HYDROLYSIS OF CONDENSED PHOSPHATES

HYDROLYSIS OF CONDENSED PHOSPHATES
IN
LAKE WATER AND WASTEWATER

BY

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SCOPE AND CONTENTS:

Nutrient enrichment through pollution causes intense aquatic growth in many of our lakes, which results in their deterioration for man's use. Phosphorus is suspected as possibly the most important element in this problem since it often is the limiting nutrient for growth. Condensed phosphates from detergents in wastewater are a major supply of phosphorus to surface waters. They hydrolyze to orthophosphate, the form most readily available to plants and organisms. The removal of phosphorus in treatment plants has therefore been suggested.

The chemical industry has carried out many studies on the rate of hydrolysis of condensed phosphate in distilled water. However few investigations have been made on this effect in natural water and wastewater. This work concentrates on studies on the rate of hydrolysis of condensed phosphates in wastewater and lake water under conditions of temperature, pH and concentration levels actually occurring in the environment.

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TABLE OF CONTENTS

Page

CHAPTER IV DEVELOPMENT OF ANALYTICAL TECHNIQUES . . 145

LIST OF FIGURES

LIST OF TABLES

I STATEMENT OF PROBLEM

Governments and the public at large have been actively concerned during the past few years about the pollution of our water resources. Nutrient enrichment through man-made pollution causes algal blooms and intense aquatic growth in many of our lakes. This in turn causes a deterioration in water quality for its use as a source of water supply for domestic and industrial purposes and for recreation and irrigation.

Phosphorus is suspected as possibly the most important element in this problem. In natural waters it may be present in inorganic form, as orthophosphate and as condensed phosphate, and in organic form. It may be dissolved in the water, precipitated to the bottom, adsorbed onto particulate matter or contained in aquatic organisms and plants. A natural cycle exists between these forms of phosphorus in the aquatic environment. The phosphorus supply to surface waters comes mainly from runoff from fertilized lands and in wastewater. Its concentration in wastewaters has increased sharply due to the use of household detergents in recent years, which contain large amounts of condensed phosphates. When these are added to water they hydrolyze to orthophosphate. Aquatic organisms and plants are reported to grow much more readily and to a greater extent on orthophosphate than on condensed phosphates. It is therefore important to know at what rate condensed phosphates revert to orthophosphate. This is particularly true for lakes, since algae blooms apparently occur only when orthophosphate concentrations exceed a certain critical level. If the rate of hydrolysis is slow enough, only a small portion will be converted to orthophosphate near shore, and dilution may solve the problem farther out in the lake. The removal of phosphates in treatment plants by several methods has received much attention in the last few years. Most of these studies were concerned with orthophosphate. Condensed phosphates may be more or less readily precipitated chemically or less readily absorbed in biological, luxury-uptake, treatment than orthophosphate. How much conversion of condensed phosphates actually takes place in the treatment plant is therefore an important point.

The chemical industry has carried out many studies on the rate of hydrolysis of condensed phosphates in distilled water. These experiments were generally carried out at high concentration, and under conditions of temperature and pH which are not representative of the natural water environment. In recent years some investigations have been made on natural waters, which showed a much faster rate of hydrolysis, attributed mainly to enzymatic activity of microorganisms, and plants. The concentration of condensed phosphates used in these experiments was generally still higher than would occur in natural waters, particularly in lakes such as the Great Lakes. Still fewer experiments were carried out with wastewater as a medium.

The object of this study is to establish rates of hydrolysis for the most widely used condensed phosphate; sodium tripolyphosphate, and to a lesser degree tetrasodium pyrophosphate. This is to be done by a comparison of existing literature values, where available, and by experimental work under the following conditions:

1. In distilled water, at low concentrations and conditions of temperature and pH similar to natural water.
2. In Lake Ontario water, at low concentrations under laboratory conditions simulating the natural environment. A field study in Lake Ontario to compare laboratory rates and *in situ* rates.
3. In wastewater, at naturally occurring concentrations and laboratory conditions, simulating conditions in a treatment plant. A field investigation at a treatment plant to compare laboratory rates and *in situ* rates.

II LITERATURE REVIEW

II-1 EUTROPHICATION

Man has been aware of the natural aging of lakes for many years. Eutrophication in a limnological sense means the natural or artificial nutrient enrichment of a water body. To persons interested in water quality management it means in addition the resulting deterioration of water quality. This aging process is normally very slow, requiring thousands of years to transform a young barren lake to marsh land, the most eutrified state. In the last quarter of a century the rate of eutrophication has increased many-fold in numerous lakes through man-made pollution. Hasler (H-5) has described the aging process of lakes and the effect of artificial fertilization. Many authors have dealt with the causes and the problems resulting from eutrophication in recent articles. Some of these are: Sawyer (S-5, S-7, S-8, S-9), Bucksteeg (B-11), Levin (L-4), Fruh (F-7), Ohle (O-1), Shapiro and Ribeiro (S-14), Neil (N-1), Frink (F-6), Webber and Elrick (W-2), Beeton (B-5) and Martin and Weinberger (M-6). The importance of this problem resulted in the gathering of 544 scientists from all over the world at Madison, Wisconsin in June 1967 for the "International Symposium on Eutrophication". Thirty-seven papers were presented under four main topics.

1. Concepts of Eutrophication and Documentation - Geographical
2. Detection and Measurement of Eutrophication
3. Prevention and Corrective Measures
4. Contributions to Science from the Study of Eutrophication.

Mackenthun (M-1) prepared a selected bibliography on the importance of nitrogen and phosphorus in water. The problems of eutrophication result mainly from luxuriant growth, or blooms, of aquatic vegetation, predominantly unicellular algae. The Task Group committee report of the American Water Works Association (A-4) conducted an extensive survey and summarized these problems as follows:

> "Fifty-six percent of the total surface water supply used for domestic purposes in the United States is affected to some extent by problems resulting from algal growth. By far the most significant problem was attributed to taste and odour production by algae."

Table I summarizes their findings.

Other algae-associated problems mentioned are:

- increased colour and turbidity
- conditions toxic for stock and wildlife caused by certain algae
- increased chlorine demand.

In addition to the algae-associated problems the report mentions problems directly associated with nutrient levels.

- Interferences in coagulation due to high condensed phosphate levels.
- Interferences in hardness removal due to high condensed phosphate levels.

Excessive eutrophication may result in the loss of recreational use of lakes. A decrease in valuable fish production

TABLE I: ALGAE-ASSOCIATED NUTRIENT PROBLEMS IN MUNICIPAL WATER SUPPLIES OF THE UNITED STATES*

ALGAE ASSOCIATED PROBLEM	PARTICULAR WATER SUPPLIES WITH ALGAE ASSOCIATED PROBLEMS (based on population equivalent served)			
	IMPOUNDED SURFACE SUPPLIES %	FLOWING SURFACE SUPPLIES %	TOTAL SURFACE SUPPLIES %	TOTAL DOMESTIC WATER SUPPLY %
Chemicals applied for algae control	43	43		
Taste and odour from algae	33	43	38	23
Chemicals for algae taste and odour control	37	49	44	26
Filter clogging by algae	12	23	17	10
Special equipment for algae removal	<5	<4	<5	<2
Total supplies with problem	62	50	56	34

* from Task Group (A-4)

through changes in species is possible even though total fish production may increase.

The nutrients necessary for the support of growth are carbon, hydrogen, oxygen, nitrogen and phosphorus, with smaller amounts of other elements required. Of the major nutrients, the supply of carbon as carbon dioxide, hydrogen and oxygen are uncontrollable. Attention has therefore been focussed on nitrogen and phosphorus. The ability of certain widely occurring algae, mainly the blue-green group, to fix nitrogen from the atmosphere has led to the conclusion that phosphorus may be the essential element in limiting the undesirable productivity of lakes. Ohle (O-1) regarded phosphate levels as the initial factor in the development of eutrophic conditions. Sawyer (S-5) in the study of seventeen Wisconsin lakes suggested that if inorganic nitrogen and phosphorus exceeded 0.30 mg/l N and 0.010 mg/l P respectively at the start of the active growing season (time of spring turnover in northern climates) a season with nuisance blooms would follow. Mackenthun (M-2) suggested that to prevent biological nuisances, total phosphorus concentrations should not exceed 0.10 mg/l P at any point within a flowing stream, nor should 0.05 mg/l P be exceeded where waters enter a lake, reservoir or other standing water body. Chu (C-4) reported that of a variety of different algae studied all flourished when phosphorus varied from 0.1 to 0.2 mg/l P, and that they were likely to suffer from a deficiency when the concentration of phosphorus was below 0.05 mg/l P. Sawyer (S-8) discussed the problem of phosphorus in water supplies, and paid particular attention to the contribution of modern household detergents to the eutrophication problem. Neil and Owen (N-2) discussed the distribution, environmental requirements and significance of Cladophora in the Great Lakes, and found phosphorus levels of prime importance. Shapiro and Ribeiro (S-14) reported on experimental work on the Potomac River and on the effluent from the Washington, D.C., Water Pollution Control Plant. They found that algal growth increased in proportion to the amount of phosphate added, and concluded that removal of phosphate from the effluent could control algal population. Bucksteeg (B-11) gave data on the problem of eutrophication in Germany. Ludwig _et al_ (L-8) discussed the nutrient balance for Lake Tahoe and indicated that nitrogen and phosphorus were retained in the lake to the extent of 89 percent and 93 percent respectively. Levin (L-4) in discussing methods of phosphorus removal pointed out that the City of Detroit and others on Lake Erie are now under orders to remove at least 80 percent of the soluble phosphate before discharge. Fruh (F-7) cited several studies where nutrients other than nitrogen and phosphorus may have been limiting. Sawyer (S-9) discussed in detail the parameters used for assessing the state of eutrophication of a lake. The nutrients, nitrogen and phosphorus and their ratio and form were considered to be the most important.

Much more research work will be necessary in the laboratory and in field investigations to establish just which nutrients may be limiting in a specific case. The major factor in the control of eutrophication is the limitation of the amount of nutrients, principally nitrogen and phosphorus, entering a lake.

II-2 PHOSPHORUS AND ITS COMPOUNDS

Van Wazer (V-2) has edited the most comprehensive work on phosphorus and its compounds. This is a two-volume book, some 2000 pages long, which deals in great detail with the chemistry, occurrence, mining and manufacture, the uses and applications, and the biological functions of phosphorus compounds. The chapters most important to this work are written by Katchman on "Phosphates in Life Processes and in Biological Synthesis" (K-4) and Van Wazer (V-2) on "Structure and Property of Condensed Phosphates". As this thesis deals with phosphorus compounds in water a short resume of parts of this comprehensive work is presented.*

II-2.1 TYPES OF PHOSPHORUS COMPOUNDS

Phosphorus, a universal constituent of protoplasm, is required for growth, health and reproduction in all forms of plants and animals. Whereas all the other elements of major biological importance, such as carbon, nitrogen, hydrogen and oxygen are readily available from the atmosphere,

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* Some of the following material is quoted verbatim without the use of quotation marks.

phosphorus is earth bound. All phosphorus deposits are in the form of orthophosphates; elemental phosphorus never occurs in nature. Both water soluble and insoluble inorganic orthophosphates are found in fresh-water lakes and the seas, as well as in the soil. The soluble orthophosphates are present in rather small amounts, the concentration being effectively controlled by the extent of the solubilization processes as well as by such cations as calcium, iron and aluminum, which are capable of forming highly insoluble orthophosphates. In plants and animals, phosphorus occurs as orthophosphates, polyphosphates of various molecular sizes, ortho- and polyphosphate esters, phosphoproteins and complex nucleoproteins.* Transformation of orthophosphate to its many derivatives represents the consequent life process.

Man utilizes phosphate rock for the manufacture of a wide variety of phosphorus compounds. Van Wazer (V-2, p.990) summarizes these. The main uses are for fertilizers and detergent builders. Some of the other uses are for animal feed, for the pharmaceutical and the food industry, for surface treatment of metals, for water softening and the plastics industry.

The basic principle of phosphate structure can be explained in the following way. By definition, the phosphates are those compounds of phosphorus in the anions of which each

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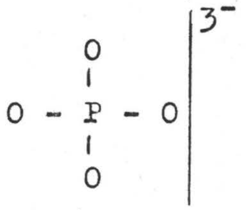
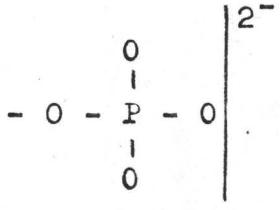
* Van Wazer (V-2, p. 570) gives a summary of the organic phosphates important in life processes.

atom of phosphorus is surrounded by four oxygen atoms arranged at corners of a tetrahedron. By sharing oxygen atoms between tetrahedra, chains, rings and branched polymers of interconnected PO_4 tetrahedra can be produced. This means that there are only several building blocks from which phosphates can be made. These are as follows:



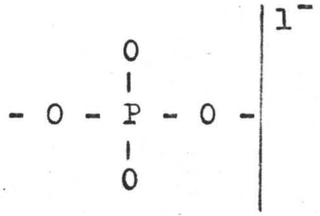
$$\left.\begin{array}{c} O \\ | \\ O - P - O \\ | \\ O \end{array}\right|^{3-}$$

orthophosphate group



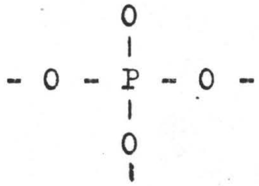
$$\left.\begin{array}{c} O \\ | \\ - O - P - O \\ | \\ O \end{array}\right|^{2-}$$

end group



$$\left.\begin{array}{c} O \\ | \\ - O - P - O - \\ | \\ O \end{array}\right|^{1-}$$

middle group



$$\begin{array}{c} O \\ | \\ - O - P - O - \\ | \\ O \\ | \end{array}$$

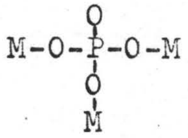
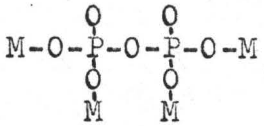
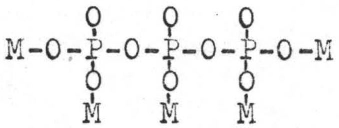
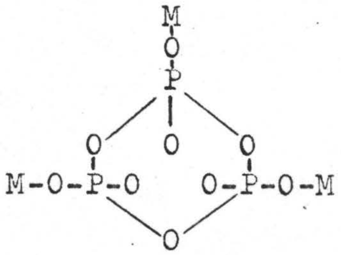
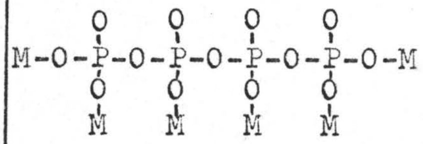
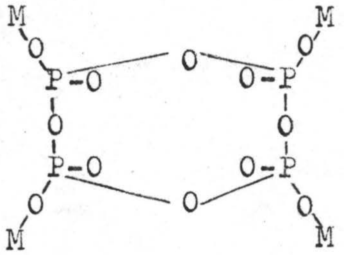
branching point

By combining end groups, middle groups and branching points in all possible ways a large number of hypothetical phosphate formulas can be devised. Only some of these compounds are actually known. The more important ones are shown in Table II, in their undissociated form.

