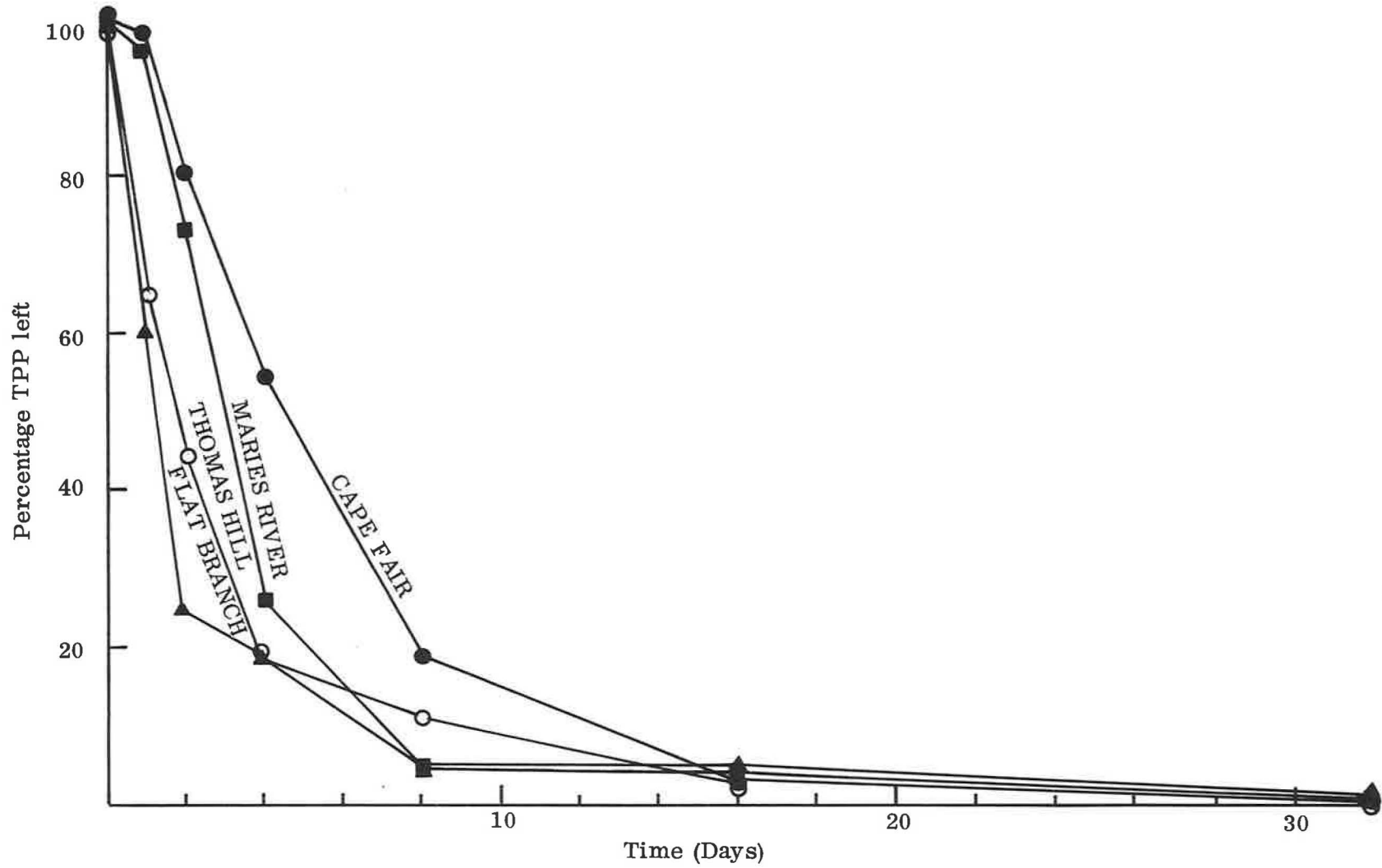
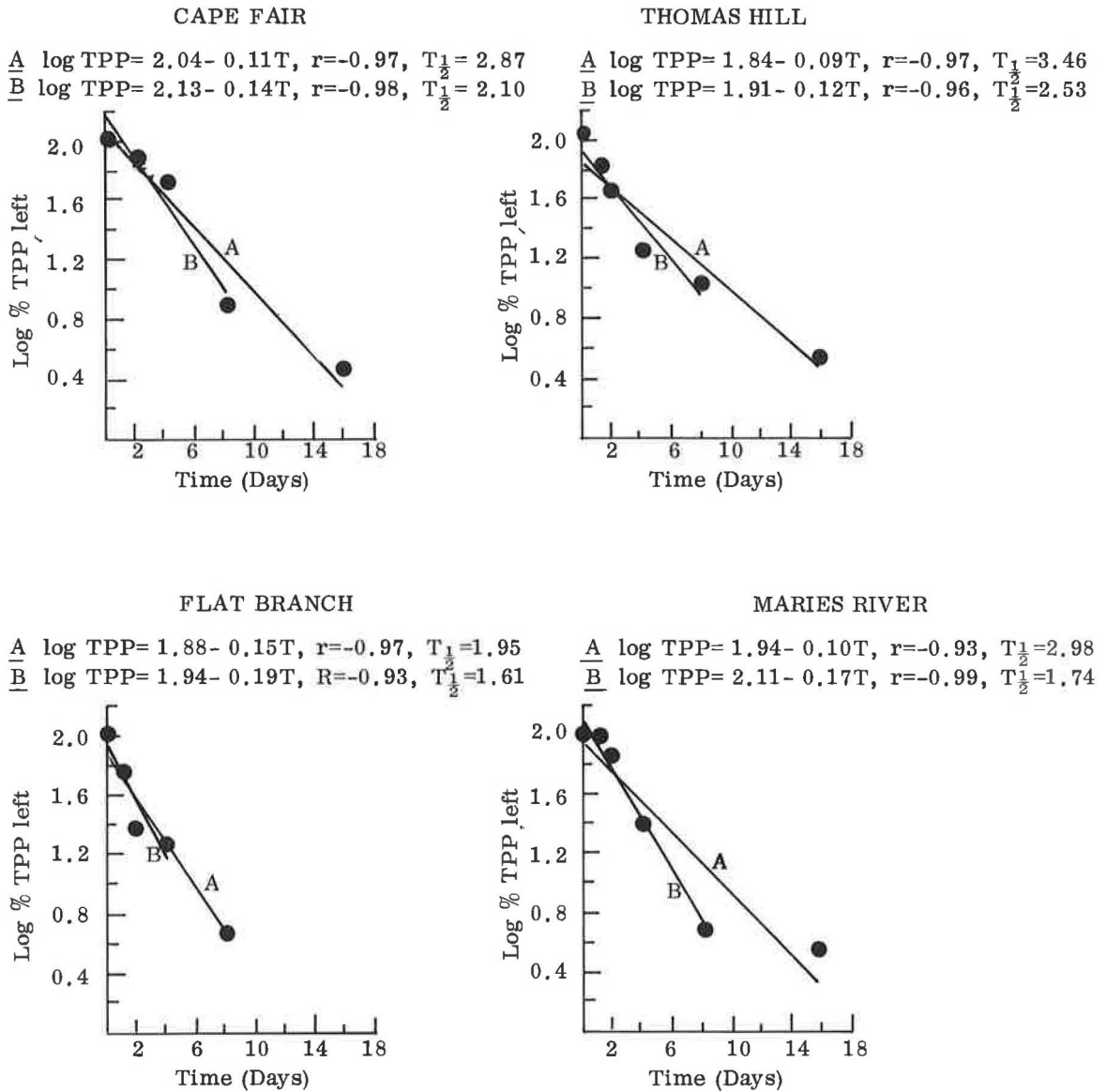


Figure 3. Hydrolysis of TPP added to Cape Fair, Thomas Hill, Flat Branch, and Maries River sediment.



**Figure 4.** A kinetic analysis of the hydrolysis of TPP added to Cape Fair, Thomas Hill, Flat Branch, and Maries River sediment.

Half-lives for the hydrolysis of TPP of 2.1 days in Cape Fair, 2.53 days in Thomas Hill Lake, 1.61 days in Flat Branch, and 1.74 days in Maries River were calculated based on line B. Using line A, half-lives of 2.87 days in Cape Fair, 3.46 days in Thomas Hill Lake, 1.95 days in Flat Branch Creek, and 2.98 days in Maries River were obtained. Longer half-lives were calculated based on 0 to 8 days of TPP hydrolysis then 0 to 4 days in all four sediments. This supported the earlier observation that the hydrolysis of TPP occurred more rapidly in the first few days.

The hydrolysis of TPP in sediments approximates the rates predicted by first order kinetics. In studies using soils, Blanchar and Hossner (1969a, 1969b) and solution studies of Van Wazer et al. (1955) reported that TPP hydrolysis followed first-order kinetics. Blanchar and Hossner (1969a) in a hydrolysis study involving 32 midwestern soils stated that half-lives of TPP hydrolysis varied from 3 to less than  $\frac{1}{2}$  days. In another study, Blanchar and Hossner (1969b) found that TPP persisted in an Elliot soil in less than 8 days and that the hydrolysis has a half-life of 1.8 days. It appears that TPP hydrolysis in sediments and soils are similar.

The hydrolysis of PP formed from TPP added to Cape Fair, Thomas Hill Lake, Flat Branch Creek, and Maries River sediment was studied, Figure 5. There is an initial build-up of PP and a maximum amount of formation was attained after 4 days. During TPP hydrolysis, the same build-up of PP, as well as orthophosphate, was observed by Van Wazer, et al.