All but the orthophosphates are made up of interconnecting groups and are given the name "condensed phosphates". Other names used for this group are "molecularly dehydrated phosphates" and "complex phosphates". The chain compounds are called polyphosphates, the ring compounds metaphosphates, and cross-linked compounds ultraphosphates.

Condensed phosphates are never found as minerals. They are involved in biological energy transfer processes, where they are formed and degraded by enzymes. In the laboratory they are usually produced by dehydration according to the

TABLE II: INORGANIC PHOSPHATE COMPOUNDS*

	NAME	FORMULA	STRUCTURE	REMARK
	Orthophosphate	M_3PO_4	 $M{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}M$	
condensed phosphates	Pyrophosphate	$M_4P_2O_7$	 $M{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}M$	
	Tripolyphosphate	$M_5P_3O_{10}$	 $M{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}M$	Chain Phosphate
	Trimetaphosphate	$(MPO_3)_3$		Ring Phosphate
	Tetrapolyphosphate	$M_6P_4O_{13}$	 $M{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}\overset{O}{\underset{\underset{M}{O}}{P}}{-}O{-}M$	Chain Phosphate
	Tetra metaphosphate	$(MPO_3)_4$		Ring Phosphate

* From Van Wazer (V-2)
m=monovalent cation

following reaction, given in terms of the sodium salts.

Polyphosphates (Chain Compounds)

$$(n-2)NaH_2PO_4 + 2Na_2HPO_4 \longrightarrow Na_{n+2}P_nO_{3n+1} + (n-1)H_2O \quad n>2$$

Metaphosphates (Ring Compounds)

$$n\ NaH_2PO_4 \longrightarrow (NaPO_3)_n + n\ H_2O$$

II-2.2 SOURCES, USES AND PRODUCTION FIGURES FOR PHOSPHORUS COMPOUNDS

Van Wazer (V-2) worked out the overall phosphorus cycle for the continental United States, with specific figures given for the late 1950's. This is shown in Fig. 1.

A study of this diagram gives a feel for the overall situation. The Task Group Report (A-5) has produced the following phosphorus estimates for the United States for 1966, and are shown in Table III.

The conclusions one must reach after a study of Fig. 1 and Table III are:

1) Surface Drainage from agricultural land is the major phosphorus contributor to surface waters.
2) Domestic Wastewater is next in importance. The contribution from it has increased sharply from the 1950's on. This is primarily due to increased use of detergents.

Calculations by the writer on detergent production for 1958, as shown in Table IV, indicate that the contribution by detergents shown in Fig. 1 should be 100 rather than 10. This would also increase the importance of sewage in Fig. 1, which would give a more accurate pattern of the relative

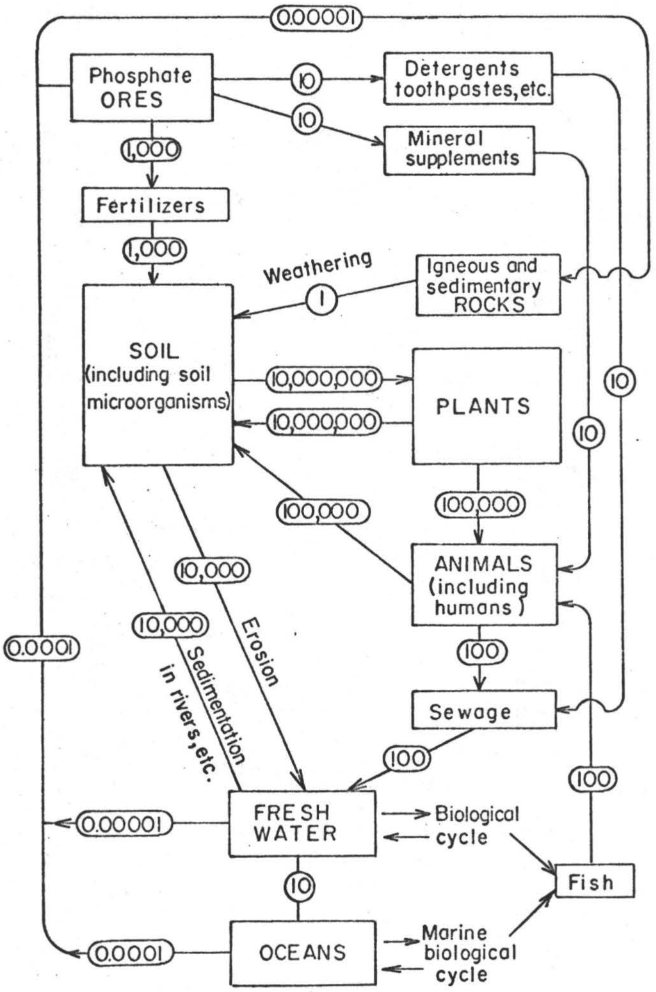


Figure 1. The over-all phosphorus cycle in the continental United States and its connections with coastal waters.*

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* The approximate rate of phosphorus transfer is given in million pounds per year of phosphorus equivalent as estimated to the nearest order of magnitude. Van Wazer (V-2)

importance of surface drainage and sewage to the overall phosphorus supply.

United States Consumption of Phosphorus Compounds for 1958 and 1966 are shown in Table IV. The compounds are essentially all phosphates.

TABLE III: ESTIMATE OF PHOSPHORUS CONTRIBUTION FROM VARIOUS SOURCES*

UNITED STATES 1966

	10^6 lbs of P/year	Usual Concentration in Discharge mg/l P
Domestic Waste	200-500	3.5 - 9
Industrial Waste	Insufficient Data	Insufficient Data
Rural Runoff		
Agricultural Land	120-1200	0.05 - 1.1
Nonagricultural Land	150- 750	0.04 - 0.2
Farm Animal Waste	Insufficient Data	Insufficient Data
Urban Runoff	11- 170	0.1 - 1.5
Rainfall	3- 9	0.01 - 0.03

* From Task Group Report (A-5, p. 363).

TABLE IV: U.S. CONSUMPTION OF PHOSPHORUS FOR 1958 AND 1966

	1958*		1966**	
	10^6 LBS AS P_2O_5	%	10^6 LBS AS P_2O_5	%
Commercial Fertilizer	4530	70	7794	70.5
Detergents	860	13.3	1228	~~13.0~~ 11,2
All other uses: (Animal feed, water softening, pharmaceuticals and food, surface treatment of metals and other uses)	1080	16.7	2000	~~16.5~~ 18.2
	6470	100.0	11022	100.0

* From Van Wazer (V-2) p. 989

** From Soap and Detergent Association (S-18)

The estimated detergent usage of various condensed phosphates for the U.S. in 1966 is shown in Table V.

TABLE V: ESTIMATED DETERGENT USAGE OF CONDENSED PHOSPHATES* IN THE UNITED STATES IN 1966

TYPE OF CONDENSED PHOSPHATE	10^6 LBS OF P_2O_5	%
Sodium Tripolyphosphate ($Na_5P_3O_{10}$)	990	80.7
Tetrasodiumpyrophosphate ($Na_4P_2O_7$)	115	9.4
Trisodiumphosphate (Na_3PO_4)	40	3.2
Potassium Pyrophosphate ($K_4P_2O_7$)	41	3.3
Sodium Metaphosphate ($NaPO_3$)	42	3.4
	1228	100.0

* From Soap and Detergent Association (S-18)

Sodium tripolyphosphate is therefore the most important condensed phosphate in the detergent industry, with tetrasodium pyrophosphate next in production. The estimated soap and synthetic detergent sales for the United States over the past twenty-five years are shown in Table VI.

TABLE VI: ESTIMATED SOAP AND SYNTHETIC DETERGENT SALES IN THE UNITED STATES*

YEAR	JULY 1st POPULATION, IN MILLIONS	NON LIQUID SOAP SALES		SYNTHETIC DETERGENT SALES		SOAP & SYNTHETIC DETERGENT SALES	
		Total 10^6lbs	Per cap. lbs.	Total 10^6lbs	Per cap. lbs.	Total 10^6lbs	Per cap. lbs.
1940	132.0	3206	24.3	30	.2	3236	24.5
1950	152.3	2882	18.9	1443	9.5	4325	28.4
1960	180.7	1230	6.8	3940	21.8	5170	28.6
1966	196.8	1100	5.6	5000	25.4	6100	31.0

* From Soap and Detergent Association (S-18)

Table VI indicates the dramatic decline of soap sales and the meteoric rise of synthetic detergent sales. Since detergents contain a considerable amount of condensed phosphate, as indicated in Table VII, the rise of detergent sales was accompanied by an equally dramatic rise in the production of condensed phosphates, primarily sodium tripolyphosphate.

The reason for the use of condensed phosphates in detergents is the synergistic effect between moderate amounts of these inexpensive compounds and relatively low percentages of expensive surfactants, which reduces the overall cost. One major and beneficial action of the phosphate is to lower the critical micelle concentration, above which the surfactants reach their maximum effectiveness as detergents. This results in a smaller surfactant requirement in the detergent. Other functions of the phosphates are:

- Removal of solid material due to adsorption.
- Reduction in the redeposition of dirt on clothes.
- Furnishing of alkalinity and acting as a buffer.
- Water softening and sequestering of calcium, magnesium and iron.

TABLE VII: PHOSPHATE CONTENT OF DETERGENTS*

Detergent Category	Phosphate Content % (as $Na_3P_5O_{10}$)
Heavy Duty Laundry Powders	35 - 57
Automatic Dishwasher Powders	25 - 55
Heavy Duty Liquid	15 - 25
Light Duty Liquid	0 - 10
Hard Surface Cleaners	1 - 20

* From the Soap and Detergent Association (S-18)

Figures on Canadian production of condensed phosphates, soaps and detergents were obtained from Dominion Bureau of Statistics publications (Q-1) and private communications from

Lever Bros. Co., (L-3) Toronto and Electric Reduction Co. of Canada Ltd., (E-2) Toronto, who are the sole producers of condensed phosphates in Canada. The figures for condensed phosphates include all types produced, however sodium tripolyphosphate is the major product and accounts for about 90 percent of production.

The other major contributor of phosphorus in domestic sewage is human waste. This is a function of protein intake. Sawyer (S-7) reported a release of 1.5 g P/person-day. The Task Group report (A-5) mentioned 1.3 lb P/person-year, or 1.6 g P/person-day. In order to be able to compare these figures to the phosphate-detergent use, the following calculations can be made.

United States 1966

Population = 196.8 million

Condensed phosphates in detergents = 1228 million lbs as P_2O_5

$$= \frac{1228 \times 10^6}{2.29 \times 196.8 \times 10^6} = 2.72 \text{ lbs P/person-year.}$$

$$= 3.38 \text{ g P/person-day.}$$

Note: 1 mg P = 2.29 mg P_2O_5

Sawyer (S-6) calculated that in 1950 the corresponding figure was 10 x 10^{-3} lb/person-day as P_2O_5 or 1.98 g P/person-day.

TABLE VIII: ESTIMATED ANNUAL PRODUCTION OF CONDENSED PHOSPHATES, SOAP AND SYNTHETIC DETERGENT POWDERS IN CANADA, 1966

Population of Canada*	20.0 Million		
Production of Condensed Phosphates in Canada**	60,000 tons (as $Na_5P_3O_{10}$)	or	69×10^6 lbs (as P_2O_5)
Imports of Condensed Phosphates to Canada (Special Products)**	1,500 tons (as $Na_5P_3O_{10}$)	or	2×10^6 lbs (as P_2O_5)
Use of Condensed Phosphates in the Detergent Industry***	55,000 tons (as $Na_5P_3O_{10}$)	or	64×10^6 lbs (as P_2O_5)
Production of Synthetic Detergents* (Household use)	201×10^6 lbs.		
	or		
	10 lbs/person-year		
Production of Soap Powders and Flakes* (Household use)	9.2×10^6 lbs.		
	or		
	0.5 lbs/person-year		

* Queens Printer (Q-1)

** Electric Reduction Co., Toronto (E-2)

*** Lever Bros. Co., Toronto (L-3)

Canada 1966

Population = 20.0 Million

Condensed phosphates in detergents = 55,000 tons = 110×10^6 lbs as $Na_5P_3O_{10}$

$$= \frac{110 \times 10^6}{3.96 \times 20 \times 10^6} = 1.39 \text{ lb P/person-year}$$

$$= 1.73 \text{ g P/person-day}$$

Note: 1 mg P = 3.96 $Na_5P_3O_{10}$

West Germany 1966

Buckstееg (B-11) provided the following figures:

Phosphorus contribution from human wastes = 1.65 g P/person-day

Phosphorus contribution from detergents = 1.57 g P/person-day

The contribution of phosphorus to domestic wastewater are thus:

	U.S. (1966)	Canada (1966)	W.Germany (1966)
	in g P/person-day		
Human waste sources	1.6	1.6	1.65
Detergents	3.4	1.7	1.57
TOTAL	5.0	3.3	3.2

Detergents containing phosphates contribute more than twice as much phosphorus as human wastes based on U.S. figures. In Canada and West Germany, the contribution of each are about equal. Sawyer and McCarty (S-10) stated that domestic sewage probably contains from two to three times as much inorganic phosphorus at the present time as it did before synthetic detergents became widely used. The figures for the United States shown above indicate that it may be slightly more than three times. Comparison of respective United States and Canadian figures for 1966 show that Canadians use considerably smaller quantities of soaps and detergents than Americans do. Even if Canadian bulk sales of detergent powders of about 50×10^6 lbs per year, and of soap powders of about 17×10^6 lbs per year would have been included, Canadian use is only about one half of the United States use. Discussions on this difference with the Electric Reduction Co. and Lever Bros. supported the figures presented but did not come up with a reason for this rather surprising difference.

Owen and Johnson (O-3) in a survey of a Metropolitan Toronto watershed estimated the annual per-capita yield of total phosphorus as 7.7 lbs PO_4 or 2.7 g P/person-day, in treated municipal wastes. The removal of phosphorus varied from 28 to 43 percent. Based on an average reduction of 35 percent, the raw waste total phosphorus contribution would be 4.2 g P/person-day and indicates that in the highly urbanized Toronto area the phosphorus contribution is much closer to the U.S. average.

Can other materials perform the same role as phosphates in detergents? The Soap and Detergent Association (S-18) provides the following answer to this question:

> "The importance of the polyphosphates lies in the synergistic effects obtained when they are used with surfactants. The net result of this synergism is the ability to use small amounts of surfactant, with attendant savings to the housewife. While the possibility of finding a material, or combination of materials, to be able to replace phosphates in detergents, cannot be ruled out, no one has yet succeeded, and the odds against success are exceptionally high. The industry possessed considerable knowledge and know-how concerning the composition of alternate surfactants, when it began its search in 1951 for an answer to the 'detergent foam problem'. Nevertheless, it still required more than a decade to find a satisfactory replacement for ABS, and to develop the technology to permit commercial production of the massive quantities of LAS required to satisfy the large volume requirements. This was true despite the fact that LAS is a member of the same chemical family as ABS. To find a non-phosphate substitute for todays detergent phosphate would be a much more difficult task, if indeed possible at all."

However, recent news reports (A-9), (A-10) mention the possibility of replacement of phosphate builders in detergent formulations by organic compounds like nitriloacetic acid (NTA), ethylenediamine-tetraacetic acid (EDTA), citrates, and malates in order to reduce the fertilization of streams and lakes.

Removal of phosphorus in present-day sewage treatment is small and only coincidental to BOD removal. While it is technically possible to remove up to 95 percent phosphorus from wastewater by special processes, they have generally not been applied up to now. This is primarily due to the fact that insufficient evidence has been presented to show that phosphate removal from wastewater will in fact solve the eutrophication problem, as phosphates would still be supplied to the aquatic environment from surface runoff. Whether in a particular drainage system the sewage treatment plant effluent or land drainage is the more important phosphorus contributor will depend on the land use. Englebrecht and Morgan (E-3), in a study of the sources of phosphorus in Illinois surface waters over a two year period (1956-1958), found that the mean percentage of orthophosphate plus maximum inorganic condensed phosphate from surface drainage amounted to forty-five percent. Missingham (M-10) in a study of the Grand River in Ontario concluded that phosphorus contributions from runoff from rural areas did not appear significant when compared to the contribution from sewage treatment plant effluents. In a report on Lake Mendota (A-7) it was concluded that a drainage area, that is nonurban, such as that of Lake Mendota, can supply by runoff through its drainage system sufficient nutrients, nitrogen and phosphorus, to fertilize the water to the nuisance producing level. Owen and Johnson (O-3) in a study of an urbanized watershed found that approximately 90 percent of the yield of phosphorus came from the sewage treatment plant effluent. Dugdale and Dugdale (D-4) in a study of lakes in Alaska showed that considerable amounts of phosphorus are contributed by the runoff of natural watersheds.

In summary it may be stated that the two principal sources of phosphorus supply to surface waters are from land drainage of fertilized agricultural areas and from sewage treatment plant effluents.

II-2.3 PHOSPHORUS CYCLE IN NATURAL WATERS

The supply of phosphorus to surface waters is mainly in the inorganic form, either as orthophosphate or as condensed phosphates. The fate of the condensed phosphates in an aquatic environment will be discussed in Chapter II-3.

When inorganic phosphorus from fertilizers is added to lake water, it disappears from solution after several days. It was thought that plant growth stimulated by the nutrient added, caused this decline. Experiments with radioactive tracer phosphorus by Hayes et al (H-7), Harris (H-3) and Rigler (R-2), (R-3) showed that it decreased in the same way as fertilizer phosphorus. Hayes (H-6) concluded from this that there is a single pool of phosphorus belonging to water and solids, which is distributed between them in a dynamic equilibrium or steady state. He summarized the findings of several workers on the transformations of phosphorus in a diagram which is reproduced in Fig. 2. Hayes (H-6) describes the process as follows:

> "It is seen that upon addition of phosphate to water the immediate reaction, within minutes, is a transfer through the bodies of unicellular floating forms of life (heavy lines to right). Next, as shown by the light solid lines to the left, there occurs within a matter of hours, ie. two orders of magnitude slower than the above, an exchange in which the floating cells and the higher aquatics compete on approximately equal terms for the PO_4. This they make into their own body structures, throwing some of it back to the water as soluble organic phosphorus. We have cancelled out the virtually instantaneous passage through floating cells and set the process down as an equilibrium between inorganic and organic phosphorus in solution, for which the turnover time is 0.3 days.

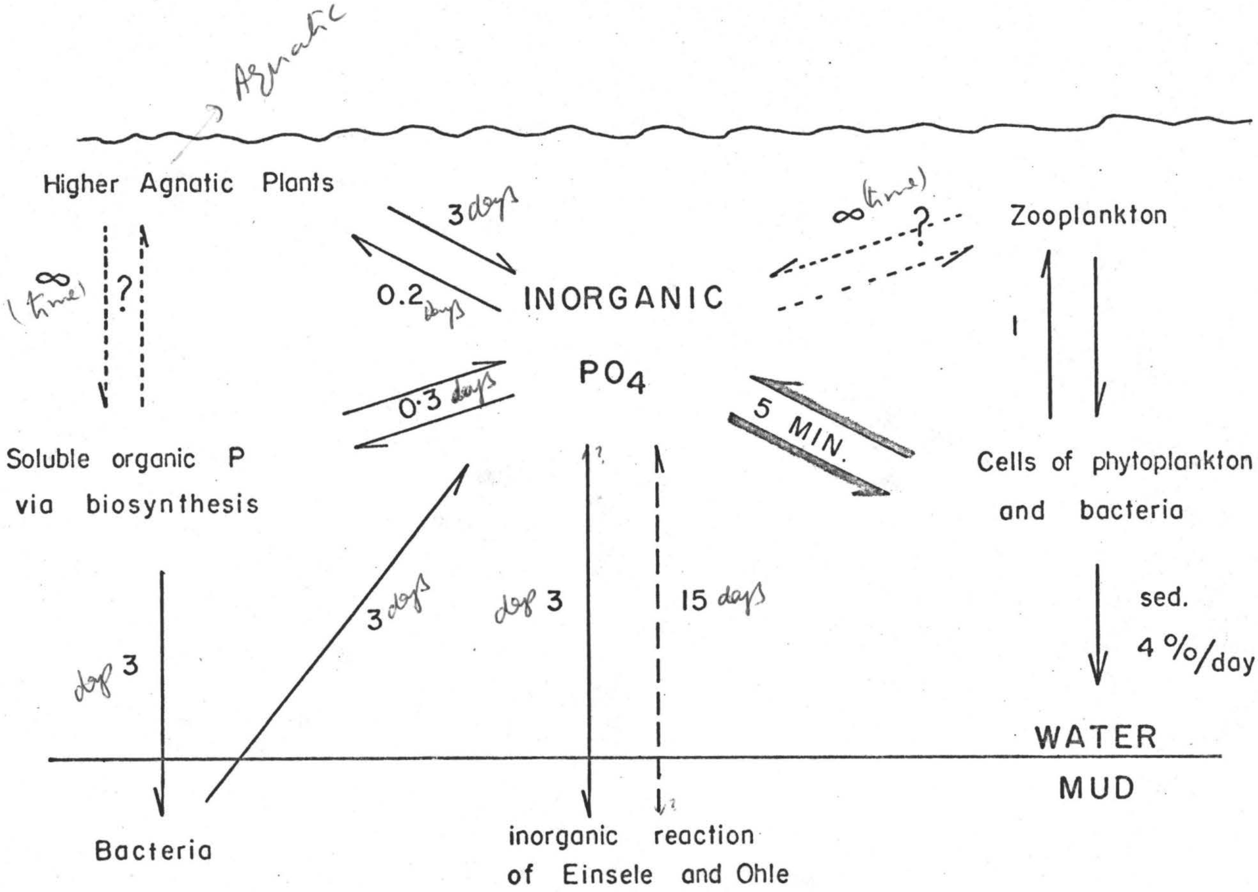

Figure 2. Transformation of phosphorus in a lake with turnover times for different equilibra. (After Hayes (H-6).*

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* Very heavy lines indicate the first action with floating cells, for which the time is given in minutes. Other times are in days. Lighter solid lines are reactions at intermediate speeds - two or three orders of magnitude slower than the initial one. Dashed line is the return from mud by inorganic release, a still slower turnover. Dotted lines at top indicate reactions too slow to measure, called infinitely slow by comparison with the rest.

> At top left is indicated a doubt as to whether higher plants can utilize organic phosphorus, and at top right the feeding of zooplankton is given a turnover time, and their inability to utilize inorganic P is noted.
>
> The lower part of Fig. 2 brings in the sediment surface. At right, bacteria are noted to fall out at a few percent per day. This is in bottles and not be read as net fallout in natural waters, which is subject to wide variation. The fallout at right probably describes the same phenomenon as the line leading down at left, ie. the settling of organic matter to be reduced again by bottom microorganisms for regeneration to the water. The turnover time for leaving the water and for return is here three days, an order of magnitude slower than for exchanges with floating life.
>
> The inorganic mechanism, which can be observed when bacteria are suppressed, is shown at lower center. The observed relations are not affected by the redox state. In taking out inorganic phosphorus the mechanism has the same turnover as the bacterial action just described, namely three days. The return to water however is much slower, at fifteen days."

Kramer (K-10) presented a theoretical model for the chemical composition of Great Lakes waters. He found that all the Great Lakes with the exception of Lake Superior had phosphorus concentrations in excess of those needed for apatite saturation. He suggested that this excess concentration might be used as an 'index of biological use' of the lake. The 'lack' of phosphorus in Lake Superior compared to that needed for apatite saturation suggested a very low biological use, whereas the excess phosphorus in Lake Erie compared to that required for saturation pointed to a very high biological use of the lake. In a subsequent work Sutherland, Kramer et al (S-21) presented a more detailed model for phosphate equilibrium. They were able to explain phosphorus concentration data for Lake Ontario by their model as a function of pH, Ca^{++}, and temperature.

The seasonal variation and the vertical distribution of the type of phosphorus compounds can be discussed together.

Mackenthun et al (M-3) presented data on the seasonal and vertical distribution of phosphorus in Lake Sebasticook, Maine. These are presented in Fig. 3. Concentration data are given in Table X. Fig. 3 shows that total phosphorus in the lake was most abundant during the summer, and lowest in autumn and winter. The soluble phosphorus however was lowest in spring and higher in winter. This variation was attributed to the changes in amounts of algal growth during the different seasons. Hutchinson (H-13) also provided a

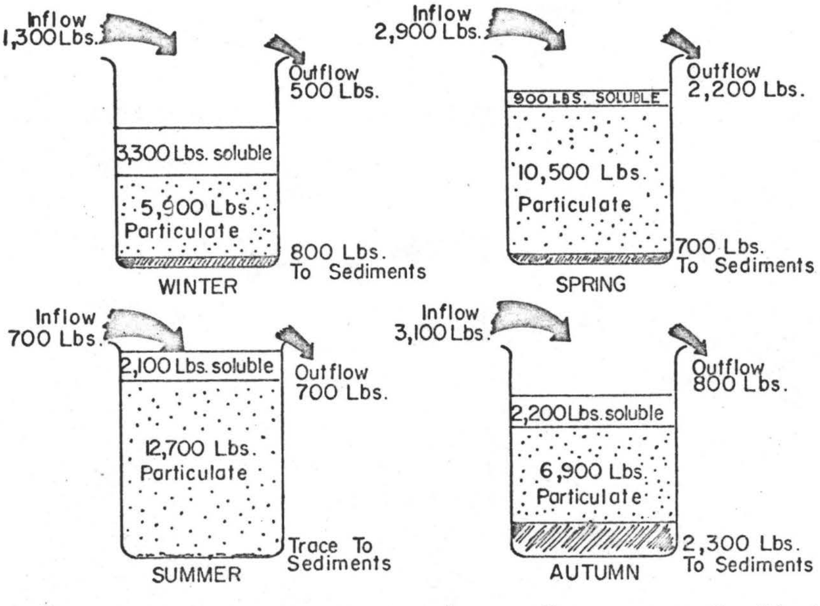


Figure 3. Representation of seasonal distribution of phosphorus in Lake Sebasticook. Inflows and outflows are total phosphorus. (After MacKenthun et al (M-3)).

graphical presentation on seasonal and vertical distribution. Heinke (H-8) found a seasonal variation of inorganic phosphorus measurements in Lake Ontario, with highest concentrations occurring in late winter months, and lowest concentrations in the summer months. Relatively uniform concentrations of phosphorus were observed with depth during the winter, whereas in the summer inorganic phosphorus concentrations in top waters (0-10m) were extremely low, with higher values at depth. Rigler (R-3) in a study of several small Ontario lakes found that inorganic phosphorus was consistently low throughout most of the year and increased to a maximum at some time between December and April.