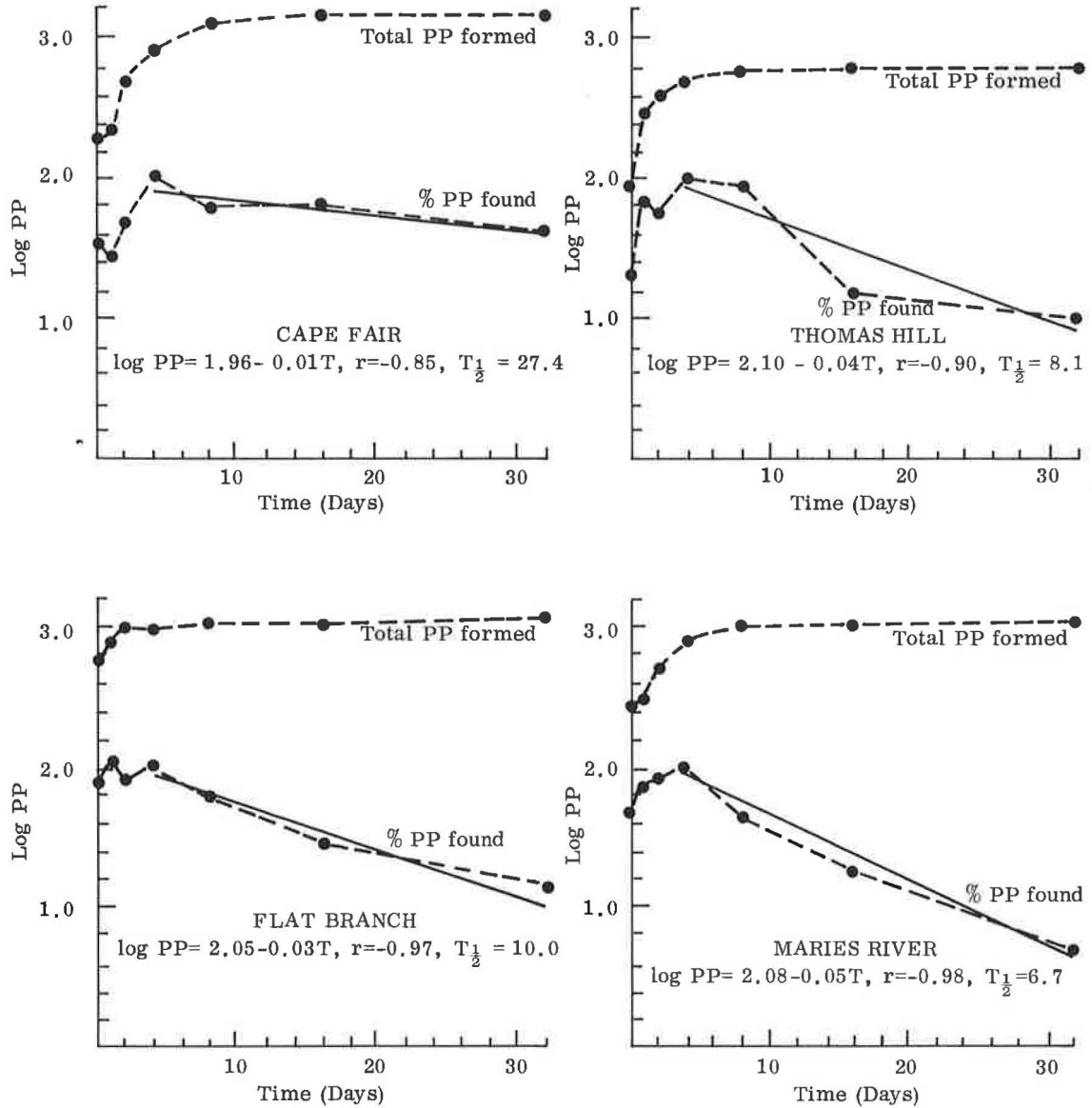


Figure 5. Percentage PP found and total PP formed from TPP added to Cape Fair, Thomas Hill, Flat Branch, and Maries River sediment.

(1955). Half-lives of 27.4 days in Cape Fair, 8.1 days in Thomas Hill Lake, 10.0 days in Flat Branch Creek, and 6.7 days in Maries River were obtained for the hydrolysis of pyrophosphate in the 4 sediments studied. Juo and Maduakor (1973) reported half-lives of 4-14 days for PP hydrolysis in the surface soils of selected Nigerian soils. Half-lives of 16-64 days were found for subsoils. Sutton and Larsen (1964) and Blanchar and Hossner (1969a) reported half-lives of 3-100 days for PP hydrolysis in soils.

Rate constants of  $1.76 \times 10^{-5} \text{ min}^{-1}$  in Cape Fair,  $5.92 \times 10^{-5} \text{ min}^{-1}$  in Thomas Hill Lake,  $7.20 \times 10^{-5} \text{ min}^{-1}$  in Maries River, and  $4.80 \times 10^{-5} \text{ min}^{-1}$  in Flat Branch Creek were obtained for PP hydrolysis in this study, Table 2. Hossner and Phillips (1971) reported rate constants of  $3.72 \times 10^{-5} \text{ min}^{-1}$  for PP hydrolysis for Katy s1 soil. Racz and Savant (1972) reported rate constants for PP hydrolysis of  $1.30 \times 10^{-5} \text{ min}^{-1}$  and  $2.00 \times 10^{-5} \text{ min}^{-1}$  for soils incubated at field capacity and flooded conditions, respectively.

Data obtained in this study showed that the hydrolysis of PP tend to follow first-order kinetics. However, Hossner and Phillips (1971) noted in their study that PP hydrolysis is not a simple first-order reaction. He attributed this to probable interactions in the soil due to precipitation and adsorption reactions. Hashimoto et al. (1969) also reported that hydrolysis of PP in soils with pH ranging from 7.0 to 7.2 did not appear to follow first order kinetics.

The hydrolysis of PP formed from TPP added to the



Table 2. Rate constants for the hydrolysis of PP and TPP  
in sediments.

	Pyrophosphate ( $\times 10^{-5} \text{ min}^{-1}$ )	Tripolyphosphate ( $\times 10^{-4} \text{ min}^{-1}$ )
Cape Fair	1.76	2.29
Thomas Hill	5.92	1.90
Maries River	7.20	2.76
Flat Branch		
15C	2.40	2.18
25C	4.80	2.99
35C	7.51	3.94
pH5	3.52	2.74
pH7	4.80	2.99
pH9	6.56	2.23
Sterile	2.88	1.96
Non-sterile	4.80	2.99
Solution	-	2.86
Precipitate	-	1.72

sediments was relatively slow. More than 10% of the pyrophosphate formed from TPP added still remained unhydrolyzed after 32 days. About 42% of PP formed was still left in Cape Fair sediment at the end of 32 days. This is in contrast to some reports made that the hydrolysis of pyrophosphate is a rapid process. Hashimoto and Lehr (1973) stated that PP initially hydrolyzed faster than TPP and tetrapolyphosphates. Hossner and Phillips (1971) contended that PP hydrolysis was more rapid in flooded soils than in soils at field capacity moisture levels. They indicated that PP was probably present as an iron phosphate and became more soluble upon flooding due to the reduction of  $Fe^{+3}$  to  $Fe^{+2}$ . Hydrolysis was 95% completed in 10 days at 25C, according to their investigation. Racz and Savant (1972) also stated that PP hydrolysis was rapid but noted that after 3 days, hydrolysis rate decreased and little hydrolysis occurred during the 30-60 day period. They disagreed, however, with Hossner and Phillip and reported that PP hydrolysis was approximately the same between soils maintained at field capacity and under flooded conditions. The half-lives for PP hydrolysis of sediments presented in Figure 5 are comparable to the range of half-lives reported for soils.

#### Influence of Temperature on TPP and PP Hydrolysis

Temperature is the most effective factor influencing the rate of hydrolysis of TPP and PP, Van Wazer (1958). The effect of temperature on the hydrolysis of TPP added to Flat Branch Creek sediment was investigated, Figure 6. The rate

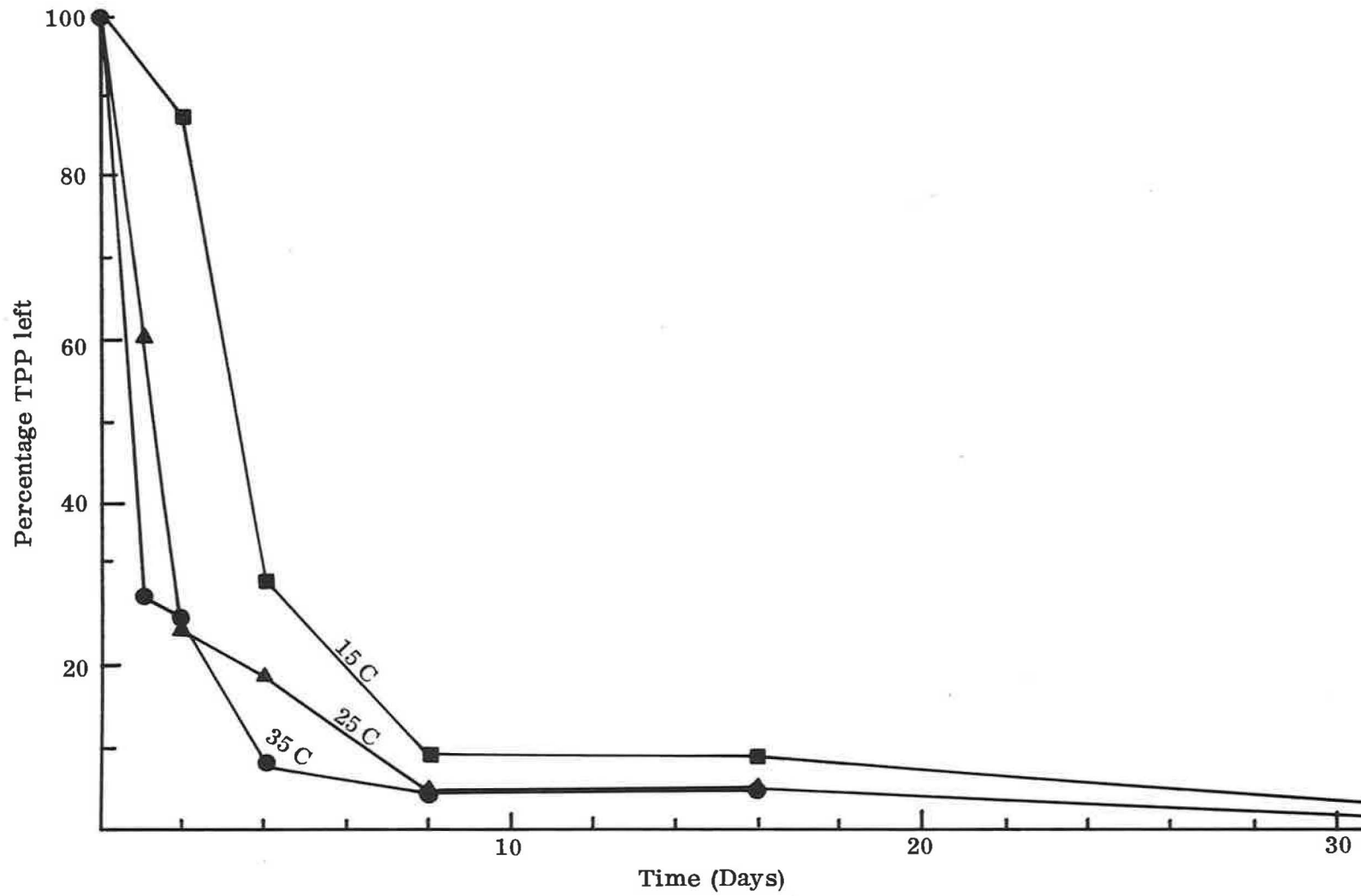


Figure 6. Effect of temperature on the hydrolysis of TPP added to Flat Branch sediment.

of TPP hydrolysis varied notable, depending on the temperature at which the sample was incubated. Hydrolysis was slowest at 15C, and rapid at 35C. At the end of 4 days of equilibration, 30% of TPP added remained unhydrolyzed at 15C while 19% and 9% still remained unhydrolyzed at 25C and 35C, respectively. As previously noted, the rate of hydrolysis was fairly rapid in the first 2 or 4 days.

The half-lives of TPP hydrolysis were estimated from data in Figure 7 to be 2.21 days at 15C, 1.61 days at 25C, and 1.22 days at 35C. The rate of hydrolysis increased with rising temperature. Reports have been published about the temperature dependence of TPP hydrolysis in solution and that the rate of hydrolysis of TPP is first-order, Van Wazer (1958), Van Wazer et al. (1952), Huffman and Fleming (1960), and Strauss and Trietler (1956). Data presented in Figure 7 shows that the same considerations apply to the hydrolysis of TPP in sediments.

The influence of temperature on the hydrolysis of PP formed from TPP added to Flat Branch Creek sediment was also investigated, Figure 8. A maximum amount of PP was formed from TPP added to the sediment after 4 days of incubation at 15C and 25C. It took only 2 days of incubation to attain maximum PP formation from TPP added at 35C. Data also clearly indicated the dependence in temperature of the hydrolytic degradation of pyrophosphate in sediments. Half-lives of 20.1 days at 15C, 10.0 days at 25C, and 6.4 days at 35C were calculated. These data clearly indicated that the rate of

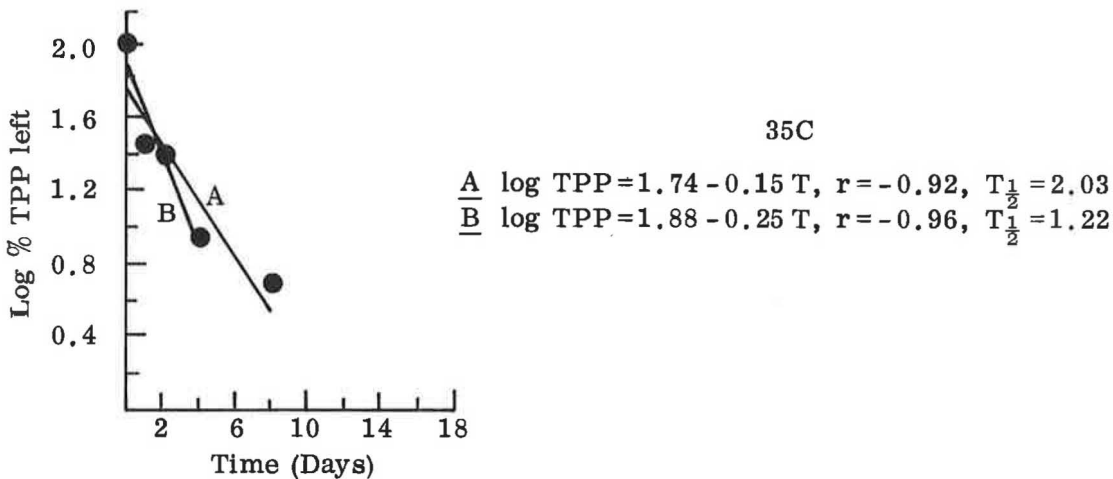
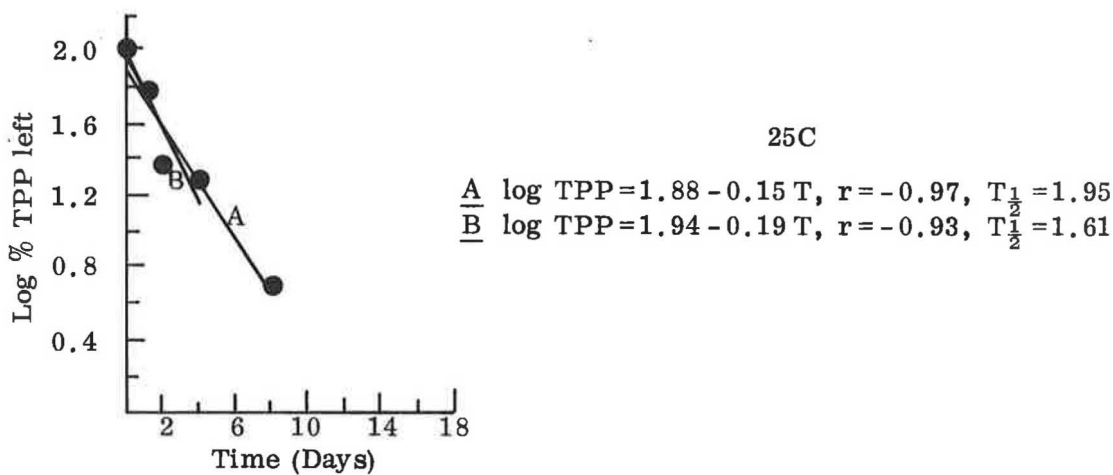
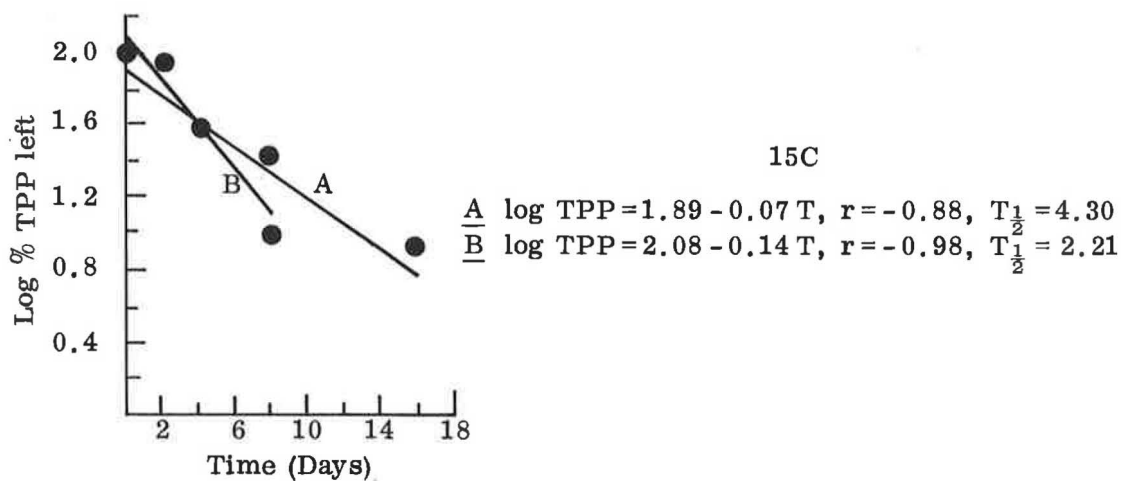


Figure 7. A kinetic analysis of the influence of temperature on the hydrolysis of TPP added to Flat Branch sediment.