An interesting experiment on interrupting the phosphorus cycle to retrieve small lakes from eutrophication was reported by Hynes and Greib (H-14). Based on preliminary laboratory evidence, they suggested that it may be possible to cut down on the further release of phosphorus from bottom muds by covering them with weighted-down polyethylene sheets. The best time to lay these would be when the lake is in full circulation and the largest amount of phosphate is in the deposits.

II-2.4 CONCENTRATION OF PHOSPHORUS IN WASTEWATER AND SURFACE WATERS

Comparison of the concentration of phosphorus found in wastewater and in surface waters by different investigators is often difficult due to the following reasons:

1. Authors have used different units to report phosphorus. In some cases it is not clear which unit has been adopted. For easy comparison all data shown in Tables X and XI have been converted to $\mu g/l$ PO_4.

2. The analytical technique used will influence the result. Lee *et al* (L-1) have shown this for total phosphorus determinations. Strickland and Parson (S-20) indicated the difficulties experienced by different contact times of the reducing agent with the sample in the analysis for inorganic phosphate due to some hydrolysis of condensed and soluble organic compounds. The size of filter used will influence the relative proportion of soluble and particulate phosphorus fractions as shown by Rigler (R-3) and others. In some cases it is difficult to establish whether the analysis was in fact made on a filtered or unfiltered sample.

3. The lack of a clear definition of the terms in which some authors report data. Some of the terms used are:
   - Total Phosphorus
   - Soluble Phosphorus
   - Particulate Phosphorus
   - Inorganic Phosphorus
   - Organic Phosphorus
   - Orthophosphate
   - Condensed Phosphate

Strickland and Parson (S-20) give an excellent breakdown of the various forms of phosphorus encountered in natural waters (seawater), with exact definitions and methods of determination for each. Their breakdown is essentially used in this thesis, and is given in Chapter IV.

4. There are seasonal and depth variations in natural waters which further complicate comparison of data.

5. The previously discussed increase in recent years in the use of detergents and fertilizers, with resulting increase in phosphorus supply to wastewaters and receiving waters makes it necessary to add the year of analysis to data to allow the assessment of this factor.

6. The relative level of enrichment will have a large influence on the local concentration of phosphorus present, eutrophic waters having high levels and oligotrophic water low levels.

The concentration of phosphorus in wastewater is caused by the contribution from human wastes, the detergent use and the volume of wastewater generated. Based on the figures calculated in II-2.2 the concentration of phosphorus can be calculated as follows:

Wastewater production (assumed) = 80 I gal/person-day.
= 362 liters/person-day.

TABLE IX: CONCENTRATION OF PHOSPHORUS IN WASTEWATER

AUTHOR	REFERENCE NO.	YEAR	LOCATION	TOTAL PHOSPHORUS CONC. RANGE (unless otherwise stated) mg/l PO_4	COMMENTS
Sawyer and McCarty	S-10	1967	General	From Human Wastes: Inorganic 6 - 9 Organic 1.5- 3 From Detergents: 12 - 27 Total: approx. 20 - 40	Textbook
Vacker et al	V-1	1964/65	Texas	27 - 51	Data collected from 9 activated sludge plants in Texas
Finstein and Hunter	F-3	1966	New Jersey	Monday: 42 - 78 Wednesday: 9 - 49 Friday: 20 - 42	Analysis on settled sewage of 6 plants. Wide variations over day and week reported. 42% (25-85 range) was in the condensed phosphate form.
Barth and Ettinger	B-4	1966/67	Ohio	8 - 33	
Missingham	M-10	1964	Southern Ontario	21 - 32 (orthophosphate only)	Data collected from four plants (weekly averages)
McGauhey et al	M-7	1963	California	25	Suggested design figure for Lake Tahoe project.
Watson et al	W-1	1965	New York State	Total: 45 - 65 Ortho: 25 - 45	Long term analysis from three individual homes
Hurwitz et al	H-17	1965	Chicago, Ill.	Raw Sewage: Total 16-20 Act.Sludge Effl: Total 4-13	Data on distribution among ortho-, condensed and organic phosph.

TABLE X: CONCENTRATION OF PHOSPHORUS IN LAKES AND RESERVOIRS

AUTHOR	REFERENCE NO.	YEAR OF SURVEY	LOCATION	CONCENTRATION OF PHOSPHORUS			REMARKS
				Type	in Authors units	μg/l PO$_4$	
Hutchinson Data of:	H-13				mg P/m^3 Mean (Range)		
Juday and Birge		1931	Wisconsin	Total Phosph.	23.0 (8-140)	70(24-428)	
Yoshimura		1932	Japan	"	14.8(4.4-43.5)	45(14-133)	
Ruttner		1937	Austrian Alps	"	20.0 (0- 46)	61(0-141)	
Lohammar		1938	Sweden	"	26.0 (4-92)	80(12-282)	
Deevey		1940	Connecticut	"	13.0 (7-31)	40(21- 95)	
Ohle		1934	Baltic Germany	Soluble Phosph.	77 (5-600)	235(15-1830)	
Beeton and Chandler	B-6	1963			ppb P		Data based on samples from various depths. Year of publication 1963. Data presumably early 1960s.
Data of U.S. Bureau of Commercial Fisheries			L.Superior	Total Phosph.	5	15	
			L. Huron	"	10	31	
			L. Michigan	"	13	40	
			L. Erie	"	61	187	
			L. Ontario	"	-	-	
Putnam and Olson	P-4	1958-59	Western Lake Superior	Total Phosph.	0.18-0.46 μg-at P/l	17-44	70-100% present in organic phosph. form
Chandler and Weeks	C-3	1942	Western Lake Erie	Soluble Phosph.	1-8 μg/l P	3-25	Data on surface waters, 29% of total phosph. in soluble form. April to October data.

TABLE X - (cont'd.)

AUTHOR	REFERENCE NO.	YEAR OF SURVEY	LOCATION	CONCENTRATION OF PHOSPHORUS			REMARKS
				Type	in Authors units	$\mu g/l$ PO_4	
Curl	C-15	1950-51	Western Lake Erie	Phosphate Phosphorus	0-4.3 μg PO_4-P/l	0-13.2	Surface Samples
Heinke	H-8	1966-67		Ortho-phosphate (unfiltered)	Depth	Mean (Range)	
			L.Superior		Surface or 10m	11(3-19)	August-December
					50m	5	
			L.Huron		Surface or 10m	20(3-70)	December
			L.Erie		Surface or 10m	48(2-99)	August-December
					50m	39(25-59)	
			L.Ontario		Surface or 10m	56(24-82)	January-February
					50m	48(37-66)	
					Surface or 10m	27(2-78)	November-December
					50m	29(14-43)	
Anderson	A-6	1950	L.Washington, Seattle	Ortho-phosphate	23 ppb PO_4-P	70	Max.hypolimnetic
		1957			89 "	272	Conc. of
		1958			74 "	226	phosphate in deepest waters.

TABLE X - (cont'd.)

AUTHOR	REFERENCE NO.	YEAR OF SURVEY	LOCATION	CONCENTRATION OF PHOSPHORUS			REMARKS
				Type	in Authors units	µg/l PO_4	
Anonymous	A-7	1945-47	L.Mendota, Wisconsin	Inorganic Phosphorus	0.008-0.082 mg/l P	25-250	
Curry and Wilson	C-16	1954	L.Zoar, Connecticut	Soluble phosphate		25(12-41)	
Rigler	R-3	1964	Ontario Lakes	Total Phosph.			Gives breakdown of total phosphorus into inorganic (5.9), Soluble organic (28.7) and Seston fraction (65.4)
			South (Hard Water)		27-133 µg/l P	83-407	
			North (Soft Water)		5-18 µg/l P	15-50	
Morgan and Englebrecht	M-12 E-3	1956-57	Illinois Lakes and Reservoirs		mg/l P_2O_5		
				Ortho-phosphate	0.036(0.0-0.108)	48(0-145)	MIC....Max. inorganic condensed
				Ortho & MIC	0.081(0.0-0.226)	108(0-303)	
Moyle	M-14	1956	Minnesota	Total Phosph.			
			North		0.058 mg/l P	177	
			South		0.126 mg/l P	385	
Neil	N-1	1952-55	Sturgeon Lake, Ont.	Total Phosph.		101-165	July to Sept. Survey
				Sol. Phosphate		23-149	

TABLE X - (cont'd.)

AUTHOR	REFERENCE NO.	YEAR OF SURVEY	LOCATION	CONCENTRATION OF PHOSPHORUS					REMARKS
				Type	in Authors units		µg/l PO_4		
Orr	O-2	1966	L.Minnetonka, Wisconsin	Total Phosph.	0.14 mg/l P		428		
Mackenthun et al	M-3	1965	L.Sebasticook, Maine		mg/l P Surface	Near Bottom	Surface	Near Bottom	
				Total Phosph.	0.05	0.37	152	1170	February
				Soluble "	0.011	0.33	34	1010	
				Total Phosph.	0.05	0.16	152	482	May
				Soluble "	0.004	0.006	12	18	
				Total Phosph.	0.07	1.36	210	4170	July-August
				Soluble "	0.01	0.11	31	337	
				Total Phosph.	0.04	0.05	122	152	October-November
				Soluble "	<0.01	<0.01	<31	<31	
Vaughan and Harlow	V-6 p.282	1964	Lake Erie, (Michigan waters)	Total Phosph.			180-300		Considerable amount of data in chart form, avg. only are quoted.
				Soluble "			50-100		

TABLE XI: CONCENTRATION OF PHOSPHORUS IN RIVERS

AUTHOR	REFERENCE NO.	YEAR OF SURVEY	LOCATION	CONCENTRATION OF PHOSPHORUS			REMARKS
				TYPE	IN AUTHORS UNITS	μg/l PO_4	
Putnam and Olson	P-4	1958-59	Minnesota	Total Phosp.	1.0-1.7 μg-at P/l	95-161	August survey
Englebrecht and Morgan	M-12	1956	Illinois	Ortho + MIC	mg/l P_2O_5 0.629(0.025-3.402)	835(33-4560)	MIC Max. Inorganic condensed
Dietz and Harmeson	D-3			MIC	0.264(0.011-0.976)	350(15-1310)	Feb. to April survey
Curl	C-15	1950-51	Detroit Riv.	Phosphate phorphorus	2.6(0-4.6)μg PO_4-P/l	8(0-14)	Surface samples only
			Maumee Riv.		43	132	
			Other Streams		16	49	
Missingham	M-10	1963-64	Grand River, Ontario	Ortho phosphate		900(90-1300)	Dec. to Feb. survey
Owen and Johnson	O-3	1964-65	Toronto, Ontario	Total phosph.		20-5000+	Predominantly urban watersheds
Shannon	S-12	1965	Wisconsin	Total phosp.	0.05-184 mg P/l	150-5600	2 week study during spring thaw period
				Ortho phosp.	0.03-1.51 mg P/l	90-4600	
				Condensed phosp.	0.02-0.25 mg P/l	60-760	
Vaughan and Harlow	V-6 p.254	1964	Detroit River	Phosphate(?)		160-520	Avg. values are presented only
Hurwitz et al	H-17	1965	Illinois Waterway	Total phosp.		1410-3870	Data on distribution among ortho-, condensed and organic phosph.

Concentration of phosphorus due to human wastes

$$= \frac{1.6 \text{ g P/person-day} \times 10^{3} \frac{\text{mg}}{\text{g}}}{362 \text{ liters/person-day}} \times 3.06 \frac{\text{g PO}_4}{\text{gP}}$$

$$= 13.5 \text{ mg PO}_4/_{\text{l}}$$

Concentration of phosphorus due to detergents (U.S. - 1966)

$$= \frac{3.4 \text{ g P/person-day} \times 10^{3} \frac{\text{mg}}{\text{g}}}{362 \text{ liters/person-day}} \times 3.06 \frac{\text{g PO}_4}{\text{gP}}$$

$$= 28.7 \text{ mg/l PO}_4$$

Total phosphorus concentration in wastewater (U.S. 1966)

$$= 42.2 \text{ mg/l PO}_4$$

Table IX shows phosphorus measurements on wastewater reported by several investigators. It represents by no means a complete summary of published data, but serves to illustrate that actual measurements are in fact around the above calculated figure.

The calculation of a concentration range of phosphorus in surface waters, similar to the above calculation for wastewater, is an impossible task. This is due to the large variability of flow and concentration in the input from surface drainage of uncultivated and agricultural land, and from wastewater, and the changes occurring during the phosphorus cycle in water bodies. A considerable number of phosphorus measurements on lakes and rivers are available in the literature. Some of these are reported in Table X for lakes and Table XI for rivers. The figures quoted are in the authors units, and converted to µg/l PO_4. Comparison of data is almost impossible due to the aforementioned reasons. However some general comments can be made:

1. Great Lakes waters have a low phosphorus concentration, Lake Erie and Ontario being highest. The range of total phosphorus is about 15 to 200 µg/l PO_4. Seasonal and depth variations are important.

2. Smaller lakes and rivers tend to have higher phosphorus concentrations, with large variations possible depending on the nature of land use in the watershed. The range of total phosphorus may be from 20 to 5000 µg/l PO_4 and higher.

3. Large seasonal differences in concentration of phosphorus occur in rivers. Owen and Johnson (O-3) reported that in three agricultural southern Ontario watersheds from 73 to 80 percent of the annual yield of phosphorus was discharged during spring runoff in February to April. Curl (C-15) found that the mean concentration of phosphorus in four Ohio streams entering western Lake Erie was five times greater in March than it was in August. Shannon (S-12) found the same trend in a Wisconsin stream.

4. The concentration of phosphorus in surface waters is increasing due to increased use of fertilizers and detergents. However, concentrations will remain relatively low due to the precipitation of phosphorus to the bottom

of lakes as part of the overall phosphorus cycle.

5. Concentration of condensed phosphates in lakes is low except near sewage treatment plant outlets. In rivers it may be considerably higher. Morgan and Englebrecht (M-12) found a mean value of 350 μg/l PO_4 for several rivers in Illinois.