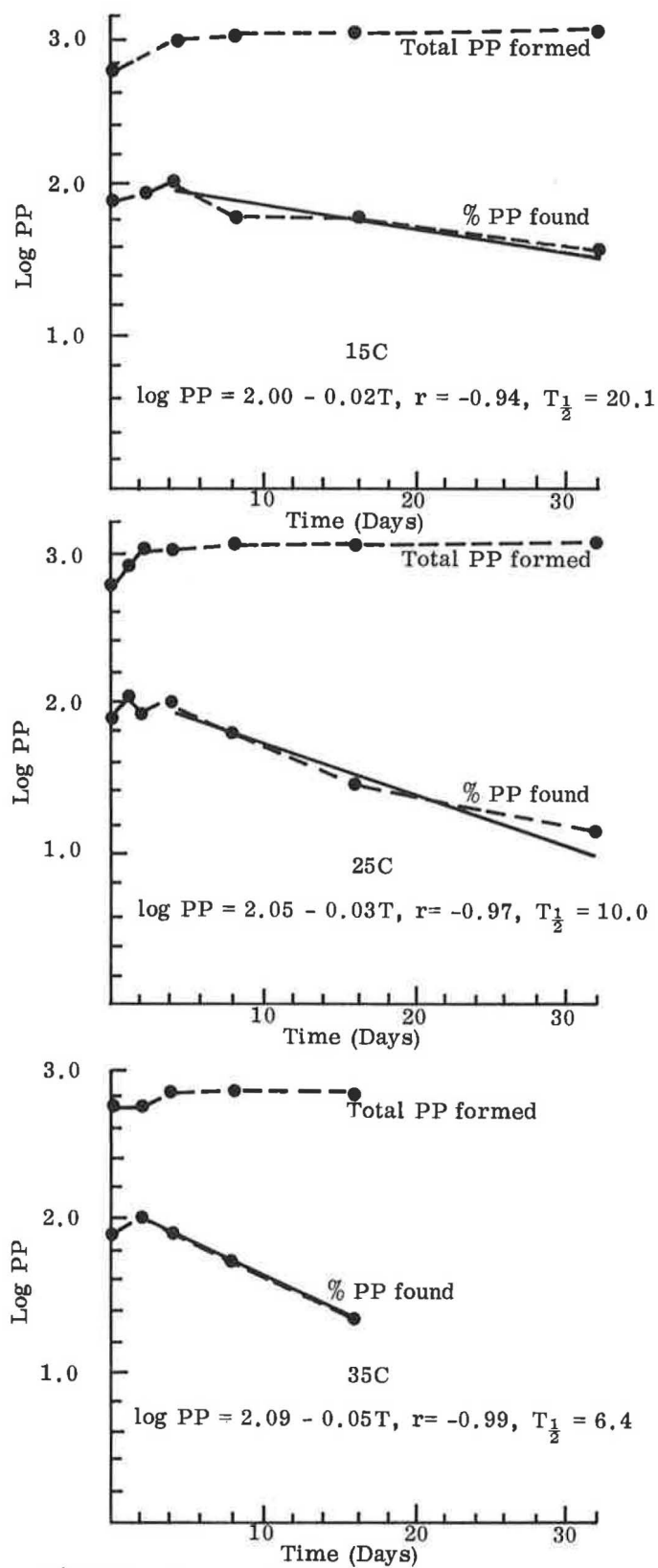


Figure 8. Effect of temperature on percentage PP found and total PP formed from TPP added to Flat Branch sediment.

PP hydrolysis markedly increased with increasing temperature. Hossner and Phillips (1971) in a study using flooded soils indicated that all PP was hydrolyzed after 4 days at 35C and 6 days at 30C. They also reported that PP hydrolysis was 84% completed in 10 days at 20C. Hossner and Phillips (1971) reported rate constants for PP hydrolysis of  $2.09 \times 10^{-5} \text{ min}^{-1}$  at 20C,  $3.72 \times 10^{-5} \text{ min}^{-1}$  at 25C, and  $14.30 \times 10^{-5} \text{ min}^{-1}$  at 35C. In this study rate constants of  $2.40 \times 10^{-5} \text{ min}^{-1}$  at 15°C,  $4.80 \times 10^{-5} \text{ min}^{-1}$  at 25°C, and  $7.51 \times 10^{-5} \text{ min}^{-1}$  at 35°C were found, Table 2. Data obtained in this study indicated that the hydrolysis of PP in sediments follow first order kinetics. However, as mentioned before, Hossner and Phillips (1971) thought that the kinetics involved were not a simple first-order reaction.

The temperature dependence of first-order rate constant k for PP and TPP hydrolysis is related to the activation energy,  $Ae^{-Ea/RT}$ , as shown by the Arrhenius Equation.

$$\ln k = -\frac{Ea}{RT} + \ln A$$

k is the rate constant of the reaction, R is gas constant, and is equal to 1.987 cal/mole, T is temperature in °K, A is the frequency factor, and Ea is the activation energy of the reaction. When ln k is plotted versus 1/T, the slope of the line is equal to -Ea/R from which the energy of activation Ea can be obtained. Ea can be used as a measure to indicate if a reaction is biologically or enzymatically catalyzed or whether the reaction is chemical. Sizer (1943) reported that Ea values for enzyme-catalyzed reactions ranged from 1000-25,000 calories.

Activation energy plots for TPP, Figure 9, and PP

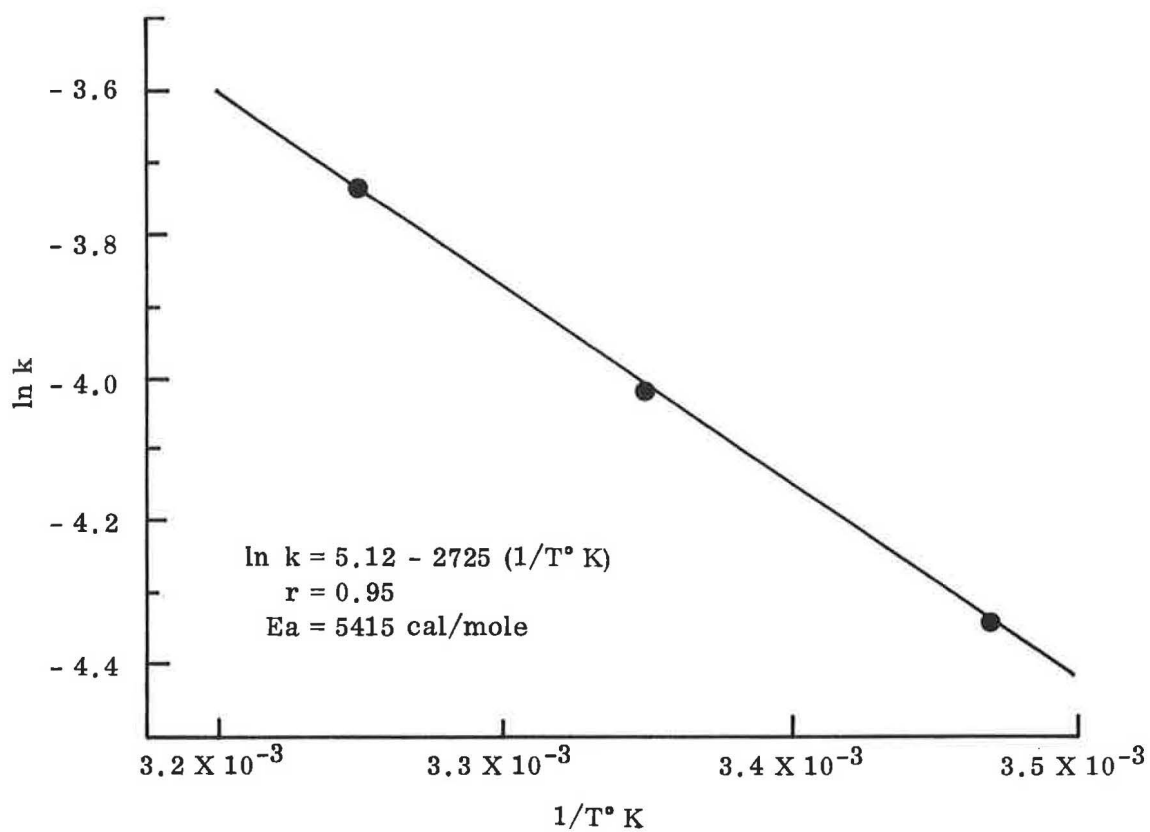


Figure 9. Arrhenius plot used to determine the activation energy of TPP hydrolysis in Flat Branch sediment.



Figure 10, were constructed in this study. An  $E_a$  value of 5415 cal/mole was calculated for TPP hydrolysis and an  $E_a$  value of 10,412 cal/mole was obtained for PP hydrolysis. These values indicated that the hydrolysis of TPP or PP in sediment was biologically or enzymatically catalyzed. Hossner and Phillips (1971) indicated that activation energy measurements for non-enzymatically catalyzed PP hydrolysis should be more than 25,000 cal/mole. Huffman and Fleming (1960) reported  $E_a$  of 15,000-22,000 cal/mole for the hydrolytic degradation of vitreous calcium polyphosphate over a range of 25C-100C temperature.  $E_a$  value of 18,900 cal/mole was calculated for polyphosphate hydrolysis at 0, 25, and 45C, Strauss and Treitler (1956). Hossner and Phillips (1971) obtained  $E_a$  of 4,500 cal/mole for the hydrolysis of PP in Katy sl soil. All of the above workers discussed the temperature-dependence of the hydrolysis and indicated that the reaction was biological or enzymatic in nature more than chemical.

#### Influence of Biological Activity on TPP and PP Hydrolysis

When activation energy of PP and TPP hydrolysis was discussed to elucidate the temperature dependence of the rate of hydrolysis, the hydrolytic degradation of PP and TPP was mentioned to be biologically or enzymatically catalyzed. Several workers have published reports about PP hydrolysis as a biological process. Juo and Maduakor (1973) found that hydrolysis of PP in some Nigerian surface soils was faster than that of the subsoils due to the high microbial activity