II-3 CONDENSED PHOSPHATES

II-3.1 PROBLEMS DUE TO CONDENSED PHOSPHATES IN WATER

The previous discussion has shown that the condensed phosphates contained in detergents are an important source of phosphorus in wastewater. Finstein and Hunter (F-3) reported that about half the condensed phosphate hydrolyzed to orthophosphate in a biological waste treatment plant, and that in the plant studied, from 5 to 40 percent of the total phosphorus leaving the plant remained in the condensed form. Several studies on the concentration of condensed phosphates in surface waters have been carried out. They have been discussed in Chapter II-2. The conclusion can be made that at least in certain surface waters, relatively close to sewage treatment plant effluents, the concentration of condensed phosphates may be high enough to cause interferences in water treatment. In many surface waters dilution and hydrolysis reduce the concentration of condensed phosphates to such levels that there would be no problems caused directly by the presence of condensed phosphates.

The problems caused by the addition of condensed phosphates to water can thus be discussed under two groupings:

a) Interferences with water and wastewater treatment caused by the presence of condensed phosphates.

b) The eutrophication problem caused by increased phosphorus available to plants and organisms, either as condensed phosphates directly or after hydrolysis to orthophosphate.

(a) INTERFERENCE WITH WATER AND WASTEWATER TREATMENT

Several studies have shown that condensed phosphates, if present in high enough concentrations, interfere with coagulation and sedimentation in water treatment because of their deflocculating properties. The recent Task Group report of the American Water Works Association (A-4) summarized the findings of several workers, such as

Smith, Cohen and Walter (S-17)
Cohen, Rourke and Woodward (C-10)
Morgan and Englebrecht (M-13)
Howells and Sawyer (H-12)

> "The studies have shown that both pyrophosphate and triphosphate decreased the efficiency of turbidity removal. Orthophosphate levels, however, up to 0.5 mg/l P showed no interference. The reduction in efficiency produced by pyrophosphate or triphosphate ranged from 0.1 - 15 percent at the 0.2 mg/l P level, and 0.6 - 20 percent at the 0.4 mg/l P level. Severe interferences with coagulation are not to be expected from the condensed phosphorus levels typically found in surface waters."

The conclusion can be drawn that while there may well be serious water treatment problems for certain local condition, they are not of great significance overall.

The removal of phosphorus from wastewaters to reduce eutrophication of receiving waters recently became an important aspect of wastewater treatment. Numerous studies have been made on which processes could economically be used to achieve desired phosphorus reductions. Barth and Ettinger (B-4) outlined the approaches taken by various investigators (Fig. 4).

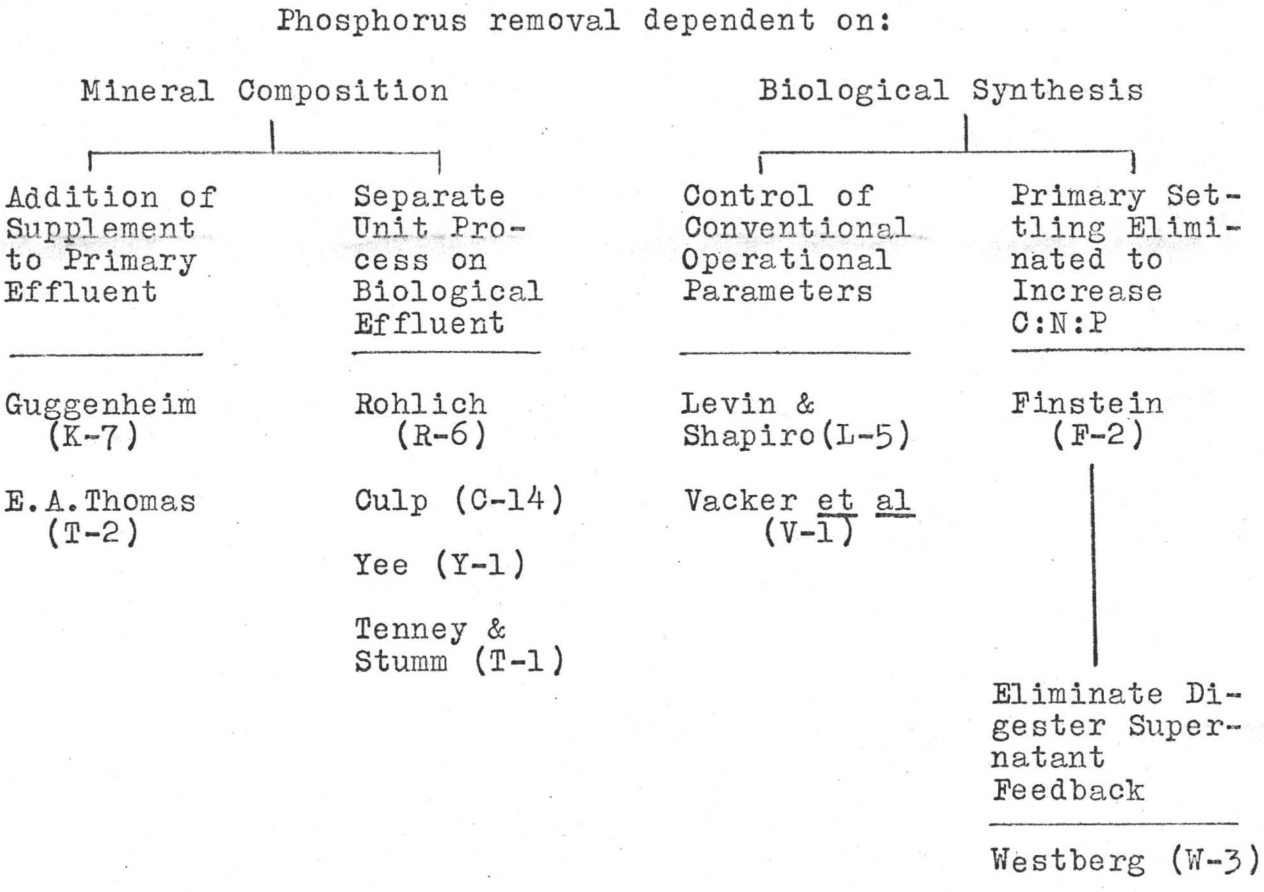


FIGURE 4. PHOSPHORUS REMOVAL BY WASTEWATER TREATMENT
(excluding lagoons and percolation)
(After Barth and Ettinger (B-4))

A recent editorial article in Environmental Science and Technology (A-8) gives costs of phosphate removal for eleven plants in the United States. For a reduction of 60 to 95 percent costs varied from 1 to 10 cents per 1000 gal. of wastewater treated.

For many of these studies the phosphorus compound under investigation was orthophosphate. Sawyer (S-6) has shown that the condensed phosphates may not be as readily precipitated as orthophosphate in wastewater. Kehren (K-6) and Klotter (K-11) reported that for the complete precipitation of phosphorus it was necessary to know not only the total amount of phosphorus but also the type of phosphorus compound present. Orthophosphate required 300, pyrophosphate and tripolyphosphate 500, and Graham salt 400 percent excess aluminum sulfate for 90 percent precipitation of the phosphorus present as P_2O_5. Hurwitz et al (H-17) reported on phosphorus removal in Chicago treatment plants and found that orthophosphate was more difficult to remove than other forms of phosphate. Yee (Y-1) removed ortho- and condensed phosphates by adsorption on activated alumina columns. With this process removal of condensed phosphates was easier than for orthophosphate. Finstein and Hunter (F-3) have shown that in settled sewage approximately half the phosphorus was in the condensed form. The extent of hydrolysis in aerobic biological treatment units was about 50 percent.

It is apparent that research on phosphorus removal should take into account that a considerable amount of phosphorus in wastewater is in the condensed form. The presently proposed methods of phosphorus removal may not achieve the efficiency reported for orthophosphate when large amounts of condensed phosphate are present. The need for studies on the rate of hydrolysis of condensed phosphates in wastewater is thus very real.

(b) THE EUTROPHICATION PROBLEM

The eutrophication problem and its relation to phosphorus has been discussed in Chapter II-1. Condensed phosphates in wastewater, whether in the condensed form or hydrolyzed to orthophosphate, are a prime source of supply of phosphorus and are therefore major contributors to the problem. The question of the availability of condensed phosphates to aquatic plants and organism will be discussed in detail in the next section. Studies on the rate of hydrolysis of condensed phosphates in natural waters are necessary to establish how long and how much of the amount of condensed phosphates leaving the wastewater treatment plants will be present in the natural water bodies.

II-3.2 AVAILABILITY OF CONDENSED PHOSPHATES TO AQUATIC ORGANISM AND PLANTS

Katchman (K-4) has written two chapters in Van Wazer's (V-2) comprehensive work on phosphorus. They deal with "Phosphates in Life Processes" and "Phosphates in Biological

Synthesis".

> "The question of the biological availability of various phosphorus-containing materials has received much attention. Generally speaking, it has been found that soluble orthophosphates are readily available to all forms of life and that phosphorus in a form other than phosphate is not immediately available to all forms of life. Some forms of life are unable to assimilate condensed phosphates; however, in the long range picture, this is no problem since all the condensed phosphates finally hydrolyze to the orthophosphate form. The soluble orthophosphate is taken up by plants and micro-organism probably through a mechanism of coupled exergonic phosphorylation reactions, which are assumed to overcome the unfavourable concentration gradient that exists between the soil or water and the living cell."

The literature contains a number of articles that indicate that phosphorus may be available to plants and microorganisms in forms other than orthophosphate. Abbott (A-2) in a study on Lake Houston, Texas, reported that planktonic algae were deriving their nutritive phosphorus from complex polyphosphates or organic phosphorus compounds without the aid of a dissolved phosphate equivalent intermediate stage. Sutton and Larsen (S-22) in a series of experiments in soil and water culture investigated the value of pyrophosphate as a plant nutrient. They found that in soils of high biological activity, pyrophosphate will not persist long enough for differences between ortho- and pyrophosphates to effect phosphorus uptake by plants and crop growth. In soils of low biological activity pyrophosphate persisted, and the phosphorus uptake recorded was lower than for orthophosphate. Water-culture experiments showed phosphorus uptake from pyrophosphate to be less by a factor of 2.4 than from orthophosphate.

Clesceri (C-6) carried out algal culture experiments using ortho-, pyro- or tripolyphosphate as the only phosphorus source. The best growth of algal occurred when the source was orthophosphate. The growth attained by the cultures utilizing pyro- or tripolyphosphate was about one half of the growth attained by the culture utilizing orthophosphate. Eppley (E-4) studied the ability of algal cells to utilize polyphosphates as a source of phosphorus. He postulated two mechanisms: 1) uptake of intact polyphosphate and its intracellular assimilation into phosphorylated metabolic intermediates, or 2) hydrolysis of polyphosphate at the cell surface and subsequent uptake and assimilation of orthophosphate. Results of his study favoured the second mechanism. He indicated higher rates of phosphate uptake from pyrophosphate and tripolyphosphate than from orthophosphate. Keck and Stitch (K-5) reported the widespread occurrence of polyphosphate in lower plants. P-O-P granules were cytochemically detected in algae, slime molds and mosses. A systematic survey was given of lower plants in which the occurrence of P-O-P had been demonstrated with their and previous studies. Within the cell P-O-P granules were observed to be present in the cytoplasm, cytoplasmic vacuoles and in the chloroplast of different algae. A possible in situ synthesis of P-O-P in chloroplasts from phosphorylated intermediates of the photosynthetic process is suggested. Chu (C-5) carried out studies on the utilization of ortho- and pyrophosphate and phytin, an organic phosphorus compound, by organisms cultured in seawater. He found that pyrophosphate could not be utilized as a source of phosphorus as effectively as orthophosphate, and phytin was about equally effective as orthophosphate. Mackereth (M-4) stated that organic phosphorus cannot be used directly by the cells as a phosphorus source. Rodhe (R-5) reported the direct incorporation of organic phosphorus by algae. Maloney (M-5) studied the effect of synthetic detergents on Chlorella pyrenoidosa, a unicellular green algae. He found that the sodium triphosphate ingredient was responsible for the increased growth. With phosphorus starved cells, only 0.05 mg/l of detergent phosphorus caused apparent growth, and at a concentration above 0.1 mg/l, algal growth was exponential. He concluded that algae are either capable of utilizing sodium triphosphate directly for growth or more likely, possess the necessary extracellular enzymes to accelerate the hydrolytic breakdown of sodium triphosphate. Davis and Wilcomb (D-1) in a study on the assimilation of condensed phosphates at a sewage level concentration range by green algae found that comparatively little of the total phosphorus was taken out of the medium, that there was an apparent preference for orthophosphate, and that in all probability, the presence of the condensed forms had an inhibitory effect on the uptake. All the species tested were shown to return some condensed phosphates to the aqueous environment during their growth cycles.

If a conclusion can be made from the somewhat conflicting reports it is that orthophosphates are the prime source of phosphorus for plants and microorganism, but in the absence of orthophosphate, other forms such as condensed phosphates and organic phosphorus compounds may also be utilized by some at a generally lower rate of growth, and with them the rate of hydrolysis is increased due to extra-cellular enzymatic activity.

II-3.3 HYDROLYSIS OF CONDENSED PHOSPHATES

Condensed phosphates in aqueous solution hydrolyze to orthophosphate (OP), the uncondensed form. Since sodium tripolyphosphate (TPP) and sodium pyrophosphate (PP) are the condensed phosphates of major importance in the detergent industry further discussion will be restricted to these compounds only. The following equations show the hydrolysis reactions.