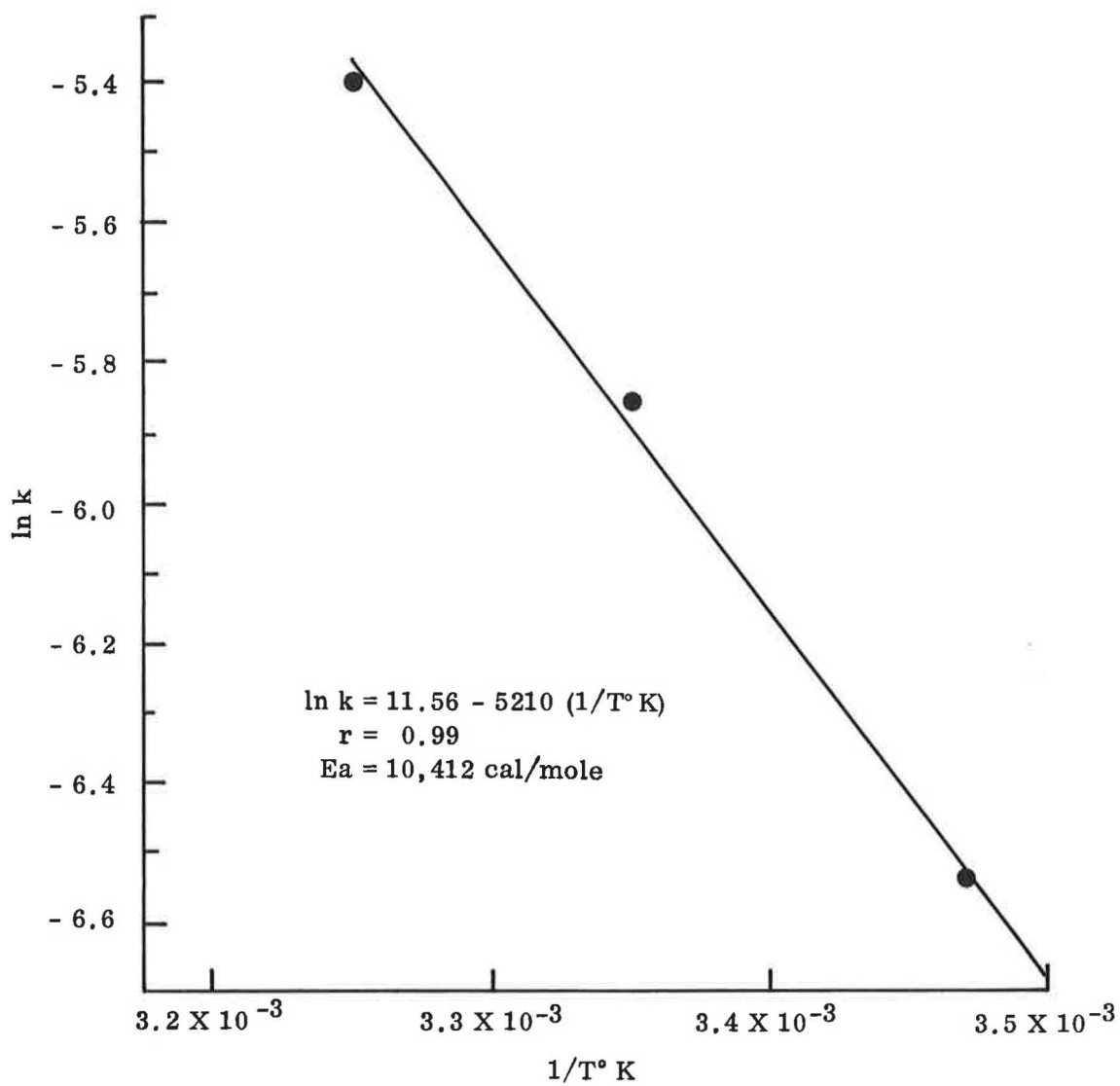


Figure 10. Arrhenius plot used to determine the activation energy of PP hydrolysis in Flat Branch sediment.

and high organic matter content or the surface soils. Sutton et al. (1966) supported this observation by stating that PP hydrolysis was proportional to CO<sub>2</sub> production of a given soil at a given temperature.

The effect of sterilization of the hydrolysis of TPP and PP was investigated. During the first 8 days, TPP hydrolysis was about 50% faster in the non-sterile sediment than the sterile sediment, Figure 11. At the end of 3 days of incubation, 64% of TPP added still remained unhydrolyzed in the sterile sediment compared to 24% left in the non-sterile sediment. After 4 days, 32% remained in the sterile sediment compared to 19% left in the non-sterile sediment. After 8 days, 11% remained in the sterile sediment while 5% was still left in the non-sterile sediment. The data presented clearly indicated that TPP hydrolysis was more rapid in non-sterile conditions than sterile conditions.

A kinetic analysis of the process showed that under both sterile and non-sterile conditions, the hydrolysis of TPP was first-order. Half-lives of 2.45 days in sterile sediment and 1.61 days in the non-sterile sediment were obtained and shown in Figure 12. This further supported the observation that TPP hydrolysis was in part a biological process.

The hydrolysis of PP formed from TPP added in both sterile and non-sterile sediment was also first-order, Figure 13. Longer half-life of 16.7 days in sterile sediment and a shorter half-life of 10.0 days in non-sterile sediment was

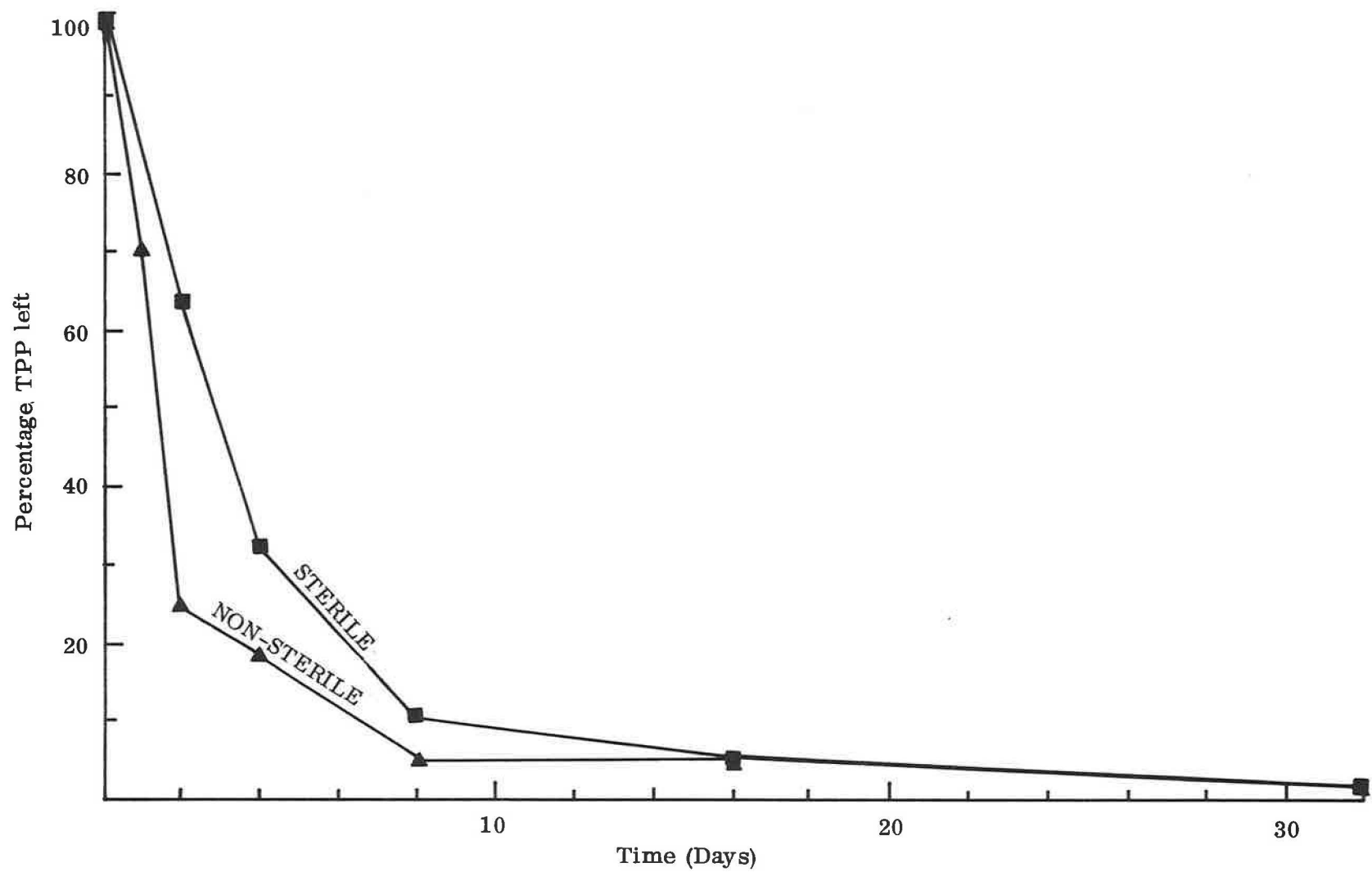


Figure 11. Effect of sterilization on the hydrolysis of TPP added to Flat Branch sediment.

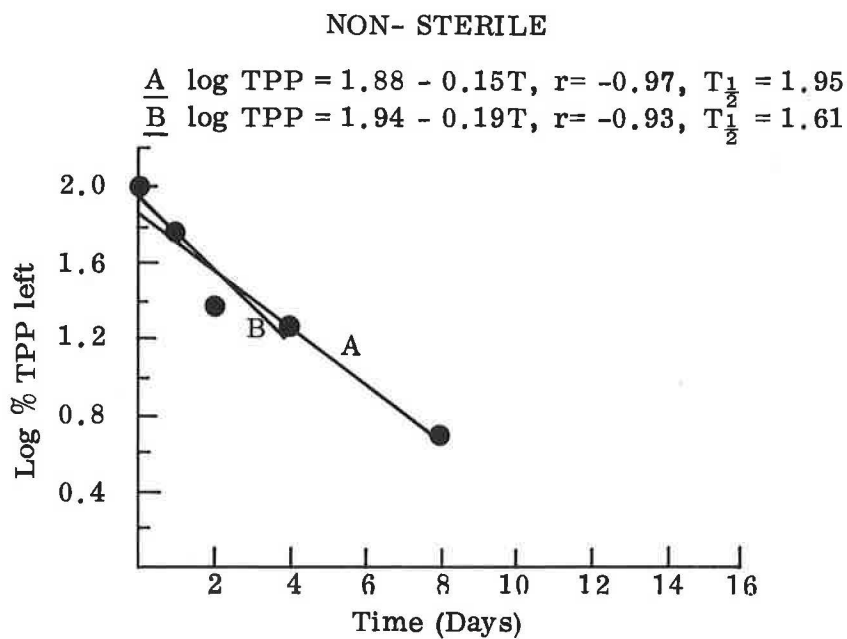
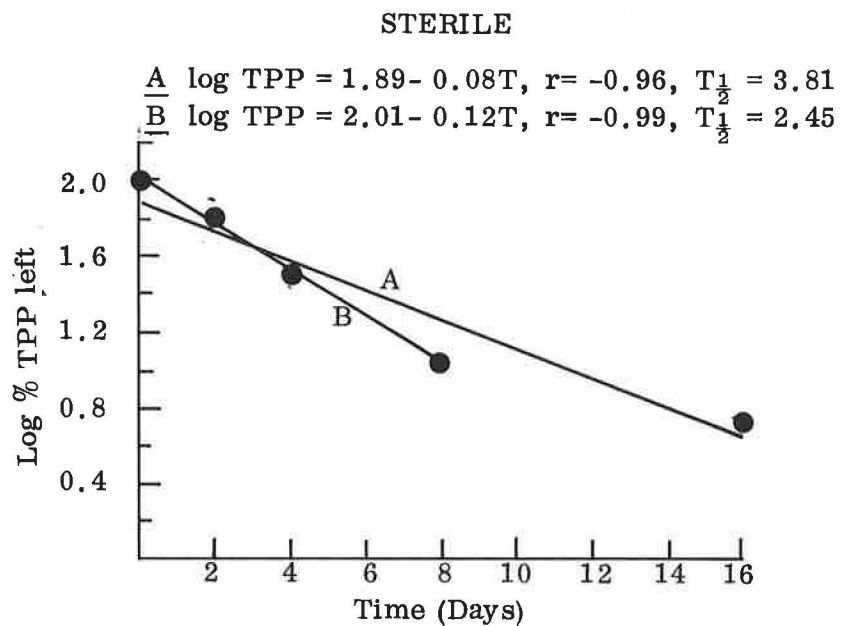


Figure 12. A kinetic analysis of the influence of sterilization on the hydrolysis of TPP added to Flat Branch sediment.

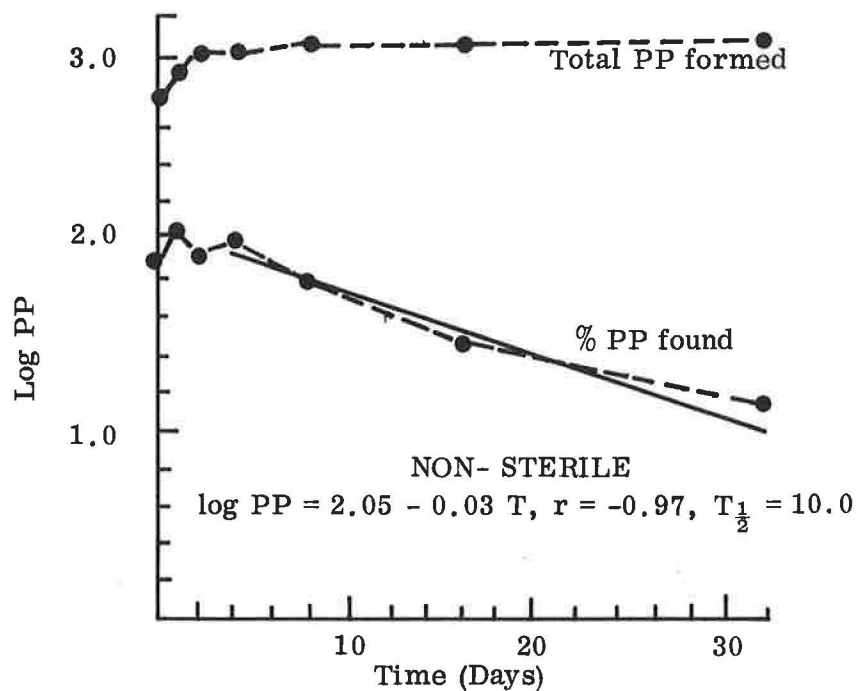
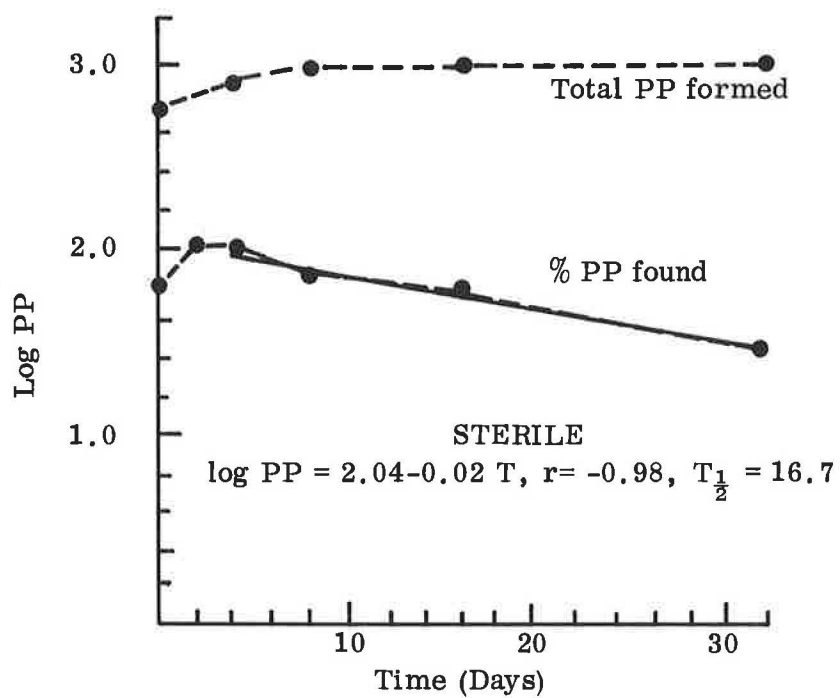


Figure 13. Effect of sterilization on percentage PP found and total PP formed from TPP added to Flat Branch sediment.

found for PP hydrolysis. These results agreed with previous reports that PP hydrolysis is biologically-catalyzed. Hughes and Hashimoto (1971) found that hydrolysis of PP to orthophosphate was rapid in soil minerals inoculated with supernatant microbial suspension extracted from a soil. Sterilization of soils by autoclaving was conducted by Hashimoto et al. (1969) and they found that autoclaving the soil reduced the rate of PP hydrolysis. Gilliam and Sample (1968) employed the technique of fumigating soil with  $\text{CH}_3\text{Br}$  to retard microbial activity. Their results indicated that sterilization slowed down PP hydrolysis. In autoclaved soil samples, the slow rate of hydrolysis was attributed to the destruction of phosphatase enzymes. The hydrolysis of PP was attributed to phosphatase activity. Gilliam (1970) supported this theory. Pyrophosphatase activity was also mentioned as an important factor in the enzymatic hydrolysis of PP by Sutton and Larsen (1964). Racz and Savant (1972) supported this finding and reported that the greater rate of PP hydrolysis in flooded soils may be due to pyrophosphatase activity.

#### Influence of pH on TPP and PP Hydrolysis

The effect of pH on the hydrolysis of TPP added to Flat Branch sediment is shown in Figure 14. Hydrolysis was fairly rapid on the first 4 days as was previously observed. At the end of 2 days of incubation, 73% was still left unhydrolyzed in the sediment at pH 5, 24% left at pH 7, and 36% at pH 9. However, after 4 days, only 13% at pH 5, 19% at pH 7, and

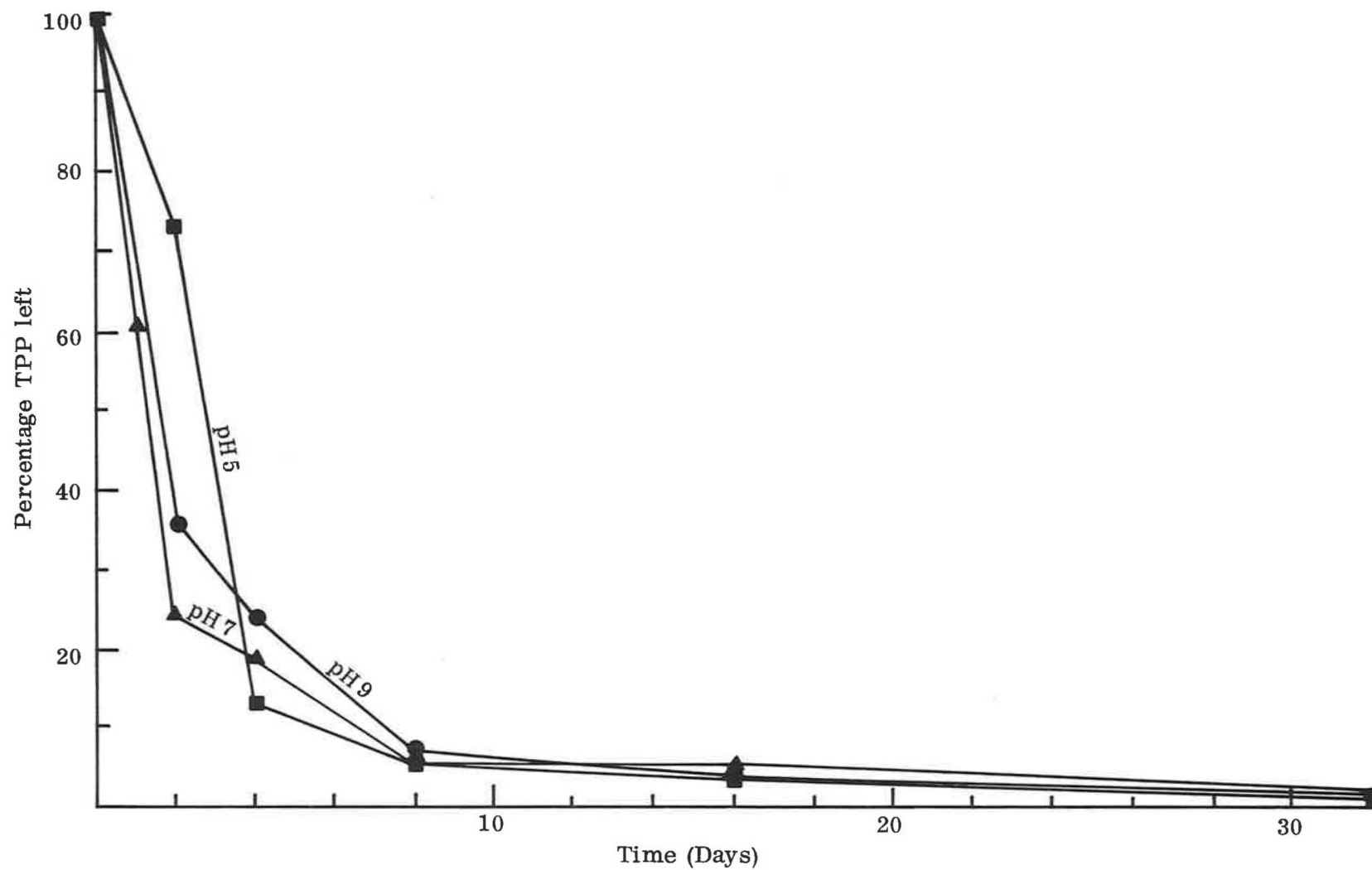


Figure 14. Effect of pH on the hydrolysis of TPP added to Flat Branch sediment.