Sodium tripolyphosphate: $Na_5 P_3 O_{10}$

$$Na_5P_3O_{10} + H_2O \xrightarrow{k_1} Na_3HP_2O_7 + Na_2HPO_4$$

and

$$Na_3HP_2O_7 + H_2O \xrightarrow{k_2} Na_2HPO_4 + NaH_2PO_4$$

Sodium pyrophosphate: $Na_4P_2O_7$

$$Na_4P_2O_7 + H_2O \xrightarrow{k_2} 2Na_2HPO_4$$

Sodium tripolyphosphate thus hydrolyzes in a series reaction to yield first one pyro- and one orthophosphate. The pyrophosphate further hydrolyzes to two orthophosphates, giving a total of three orthophosphate ions from one tripolyphosphate ion. Tripolyphosphate and pyrophosphate hydrolyze independently of each other when they are mixed. This statement is supported by several workers, among them Crowther and Westman (C-12) and Van Wazer, Griffith and McCullough (V-5). Under identical experimental conditions the k_2 values in the two reactions will therefore be the same. The inability to measure tripolyphosphate, pyrophosphate and orthophosphate separately in a mixture necessitated several workers to represent the hydrolysis of tripolyphosphate as follows:

$$\text{TPP} \xrightarrow{\text{k avg.}} 3\ \text{OP}$$

The samples were analysed for total phosphorus and orthophosphate. The sum of tripoly- and pyrophosphate was obtained as the difference.

For purposes of comparison the literature data will be divided on the basis of the aqueous medium used into studies on distilled water, surface water, and wastewater and algal cultures.

DISTILLED WATER STUDIES

Numerous studies have been carried out over the past one hundred years on this subject. Wide variation in experimental conditions were employed. A summary of the most pertinent work of the more recent past is given in Table XII for tripolyphosphate and Table XIII for pyrophosphate.

The experimental conditions and the units employed vary widely.

Temperature range: 4° - $90^\circ C$

pH range : 0.7 - 12

Initial Concentration of condensed phosphate : 1.5 - 77,000 mg/l PO_4

Most workers report the rate of hydrolysis as a first-order response, and give k_1 or $k_{avg.}$ (TPP), values and k_2 (PP) values in units of min^{-1}, hrs^{-1} or $days^{-1}$, or report half-life. Two workers, Quimby (Q-2) and Shannon (S-12), report a zero-order response. However, Quimby (Q-2) stated that he ignored the effect of change in pH, which had fallen to about 7.5 from original 10.0 by the end of the first day. In the detailed analysis of literature data in Chapter III, it is shown that if the pH effect is taken into account, Quimby's data check in well with the rest of the worker's first-order k_1-values. Shannon (S-12) reported his rate data as mg P/l-500 hrs. This implies a zero-order response, without actually being stated as such in his work. The experimental data in fact show some variation from the linear response. The rates of hydrolysis were computed from the initial and final concentrations of condensed phosphate assuming linearity over the duration of each study. Shannon's work was the most dilute solution, 0.5 mg/l P.

SURFACE WATER AND WASTEWATER OR ALGAL CULTURES STUDIES

Few studies have been made on the rates of hydrolysis of condensed phosphates in natural surface waters, wastewaters or algal cultures. The pertinent literature is summarized in Tables XIV and XV.

The variations in temperature, pH and concentration are not as wide as in the distilled water studies. The temperature range of 4°C to 35°C is representative of seasonal variations. The pH values are those of the natural water environment and vary from 6.1 to 8.6, with two workers not reporting pH values. The initial concentration of condensed phosphates employed is representative of wastewater, but generally too high to be representative for surface waters. With the exception of Karl-Kroupa (K-3) none of the investigators were able to employ differential analysis of condensed phosphates. Karl-Kroupa used paper chromatography in her work to measure ortho-, pyro- and tripolyphosphate separately.

The presence of organisms in surface water, wastewater or algal cultures effectively increases the rate of hydrolysis of condensed phosphates. The variation in experimental conditions such as

- source of sample
- sterile or nonsterile sample
- filtered or nonfiltered sample
- pH
- temperature
- lighting condition
- aeration condition
- addition of food (glucose)

will account for variations in the reported rates.

A direct comparison of the reported rates by the workers stated in Table XIV and XV is thus not possible. The effect of the environmental factors on the rate of hydrolysis as reported in the literature is discussed in the next section in general form. In Chapter III the quantitative effect of temperature, pH, concentration and enzymatic activity is evaluated from the literature data.

These relationships are then used to recalculate rates at a standard temperature of 20°C and a standard pH of 7 and standard units to allow direct comparison.

TABLE XII: HYDROLYSIS STUDIES ON TRIPOLYPHOSPHATE (TPP) IN DISTILLED WATER

AUTHOR	REFERENCE NO.	TEMPERATURE °C	pH	INITIAL CONCENTRATION	RATE DATA AS	REMARKS
Karl-Kroupa et al	K-3	24	6.9-6.1	5.5 mg/l P	k_1 as $t_{\frac{1}{2}}$* in hrs.	Sterile Distilled reports 1st order response
Friess	F-5	40-50	0.8-1.0	.0219 M	k_1 in Sec^{-1}	reports 1st order response
Van Wazer, Griffith and McCullough	V-5	60, 90	4, 7, 10	1% sodium tri.	k_1 in hrs^{-1}	reports 1st order response
Smith	S-16	65.5	1.4,3.0,4.4,4,7,5.0,5.3	0.05 at. wht. of P/liter	k_1 in min^{-1}	reports 1st order response
Shannon	S-12 S-13	20, 4	6.3	~0.5 mg/l P	$k_{avg.}$ as mg P/l-500 hrs.	reports data as 0-order response
Quimby	Q-2	25-28, 82	10.0 initially, but was not kept constant	0.1-10 g/100 ml as $Na_5 P_3 O_{10}$	k_1 as % $Na_5 P_3 O_{10}$/day	Reports 0-order response
Green	G-6	65.5 87.8	5, 7, 9	50,5 mg/l PO_4	$k_{avg.}$ in hrs^{-1}	Reports 1st order response, but indicates variations from this at lower concentrations
Crowther and Westman	C-12	65.5	2,3,5,9.3, 12	0.0951 g-moles P/l 0.190 "	k_1 in min^{-1}	reports 1st order response, but indicates variations from this at lower concentrations
Van Wazer, Griffith and McCullough	V-3	90	7	1% as PO_4	k_1 in hr^{-1}	reports 1st order response

* $t_{\frac{1}{2}}$ means halflife

TABLE XIII: HYDROLYSIS STUDIES ON PYROPHOSPHATE (PP) IN DISTILLED WATER

AUTHOR	REFERENCE NO.	TEMPERATURE °C	pH	INITIAL CONCENTRATION	RATE DATA AS	REMARKS
Campbell and Kilpatrick	C-1	49.83, 59.87 and 69.40	0.7,1.1, 1.3 calc. from H+ conc.	1x10^{-5} to 2x10^{-4} moles P_2P_7/liter	k_2 in hr^{-1}	reports 1st order response. Large amount of data.
Friess	F-5	40-50	0.8-1.0	0.0232 M	k_2 in sec^{-1}	reports 1st order response
Van Wazer, Griffith and McCullough	V-5	60	1, 4	1% sodium pyro	k_2 in hr^{-1}	reports 1st order response
Smith	S-16	65.5	2.8, 4.9, 5.0	0.05 at wht. of P/liter	k_2 in min^{-1}	reports 1st order response
Shannon	S-12 S-13	20, 4	6.3	0.454 and 0.704 mg/l P	k_2 as mg P/l-500hrs	reports data as 0-order response
Green	G-6	65.5 87.8	5, 7, 9	50 mg/l PO_4 5 mg/l PO_4	k_2 in hr^{-1}	reports data as 1st order response, but indicates variation from this at lower concentrations
Crowther and Westman	C-12	65.5	2,3,6,9.3 10.9	0.082-0.245 g-moles P/l	k_2 in min^{-1}	reports data as 1st order response, but indicates possibility of variation from this at lower concentrations.

TABLE XIV: HYDROLYSIS STUDIES ON TRIPOLYPHOSPHATE (TPP) OR PYROPHOSPHATE (PP) IN NATURAL WATERS

AUTHOR	REFERENCE NO.	TYPE OF SAMPLE	TPP OR PP ADDED	TEMP. °C	pH	INITIAL CONC.OF ADDED COND.PH.	RATE DATA AS	REMARKS
Clesceri	C-6 C-8 C-9	Lake Mendota (sterile and nonsterile)	TPP	23	8.3	~0.5 mg/l P	In graphical form for nonsterile lakewater. As 1st order $k_{avg.}$ for sterile lakewater. 1st order k_1 calculated from k_2 and $k_{avg.}$	Cont. aeration and lighting
"	"	"	PP	23	8.3	"	In graphical form for nonsterile lakewater. As 1st order k_2 for sterile lakewater.	
Englebrecht and Morgan	E-3	Illinois River and Reservoir Water Samples	TPP and PP	29	7.3-8.6	2.2-9.16 mg/l P_2O_5	Halflife in days (ie 1st order response) No differential analysis	Several pretreatment (filter, unfiltered) and storage (quiescent, semiquiescent, turbulent) conditions. No information on lighting condition
Smith, Cohen and Walton	S-17	Ohio River and Local Stream	TPP and PP	5,20, 35	7.5, 8.1	20 mg/l PO_4	Halflife in days (ie 1st order response) No differential analysis	Settled, unfiltered samples. No information on aeration or lighting condition.
Shannon	S-12 S-13	Lake Mendota, Local Stream Low Hardness Water (artificial)	TPP and PP	4, 20	8.4 7.4 8.6	~0.3-0.7 mg/l P	mg P/l-500 hrs (ie 0-order response) No differential analysis	Unfiltered samples, aerated daily for 30 minutes, incubated in dark

TABLE XV: HYDROLYSIS STUDIES ON TRIPOLYPHOSPHATE (TPP) OR PYROPHOSPHATE (PP) IN WASTEWATERS OR ALGAL CULTURES

AUTHOR	REFERENCE NO.	TYPE OF SAMPLE	TPP OR PP ADDED	TEMP. °C	pH	INITIAL CONC. OF ADDED COND. PH.	RATE DATA AS	REMARKS
Sawyer	S-6	Batch study on domestic sewage	TPP and PP	5 20	not report.	10 mg/l P	In graphical form. No differential analysis	No information on aeration or lighting conditions given. No information if filtered or unfiltered
Finstein and Hunter	F-3	Field study on activated sludge treatment plants	none added	not report.	not report.	none added	In graphical and tabular form. No differential analysis	Study on the concentration of ortho- and condensed phosphates on settled sewage and after biological waste treatment.
Finstein and Hunter	F-3	Batch study on activated sludge. Mixed Liquor	none added	20	not report.	none added	In tabular form. No differential analysis	Short term (3 hr.) study on unfiltered and filtered mixed liquor. No information on aeration or lighting conditions.
Karl-Kroupa	K-3	Batch study on pure cultures of algae, plants, fungi & bacteria	TPP	24	6.1-6.9	5.5 mg/l P	Halflifes in hrs. (ie 1st order). Differential analysis	Sterile distilled water + organisms. No aeration. No information on lighting conditions. Induction (Delay of Hydrolysis) was observed.

cont'd. ...

TABLE XV - Cont'd.

AUTHOR	REFERENCE NO.	TYPE OF SAMPLE	TPP OR PP ADDED	TEMP. °C	pH	INITIAL CONC. OF ADDED COND. PH.	RATE DATA AS	REMARKS
Clesceri	C-6 C-8 C-9	Batch study on culture of chlorella (sterile and non-sterile)	TPP and PP	23	8.4	0.5 mg/1 P	In graphical form for nonsterile cond. As $k_{avg.}$ and k_2 for sterile cond. k_1 calc. from k_2 and $k_{avg.}$ No differential condensed phosphate analysis.	Mofidied Allen and modified Gorham's algal medium was used. Continuous aeration. Continuous lighting.
Davis and Wilcomb	D-1	Batch studies on domestic waste, synthetic sewage and cultures of green algae cultures. Column studies on green algae cultures.	TPP, PP SHMP (Sodium hexa metaphosphate)	28	7.5	4-10 mg/1 P	In graphical or tabular form. No differential condensed phosphate analysis.	Day-night lighting. Main emphasis was on phosphorus uptake rates for which values are given.

II-3.4 EFFECT OF ENVIRONMENT ON THE RATE OF HYDROLYSIS

General

Van Wazer (V-2), p. 453, lists the major environmental factors that affect the rate of hydrolysis in what is believed to be their decreasing order of effectiveness.

Factor	Approximate Effect on Rate
1. Temperature	10^5-10^6 faster from freezing to boiling
2. pH	10^3-10^4 slower from strong acid to base
3. Enzymes	As much as 10^5-10^6 faster
4. Colloidal Gels	As much as 10^4-10^5 faster
5. Complexing Cations	Very many-fold faster in many cases
6. Concentration	Roughly proportional
7. Ionic Environment in the solution	Several fold change

The majority of studies on which the above information is based have been carried out on artificial, distilled water, samples. In these the effect of one factor alone is easier to study. In natural water samples it becomes more difficult to separate the effects of several factors acting at the same time. The effect of temperature, pH and concentration at high levels in distilled water samples seems to be reasonably well defined. However there is little or no information available if and how the presence of organisms in natural waters and wastewaters changes the temperature and pH dependence. Almost all distilled water studies and some of the few natural water studies have been carried out at concentrations of condensed phosphates that are higher than would occur in natural waters.

The first-order response, in which the rate is exactly proportional to concentration, found at these higher concentrations may not necessarily hold at the low concentrations characteristic of most surface waters. The presence of organisms (enzymes) has been found to greatly accelerate the rate of hydrolysis. But too few data are available to assess quantitatively the effect of the varying concentration and type of organisms present in surface waters, wastewaters and algal cultures on the rate of hydrolysis. The effect of colloidal gels, complexing cations and the ionic environment cannot be assessed conclusively even for distilled water studies as very few workers have dealt with these factors.

Van Wazer (V-2) and more recently Clesceri (C-6), have reviewed the literature on the environmental factors. The purpose of this literature review is not only to present the results and conclusions of previous workers, but to extract from their joint data a means of quantitatively reducing their results at varying experimental conditions to a standard condition for the purpose of direct comparison. This is reported in Chapter III, Analysis of Literature Data, for the factors, temperature, pH and concentration, where sufficient data were available to allow this. The effect of the presence of organisms (enzymes) can best be looked at by grouping the data into distilled water, surface water and wastewater or algal culture studies.