24% at pH 9 remained unhydrolyzed.

Hydrolysis of TPP added to Flat Branch sediment had half-lives of 1.76 days at pH 5, 1.61 days at pH 7, and 2.16 days at pH 9, Figure 15. The data showed that the hydrolysis of TPP was slower at pH 9. Van Wazer (1958) and McCullough et al. (1956), showed that the hydrolysis of TPP is acid-catalyzed. McCullough et al. (1956) reported that hydrolysis rate of long-chain polyphosphates increased rapidly from pH 7 to pH 4 and does not change much from pH 7 to pH 10. TPP solution was found to be most stable at pH 9 and 10, Crowther and Westman (1954). Blanchar and Hossner (1969a) indicated in their study that hydrolysis rate of TPP was more rapid between pH of 7.7 to 6.8 than at either higher or lower pH. This observation is consistent with the variation of TPP half-life with pH in sediment report here.

The effect of pH on the hydrolysis of PP formed from TPP added to the sediment was in contrast to that observed for TPP hydrolysis. The degradation of PP increased with increasing pH of sediment, Figure 16. Half-lives of 13.7 days at pH 5, 10.0 days at pH 7, and 7.3 days at pH 9 were obtained. It was also noted that at pH 9, maximum PP formation from TPP added was attained after only 2 days. PP was formed at a maximum after 4 days at pH 5 and 7. These findings agreed with the observation of Sutton and Larsen (1964) that there was a positive correlation between hydrolysis rate of PP and increasing soil pH. Their study showed that PP breakdown was more rapid the higher the soil pH.

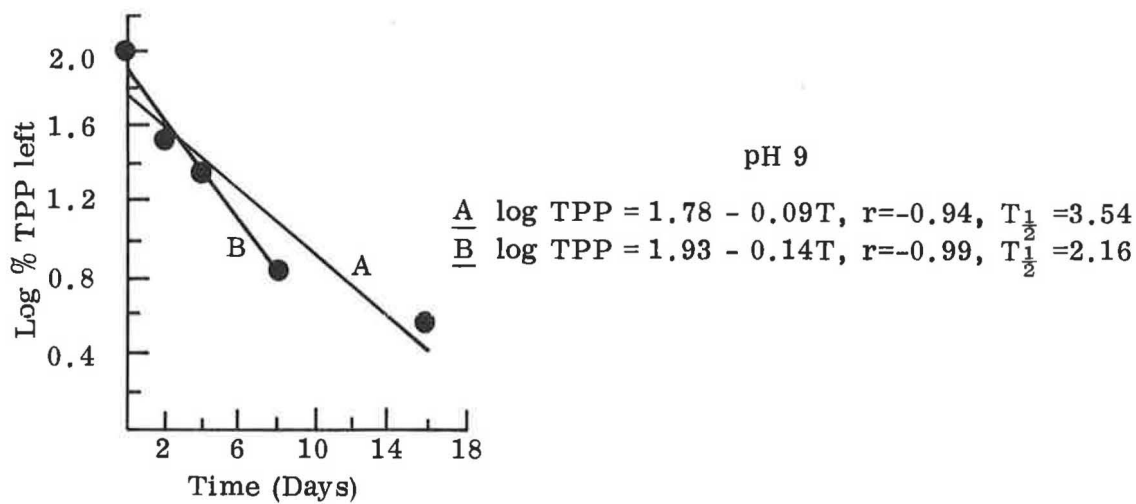
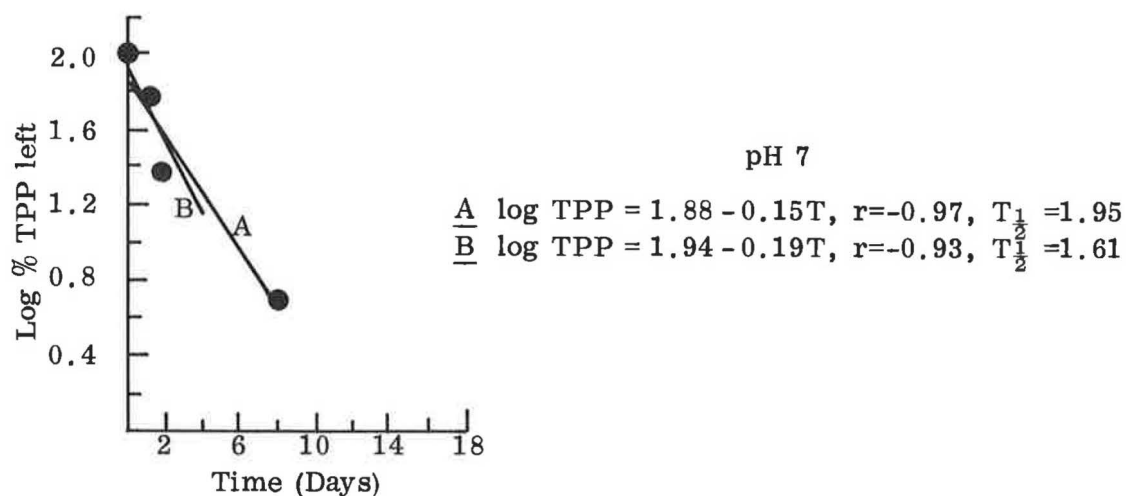
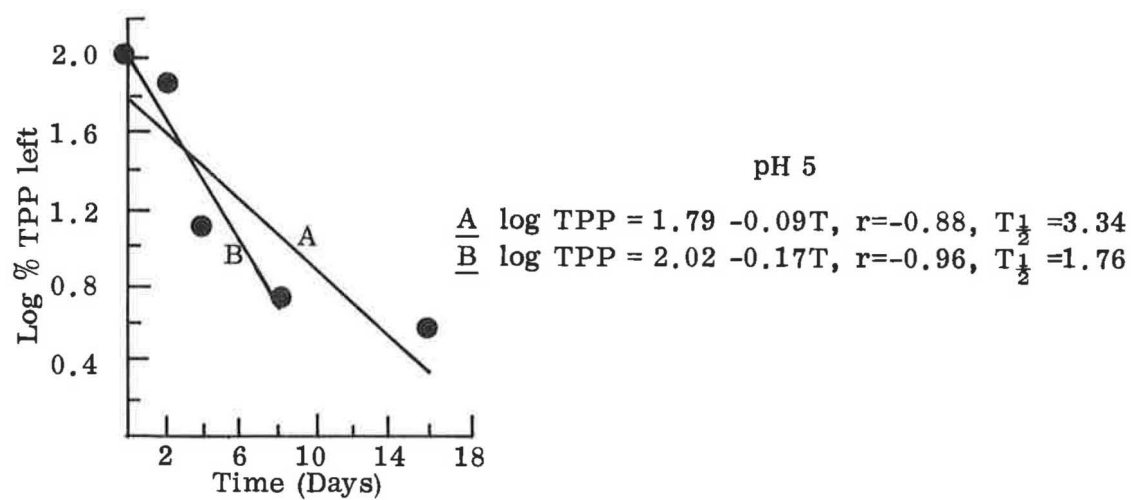


Figure 15. A kinetic analysis of the influence of pH on the hydrolysis of TPP added to Flat Branch sediment.

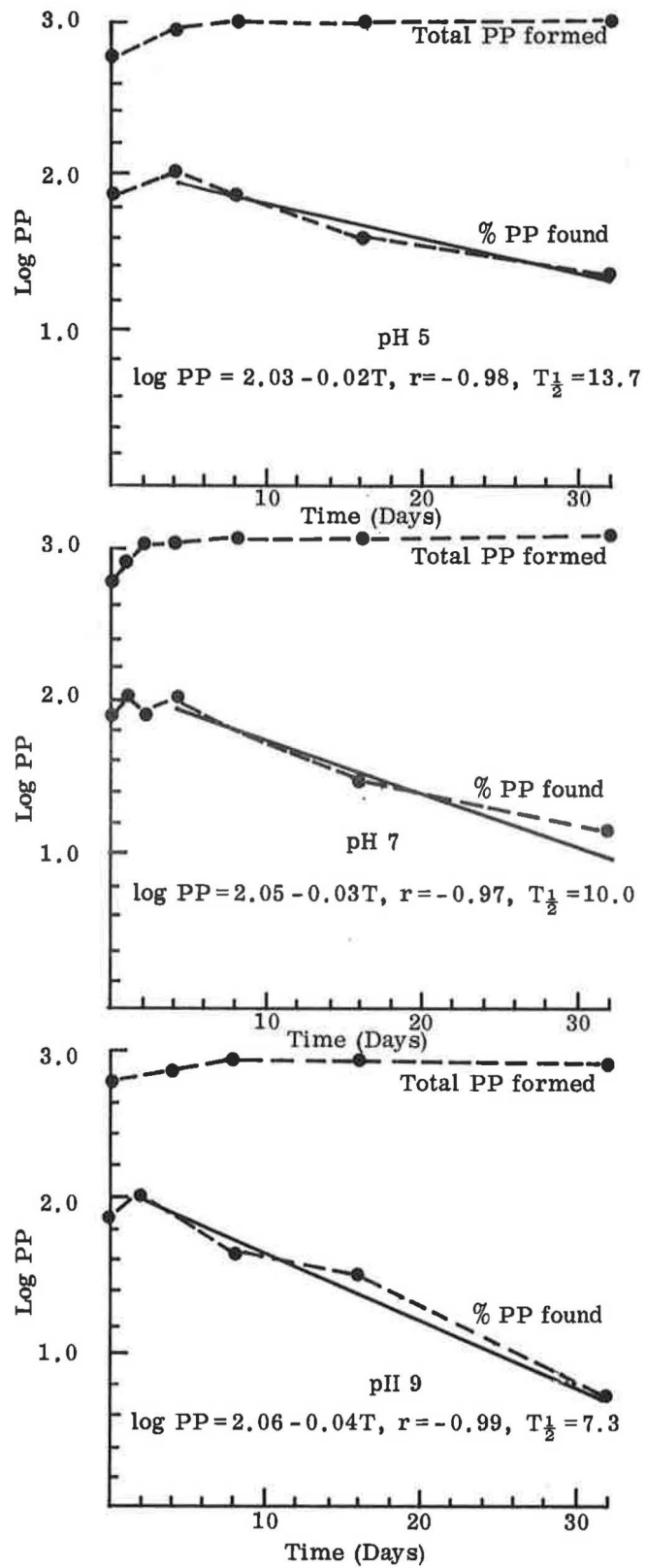


Figure 16. Effect of pH on percentage PP found and total PP formed from TPP added to Flat Branch sediment.