The effect of temperature, pH, concentration and organisms (enzymes) will therefore be discussed now only briefly and in general form with detailed references and analysis given in Chapter III. The effect of the other factors will be discussed in the present chapter.

Temperature

Van Wazer (V-2), p. 453, provides the following summary:

> "The effect of temperature is probably the best defined of all of the major factors affecting the rate. As is the usual case, the variation of the rate constant, k, with temperature can be denoted by the Arrhenius equation.
>
> $$k = Ae^{-E/RT}$$
>
> where the temperature independent term, A, is called the frequency factor, E is called the activation energy; and R and T are the gas constant and the absolute temperature, respectively."

The range of values found for the activation energy E, for the splitting of P-O-P linkages in distilled water studies is 20 to 40 kcal per mole of linkages, with an average value of 25 kcal per mole. This corresponds to a doubling of the rate for every 5°C rise in temperature.

The temperature effect in natural water and wastewater studies has been dealt with only by reporting rate data in graphical or mathematical form at various temperatures.

pH

Hydrogen ions are a strong catalyst for the hydrolysis of condensed phosphates. Van Wazer, Griffith and McCullough (V-3, V-4) and others showed that there is a logarithmic dependence of the rate on pH with a 10,000 fold decrease of the rate constant over the pH range of 0 to 14. The pH effect in natural water and wastewater is dealt with by reporting at most the pH of the experiments.

Concentration

Most workers report that the hydrolysis of pyro- and tripolyphosphates is a first-order process, so that the rate is exactly proportional to the concentration. Green (G-6), and Crowther and Westman (C-12) however suggest the possibility that in very dilute solutions of tripolyphosphate (less than 50 mg/l PO_4) the reaction may not be first-order. Shannon (S-12) presented his data on tripolyphosphate and pyrophosphate hydrolysis (at an initial concentration of approximately 1.5 mg/l PO_4) as mg P/l-500 hrs. Without saying so directly, this implies a zero-order response. Karl-Kroupa (K-3) represented the rate of hydrolysis in sterile distilled water (at a concentration of approximately 15.5 mg/l PO_4) in reporting half-life, which implies a first-order response. Clesceri (C-6) did not carry out any distilled water experiments, but presented the rate data in sterile lake water and algal cultures as first-order rate constants. There is therefore some doubt as to whether the rate at very low concentrations still follows a first-order response.

Enzymes (Organisms)

Van Wazer (V-2), p. 456, states that

> "the hydrolysis of condensed phosphates is greatly accelerated due to enzymatic activity of organisms. The action of the enzymes, phosphatase, is affected by temperature, pH and the presence of certain

> metal ions, such as magnesium. In spite of the fact that enzymatic hydrolysis of the condensed phosphates is extremely fast under optimum conditions, chance microbiological contamination of phosphate solutions will not cause unduly rapid hydrolysis if the concentration of the solutions is reasonably high (greater than 1 percent). However, Karl-Kroupa et al (K-3) report that unless special care is taken to ensure that the system is sterile, solutions of phosphates in the parts per million concentration range undergo very rapid hydrolysis because of the action of the phosphatases liberated by microorganisms."

Eppley (E-4) showed that the appearance of orthophosphate in solutions of condensed phosphates was much greater when living seaweed tissues (Porphyra perforata) were present than boiled tissue. Englebrecht and Morgan (E-3) found that the filtration of Illinois river waters definitely decreased the rate of degradation of sodium tripolyphosphate and sodium pyrophosphate. Membrane filtration was employed to produce a 'sterile' river water. They concluded that biological life exerted an effect on the rate of degradation.

Colloidal Gels

Colloidal gels such as the hydrated oxides of iron, cobalt, nickel, aluminum, and rare earths, were investigated by Bamann and Meisenheimer (B-2), in Germany in 1938. Van Wazer (V-2), p. 457 reports that this was the only investigation on the effect of colloidal gels on the rate of hydrolysis. They found that in particular lanthanum hydroxide increased the rate of hydrolysis of pyro- and tripolyphosphates, as well as other phosphates tested. The catalysis due to these oxides represents a process which occurs simultaneously and independently from any enzymatic catalysis due to the presence of organisms. However, there are insufficient data to allow a quantitative assessment of the importance of the two catalytic processes. Bamann and Novotny (B-3) did further work on the catalytic action of lanthanum and found that in neutral and alkaline media the hydrolysis of condensed phosphates is speeded up the presence of lanthanum. In strongly acidic media on the other hand, the presence of lanthanum reduced the rate of hydrolysis. The action of lanthanum salt was catalytic with no precipitation of insoluble lanthanum phosphate.

Complexing Cations and Ionic Environment in the Solution

The effect of complexing cations is difficult to separate from the effect of the ionic environment of the solution, and for this reason is discussed together. The cations that have been investigated are calcium, magnesium, sodium, tetramethylammonium and lanthanum.

The earliest report on the effect of calcium and magnesium on the rate of hydrolysis of condensed phosphates is reported by Abbot (A-1). He found that the presence of the calcium ion increased the rate, and the presence of magnesium retarded the rate of hydrolysis.

Green (G-6) investigated the effect of calcium on the rate of hydrolysis of sodium tripolyphosphate and tetrasodium pyrophosphate at pH of 5, 7 and 9 and temperatures of 150 and 190°F. With the exception of the behaviour of tetrasodium pyrophosphate at pH 5, the effect of the calcium ion was to increase the rate of hydrolysis. The magnitude of this effect increased with pH. However, the presence of magnesium, under pH conditions of 5 and 7, and temperatures of 150 and 190°F increased the stability of the condensed phosphates. Green concluded:

> "It seems reasonable to assume that in many instances the influence of calcium and magnesium on the rate reversion is related to the tendency of many of the molecularly dehydrated phosphates to form soluble complexes with these ions. When appreciable concentrations of such complexes are present, the rate of reversion would be affected by the ease with which the complex is hydrated. Unfortunately little quantitative information is available concerning the equilibria of these complexes in aqueous solutions."

Clesceri (C-6) noted a dependency of rate of hydrolysis of sodium tripolyphosphate and sodium pyrophosphate on the calcium concentration. This is shown in Table XVI.

TABLE XVI: RATE CONSTANTS FOR THE HYDROLYSIS OF PYROPHOSPHATE AND TRIPOLYPHOSPHATE AT 25°C*

Sterile Medium	Ca^{++} mg/l	Pyrophosphate	Tripolyphosphate
Lake Water	32	$6.1 \times 10^{-5} min^{-1}$	$1.4 \times 10^{-4} min^{-1}$
Modified Allen's	18	$7.4 \times 10^{-6} min^{-1}$	$5.5 \times 10^{-5} min^{-1}$
Modified Gorham's	10	$6.1 \times 10^{-6} min^{-1}$	$1.9 \times 10^{-5} min^{-1}$

* From Clesceri (C-6), p. 187.

Although not shown in this table, the pH of the three media was the same at 8.4. A decrease in the calcium concentration is accompanied by a decrease in the rate constant, although the decrease for pyrophosphate does not correspond as well as in the case of tripolyphosphate. Shannon (S-12) reported the following data, given in Table XVII. His conclusions on the calcium and magnesium effect are:

> "In this investigation the high and low hardness waters at 20°C showed no apparent calcium or hardness effect. The lack of evidence in this study for the calcium effect at 20°C could be due to the inhibitory effect on the rate of hydrolysis of condensed phosphates by magnesium reported by Green (G-6) or due to the complex character of the natural waters being studied. However, there was an increase in the rate of hydrolysis of the condensed phosphates in the low hardness waters when compared with the high hardness Black Earth Creek and Lake Mendota water samples at 4°C. This increase in the rate of hydrolysis of the condensed phosphates correlates with the increase in the Ca/Mg concentration ratio in the waters studied. The increase in rate of hydrolysis of the condensed phosphates in Black Earth Creek over the rate in Lake Mendota water at 4°C best illustrates the co-called calcium effect, since both waters have similar pH and magnesium concentrations."

As shown in Table XVII, the pH of the natural water samples varied from 7.4 to 8.6; a direct comparison without adjusting for pH variations should therefore not be made. In the absence of data on pH effect on natural waters, Shannon's rate data were adjusted to a pH 7 value according to Griffith nomograph line (G-7) given in Figures 11 and 12, Chapter III-3. The adjusted rate data are shown in Table XVII in brackets. An analysis of the adjusted data does not allow a markedly different conclusion from Shannons. Eppley (E-4) studied the hydrolysis of condensed phosphates in seawater in the presence of algal cells, porphyra perforata. He found

TABLE XVII: RATE CONSTANTS FOR THE HYDROLYSIS OF PYROPHOSPHATE AND TRIPOLYPHOSPHATE AT 20°C AND 4°C FOR VARIOUS MEDIA*

MEDIUM	Ca mg/l	Mg mg/l	Ca/Mg	pH	20°C RATE DATA in mg P/l-500 hrs.		4°C RATE DATA in mg P/l-500 hrs.	
					PP	TPP	PP	TPP
Black Earth Creek	45.4	36.8	1.23	8.6 (7.0)	0.232 (0.495)**	0.388 (0.835)	0.099 (***)	0.114 (0.199)
Lake Mendota	25	36.2	0.69	8.4 (7.0)	0.472 (0.920)	0.339 (0.655)	0.075 (***)	0.072 (0.122)
Low Hardness Water	5.65	3.62	1.56	7.4 (7.0)	0.407 (0.501)	0.500 (0.595)	0.211 (0.454)	0.224 (0.269)
Distilled Water	-	-	-	6.3 (7.0)	0.163 (0.113)	0.370 (0.260)	0.020 (0.016)	0.013 (0.010)

* Prepared from Data of Shannon (S-12)

** Rate data adjusted to pH acc. to Figures 11 and 12 and shown in brackets.

*** Outside of range of adjustment.

that both calcium and magnesium salts must be present in the medium, and that maximum rate of hydrolysis occurred at the Ca/Mg ratio found in seawater (about 0.19).

The effect of sodium and tetramethylammonium was investigated by Van Wazer, Griffith and McCullough (V-3, V-4, V-5) in distilled water medium. They found

> "that an ionic atmosphere of tetramethylammonium bromide decreases the rate of hydrolysis in both acidic and basic solutions. On the other hand, substitution of the tetramethylammonium ion by sodium ion increased the rate of hydrolysis and this increase is intensified by the presence of excess sodium. In highly acidic solutions, the hydrogen ion seems to displace the sodium ion as a catalyst, so that the addition of a sodium salt as swamping electolyte results in a diminution in reaction rate in opposition to its accelerating action under less acidic conditions. The work by Friess (F-5) and Campbell and Kilpatrick (C-1) describes this effect in more detail; but these authors do not show the accelerating action of sodium salts in mildly acidic, neutral and basic solutions, since the pertinent part of their work was done under conditions (strong acid) where the hydrogen ion was dominant."

II-4 ANALYTICAL METHODS FOR THE DETERMINATION OF PHOSPHORUS

The current edition of Standard Methods (A-3) gives methods for the various forms of phosphorus in natural and treated waters in the absence of gross pollution, but does not give a method for wastewater. Almost all of the literature deals with a variety of methods, applicable for natural waters, with few articles discussing the measurement of phosphorus in wastewater. Many investigators are using methods, developed for natural waters, for the analysis of phosphorus in wastewaters without showing that materials in sewage do not interfere.

A further difficulty in summarizing the literature lies in the fact that there is considerable confusion in the terminology of the various forms of phosphorus measured by each technique. A definition of terms as used in this work is given under IV-1. Examples of the kind of confusion encountered are discussed below.

(1) The terms "Soluble Phosphorus" and "Insoluble (or Particulate) Phosphorus" are not defined unless the type of filter and pore size are stated. A variety of filters are used, and in some articles it may not be clear which was used.

(2) The term "Total Phosphorus" means just what it says; the total amount of all forms of phosphorus in a sample. However, different methods employed differ in their ability to mineralize and bring into solution all forms of phosphorus for further colour development. Thus the amount of total phosphorus reported on an identical sample will differ for the Autoclave Method, the Ashing Method, the Sulfuric-Nitric Acid Digestion Method, the Persulfate Digestion Method, the Perchloric Acid Digestion Method, etc.

(3) The terms "Orthophosphate" and "Condensed (or Complex, Poly-) Phosphates" need some clarification. In some methods there is sufficient length of time in the analysis to convert some of the condensed phosphates to orthophosphate by contact with the acidic solution employed. For this reason, Strickland Parson (S-20) use the term

"Soluble Reactive Phosphate", to describe what is actually measured by their technique.

(4) The terms "Inorganic Phosphorus" and "Organic Phosphorus" are often unclear. Inorganic Phosphorus is often defined as the sum of orthophosphate and condensed phosphates, which are both soluble. Then "Organic Phosphorus" is defined as total soluble phosphorus minus inorganic phosphorus. However, Strickland and Parson (S-20) point out that there may well be organic, soluble and reactive material as well as inorganic, particulate, unreactive material in a sample, in which case the above definitions for inorganic and organic phosphorus are incorrect.

The desire for rapid analysis of many samples has introduced the use of automatic analysis to the field. There is considerable literature on the application of automatic analysis for phosphorus. The equipment to carry out automatic analysis was available for this work and the pertinent literature is therefore reviewed.

The literature on the differential analysis of mixtures of condensed phosphates and other phosphorus forms was reviewed in order to select the technique which, after modification, would most likely allow quantitative results at the low levels under investigation in this work.

In light of the above, the literature survey on analytical methods for phosphorus determination is discussed under the following headings:

II-4.1 APPLICATION TO WATERS IN THE ABSENCE OF GROSS POLLUTION

Manual Orthophosphate Determination
Automatic Orthophosphate Determination
Total Phosphorus Determination
Condensed Phosphate Determination
Differential Analysis of Condensed Phosphates

II-4.2 APPLICATION TO WASTEWATER

II-4.1 APPLICATION TO WATERS IN THE ABSENCE OF GROSS POLLUTION

Manual Orthophosphate Determination

The reagents for orthophosphate determination form a phosphomolybdate complex, which is subsequently reduced to a highly coloured blue compound, molybdenum blue. The methods differ in the reducing agent employed.