However, there were some contradicting reports on this matter. Crowther and Westman (1954) and Van Wazer (1958) reported that PP hydrolysis was acid-catalyzed. Gilliam and Sample (1968) also disagreed with Sutton and Larsen then they found that increasing the pH above 7 markedly decreased PP hydrolysis. Hossner and Melton (1970) supported Gilliam and Sample by reporting that PP was hydrolyzed more rapidly in acid soils than in basic soils.

#### Influence of Precipitates on TPP Hydrolysis

PP and TPP are used as fertilizers in the form of solid precipitates, Terman and Engelstad (1966), Getsinger, et al. (1962), Hossner and Blanchar (1968), Giordano and Mortvedt (1969), and Dobson, et al. (1970). In some of the work done by these investigators, PP and TPP were used as solid fertilizers. However, addition of solutions of PP and TPP was also done in experiments of Blanchar and Hossner (1969a and 1969b), Hossner and Melton (1970), and Hossner and Phillips (1971). Perhaps the way that phosphorus is added to the sediment influences the rate of TPP hydrolysis.

An insoluble calcium polyphosphate,  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$ , was prepared as described by Bobtelsky and Kertes (1954). The rate of TPP hydrolysis was slower when TPP was added as  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  than TPP added in solution. After 4 days, 37% of the TPP added as  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  and 5.1% of the TPP added in solution was still left unhydrolyzed, Figure 17. The half-life of the hydrolysis when the standard was added as  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  was 2.79 days compared to 1.68 days when TPP was

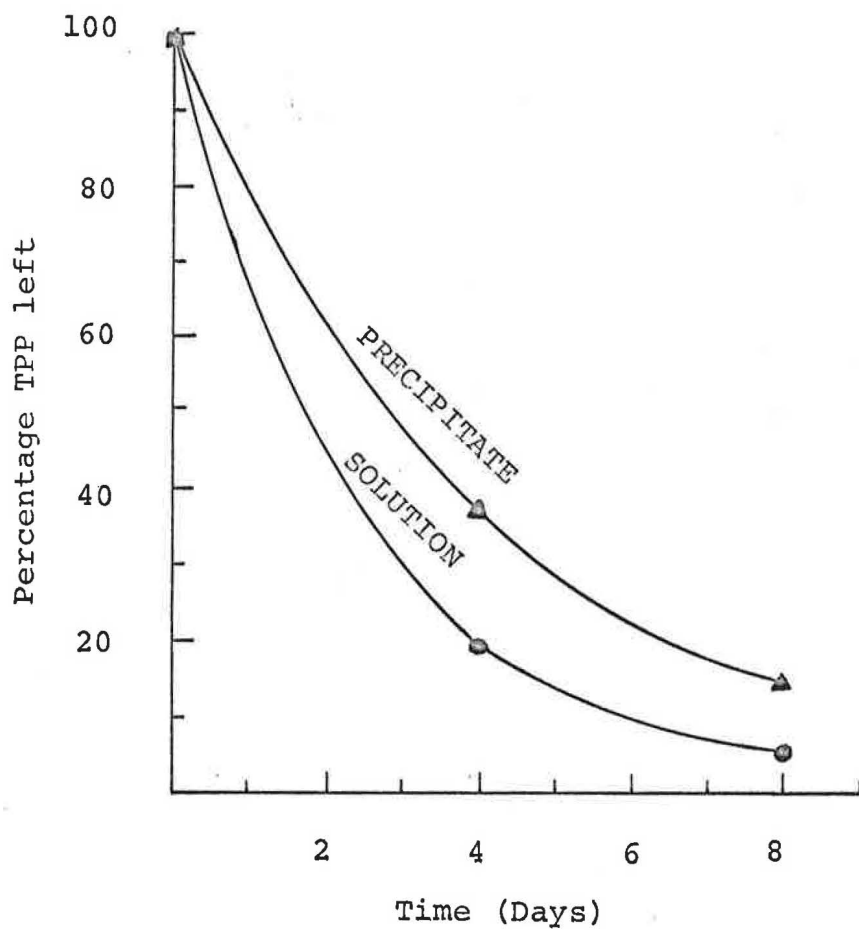


Figure 17. Hydrolysis of TPP added to Flat Branch sediment either as solid precipitate or solution.

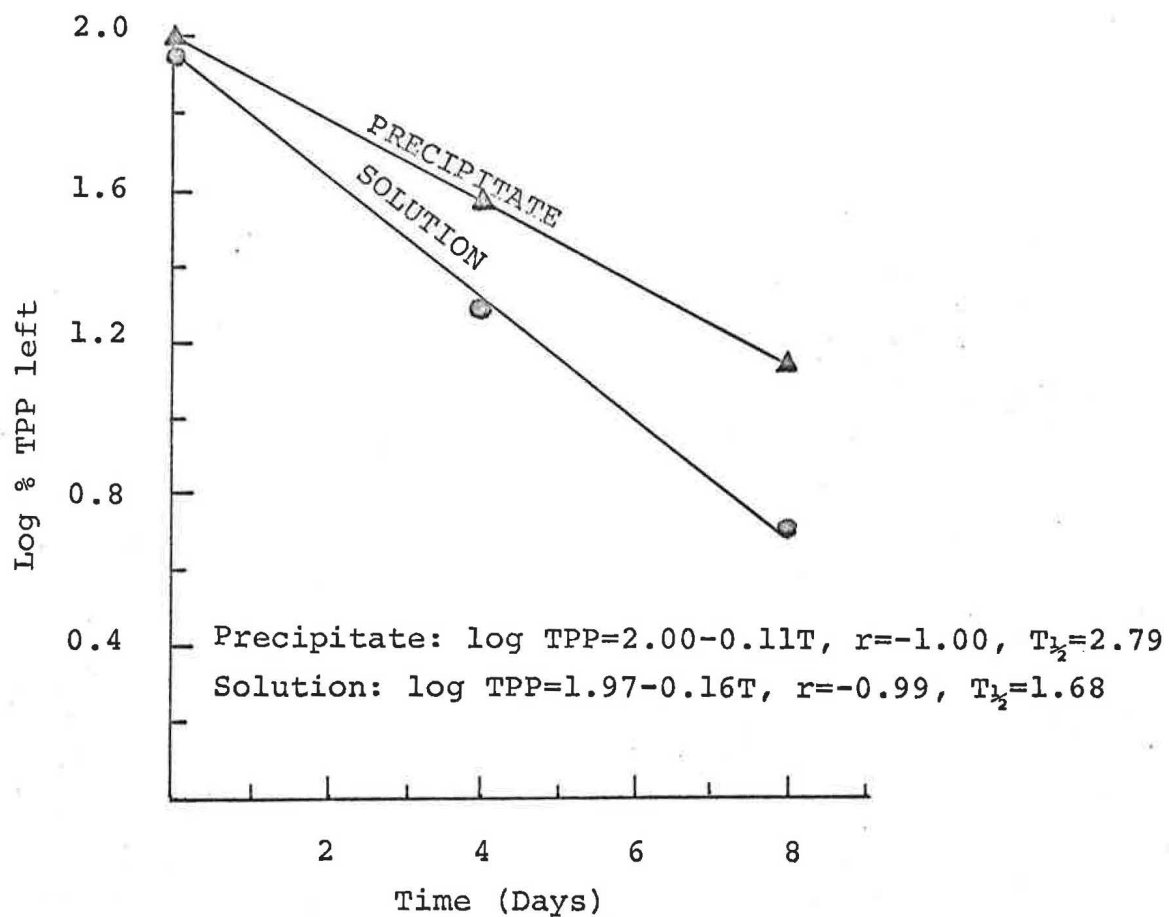


Figure 18. A kinetic analysis of the hydrolysis of TPP added either as solid precipitate or solution to Flat Branch sediment.

added to the sediment as a solution, Figure 18. These data indicate that the rate of hydrolysis of TPP was slower when added to the sediment as  $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$  rather than in solution. The hydrolysis seemed to follow first-order kinetics whether tripolyphosphate was added in solid or solution form.

Precipitation may influence the retention of TPP by soils by preventing its rapid hydrolysis. This factor may account for the fact that amounts of TPP in excess of those predicted to remain in sediments at longer time periods were found. However, the rapid rate of TPP hydrolysis with no half lives longer than 3 days indicate that after two weeks less than 10 percent of the original TPP may be present. With this rapid a breakdown it is predicted that TPP would not accumulate in sediments. However, it is probable that the cyclic formation of long chain polyphosphates and its subsequent breakdown to TPP, PP, and OP will play a role in dilute solution chemistry of phosphorus and its subsequent availability as a nutrient for aquatic vegetation and bacteria.

## TRAINING ACCOMPLISHED

Domingo Riego has done the research contained in this report. This research will apply as approximately one half his Ph.D. research requirement. He has developed an understanding of aspects of water quality that will enable him to deal much more effectively with future water quality problems.

Thomas Morton, an undergraduate student, worked closely with Domingo Riego on this project. Tom is now manager of two municipal golf courses in St. Louis, Missouri. His awareness of water quality considerations will be put to good use in this capacity.

Kenneth Koelkebeck is an undergraduate student who has worked with Domingo Riego on this project. Ken is continuing his study for the B.S. degree and is working in this laboratory on arsenic in soil-water systems.

William Brook, a freshman, has begun work in our laboratory and has helped with this project. Bill is majoring in Soil Science and will continue to work in this laboratory.

Mary Lindeman worked for several months in this project. Mary is currently analyzing run-off water samples for ammonium, nitrate, and phosphorus. Mary will graduate this spring and begin a career in child development work.



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