Standard Methods (A-3) recommend the use of the Aminonaphtolsulfonic Acid Method in the range of 0.1 to 30 mg/l PO_4 and the Stannous Chloride Method in the range of 0.05 to 3 mg/l PO_4. With extraction the range of the latter method can be extended to 0.01 mg/l PO_4. The Association of American Soap and Glycerine Producers Committee Report (A-11) recommends a modified extraction and hydrolysis procedure, which eliminates the danger of hydrolysis of the condensed phosphates during analysis because the contact time of the acid solution with the sample is reduced to 60 - 90 seconds. The extraction step also eliminates interference by other ions. The range for the method is 0.8 to 43 mg/l PO_4 without extraction and 0.067 to 0.8 mg/l PO_4 with extraction. Murphy and Riley (M-15) used ascorbic acid as a reducing agent and later (M-16) described a modified method using a single solution of sulfuric acid, ammonium molybdate, ascorbic acid and potassium antimony tartrate. This reduced the time for colour development to 10 minutes at room temperature. Beer's law was reported to be followed up to 0.76 mg/l PO_4. Edwards, Molof and Schneeman (E-1) modified this method slightly to extend the range upwards to 2.0 mg/l PO_4, as they were interested in polluted waters. Stephens (S-19) added an isobutanol extraction step, and thus extended Murphy and Riley's method to a lower limit of 0.001 mg/l PO_4. Kramer (K-9) reported the use of a somewhat altered Stephens modification of Murphy's and Riley's method, from now on referred to as "Ascorbic Acid Method with extraction", for orthophosphate measurement in Great Lakes waters. Strickland and Parson (S-20) recommend the use of the Ascorbic Acid Method, with and without extraction, for low level orthophosphate analysis, as they consider it far superior to other methods. Their book contains a very complete write-up including helpful hints and suggestions. A program of comparative tests with several different methods has been described by Jones and Spencer (J-3).

Automatic Orthophosphate Determination

To be able to handle large numbers of samples an automatic method is desirable. This can be done by the use of an instrument, called Autoanalyzer. Skeggs (S-15) described the autoanalyzer and its use in detail. Flannery and Steckel (F-4) used this instrument for samples in the range of 0.46 to 12 mg/l PO_4. Lundgren (L-9) used an automatic method for phosphate analysis in the detergent industry. As expected his range, 13.4 to 535 mg/l PO_4, was considerably higher than desired for lake water or wastewater analysis. Henricksen (H-9) used the Ascorbic Acid Method with extraction in conjunction with an autoanalyzer and reported good results on surveys of lakes and ocean waters in Norway. He was able to detect as low as 0.003 mg/l PO_4. Chan and Riley (C-2) reported that it was not possible to obtain reliable results with Henricksen's method due to the large number of tubes required with the extraction step. They used a non-extraction Ascorbic Acid Method, slightly modified, to obtain results in the range of .025 to 0.200 mg/l PO_4, employing a 15 mm flow cell with 10x range expansion. Molof, Edwards and Schneeman (M-1) used the Ascorbic Acid Method in the range of 0.3 to 6.0 mg/l PO_4 with good results. This range will be of interest for highly polluted waters only. Gales and Julian (G-2) used a stannous chloride method for stream and lake water analysis. With a 15 mm flow cell and 2x range expansion they were able to obtain good results in the range of 0.050 - 1.0 mg/l PO_4.

Total Phosphorus Determination

In order to be able to determine the total phosphorus content of a water, it is necessary to convert all of the condensed and organic phosphorus compounds to orthophosphate. Standard Methods (A-3) recommends the use of a simple acid hydrolysis with a strong sulfuric acid solution. The acidified sample is boiled for 90 minutes or autoclaved for 30 minutes, followed by neutralization and orthophosphate analysis. The Association of American Soap and Glycerine Producers Committee Report (A-11) demonstrated that the simple acid hydrolysis will hydrolyze any P-O-P bonds in organic compounds, but will not give the total phosphorus content of the sample when bonding in the organic molecule is due to P-O-C or P-C bonds. They recommend wet ashing the sample and the use of a combination of nitric and perchloric acid. Strickland and Parsons (S-20) also use perchloric acid digestion. Their method is a modification of Hansen and Robinson (H-2). Menzel and Corwin (M-9) used digestion with potassium persulfate. Gales, Julian and Kroner (G-1) proposed a simplified potassium persulfate digestion procedure. Jenkins (J-2) gives a good summary of the above methods and an evaluation of each. The persulfate digestion technique was selected by him as the one that gave the best results and had a simplicity in execution that made it especially attractive for routine analysis. Sanning (S-2) evaluated the persulfate digestion method on a number of mud and water samples. Lee, Clesceri and Fitzgerald (L-1) compared four methods: Standard Methods, Ashing Method, Perchloric Acid Digestion Method and Sulfuric-Nitric Acid Digestion Method. They obtained equally good results with the last two, and selected the Sulfuric-Nitric Acid Digestion Method over the more dangerous Perchloric Acid Digestion Method.

Lundgren (L-9) provides a flow diagram for total inorganic phosphate determination using a Technicon Autoanalyzer. The quantitative degradation of the condensed phosphates is carried out with a sulfuric acid solution, in a 95°C heating bath, followed by dialysis and colorimetric development, using ammonium molybdate and hydrazine sulfate, and measurement of the orthophosphate concentration.

Gales and Julian (G-2) adopted their manual persulfate digestion procedure, followed by automatic analysis of the resulting orthophosphate to provide a semi-automatic total phosphorus method. Grasshof (G-5) reported on the use of an automatic total phosphorus determination in seawater, by decomposition of plants and organism with ultra violet light.

Condensed Phosphate Determination

Standard Methods (A-3) obtains the condensed phosphates (or polyphosphates) by difference of the total phosphate and orthophosphate results. AASGP (A-11) recommends boiling the sample in aqueous acid for 40 minutes. Hydrolyzable P_2O_5 either from inorganic condensed phosphates or from organic compounds which have condensed phosphate groups is then obtained by subtracting the orthophosphate value from the result of the acid-boiled sample. Jenkins (J-2) adopted this same procedure. Gales and Julian (G-2) recommends the addition of one ml of a sulfuric acid solution (310 ml conc. H_2SO_4 per liter of solution). Overnight standing will hydrolyze the condensed phosphates present. Lee, Clesceri and Fitzgerald (L-1) hydrolyzed the condensed phosphates to orthophosphate by heating the mixture in an autoclave for 30 minutes at 120°C and 15 psi. Clesceri (C-6) indicated that these hydrolysis conditions were not vigorous enough to hydrolyze all of the phosphorus in organic compounds. Shannon (S-12) used the same procedure. Englebrecht and Morgan (E-3) obtained hydrolyzable P_2O_5 by boiling an acidified solution of the sample, running the colourimetric determination and subtracting the orthophosphate value. Realizing that by this procedure some hydrolysis of P-O-P bonds of organic compounds may take place, they referred to this result as "maximum inorganic condensed P_2O_5 (MIC).

Differential Analysis of Condensed Phosphate Mixtures

The Phosphorus Methods discussed up to now allow the determination of the sum of all types of condensed phosphates in a sample. In particular for work in this dissertation, they give the sum of pyrophosphate and tripolyphosphate. In order to follow the series reaction $TPP \longrightarrow PP + OP$, and $PP \longrightarrow 2\ OP$, it is desirable to be able to differentiate between the amounts of TPP and PP present.

A literature survey revealed the following possible methods to achieve this. Van Wazer (V-2) and Clesceri (C-6) give a general review of methods used. Each type of method is discussed briefly in turn.

Type of Method	References
Wet Chemical Methods	Numerous papers, refer only to B-7, B-8, B-9, D-2, V-4.
Paper Chromatography	C-11, H-1, H-11, K-2, K-3, K-7, W-6, W-7.
Paper Electrophoresis	S-3, S-4.
Thin Layer Chromatography	C-6, C-7, F-1.
Ion Exchange Chromatography	B-10, C-17, G-4, L-6, L-10, P-1, P-2, S-1, S-11.
Radioactive Tracers	C-1, C-6, Q-3, R-4, V-2.

In searching the literature the aim was to find the method which would most likely lead to successful application for the following conditions:

1. Concentrations of condensed phosphate mixtures in the range of 0.01 - 50 mg/l PO_4 (Lakewater and Wastewater).
2. Distilled water, lake water, river water and wastewater as medium.
3. Phosphate mixture confined to orthophosphate, pyrophosphate and tripolyphosphate.
4. Require the least expenditure of additional equipment.

Wet Chemical Methods

The literature on this method is numerous. Van Wazer (V-2) gives a summary of the more useful procedures. Until approximately 1950 all of the work on differential analysis of phosphate mixtures was based on wet chemical techniques.

These methods include precipitation with albumen, barium, silver, manganese, luteocobaltic chloride and a number of organic cations. One of the more recent methods is given by Bell (B-7, B-8, B-9). It is a zinc titration for the determination of pyro- and tripolyphosphate. Van Wazer et al (V-4) used pH-titration in the analysis of phosphate mixtures. Dewald (D-2) points out that several of the wet chemical techniques are not satisfactory for quantitative work on mixtures of pyro- and tripolyphosphate.

The conclusion was reached that wet chemical methods will not likely be a useful method for this work; therefore further investigation was not carried out.

Paper Chromatography

Early work on the use of paper chromatography for differential analysis of phosphate mixtures was done by Hanes and Isherwood (H-1), Westman and Scott (W-6) and Westman, Scott and Pedley (W-7). The separation of the phosphorus compounds is obtained on a chromatogram due to their different velocities of flow. The procedure consists of identifying the phosphate bands on the chromatogram, cutting out the bands, eluting the phosphates from the paper and colorimetrically determining the amount of phosphorus in each band after digestion. Crowther (C-11) using descending chromatography, identified the phosphate bands by spraying with an acid molybdate solution and heating the chromatogram to form the phosphomolybdate complex. Exposure to ultra-violet light reduces the complex to a blue colour. The samples analyzed were household detergent mixtures of high phosphorus concentrations. Karl-Kroupa (K-2) used ascending chromatography with shorter separation times, during which less hydrolysis takes place. The experimental work is claimed to be somewhat easier. Most of her work was on the analysis of detergent mixtures of high phosphorus concentrations, but some data are given on dilute solutions (10 mg/l P). This value is just below the upper range of concentration of interest in this work. Two-dimensional chromatography was used to distinguish between the family of ring and the family of chain phosphates. Karl-Kroupa et al (K-3) also used paper chromatography to study the stability of sodium tripolyphosphate in aqueous solutions containing various common living organisms. This involved the separation of the mixture in 2½ - 3½ hour runs into bands containing the ortho-, pyro-, and tripolyphosphates, followed by strip cutting and colorimetric analysis. The reliability of the method was ±0.1 mg/l P in the range of 1 to 5 mg/l P.

Hettler (H-11) gave a summary of all literature up to 1958 on the use of paper chromatography for phosphorus analysis. Koloff (K-8) reported the use of a high capacity chromatographic paper and modified solvent to make possible a more rapid and quantitative densitometric determination of pyro- and orthophosphate mixture. However, the concentration of phosphorus was quite high.

The conclusion was reached that paper chromatography may be a feasible method for this work, but that it would require the purchase of additional equipment and probably a considerable amount of time to acquire the technique to be able to extend it to lower ranges of concentration. It seemed unlikely that quantitative results at the lake water level of phosphorus concentration could be obtained.

Paper Electrophoresis

Work on this method was carried out by Sansoni and Klement (S-3, S-4) in Germany. In continuous paper chromatography, the long chain phosphates do not move from the point of application, whereas in paper electrophoresis, even the highest molecular weight chain phosphates are found to move. However, for the problem at hand in this work, this difference is of no importance.

Thin Layer Chromatography

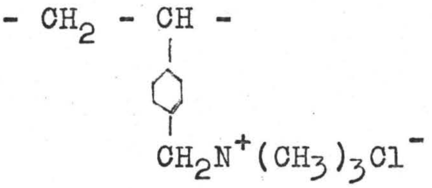
Farr (F-1) described the thin layer chromatographic technique as applied to the separation of closely-related compounds. Thin layers of powdered chromatographic adsorbents are spread on glass plates. Simpler operation, sharper separation, higher sensitivity and shorter time are claimed for thin layer chromatography over paper chromatography.

Clesceri and Lee (C-7) developed a preliminary method for the thin layer chromatographic separation of phosphates. The method was evaluated by using P-32 tagged compounds and autoradiograms of the chromatogram. Further work on this was done by Clesceri (C-6) during his doctoral research work. He used cellulose powder as an adsorbent, spread on glass plates. The solvent system used was a modification of Koloff (K-8). Distinct separation of orthophosphate and pyrophosphate was obtained. However, the molybdate spray normally used to locate the phosphate spots in paper chromatography did not yield a suitable reaction in the thin layer chromatographic method. Other sprays were tried without success. Work on thin layer chromatography was abandoned due to lack of time.

Ion Exchange Chromatography

Samuelson (S-1) in his book on "Ion Exchange Separations in Analytical Chemistry" discusses ion exchange chromatography in great detail. It can be used to separate ionic mixtures for which the ion exchange resin exhibits even only slight differences in selectivity. Two general methods used are adsorption and elution chromatography. Adsorption chromatography is used for the separation of mixtures which exhibit reasonably different selectivities for a resin, such as the separation of mono- and divalent ions. Elution chromatography applies to the fractionation of more closely related species. An elution agent is used to selectively remove several adsorbed species. Gradient elution is often used and consists of progressively increasing the concentration of the eluting agent, to avoid excessive broadening of the elution curves.

The condensed phosphates are a closely related group of anions, which can be separated by elution chromatography. The principle of the method is the adsorption of the condensed phosphates species in a mixture on an anion exchange resin followed by selective elution with a suitable medium. The anion exchange resin used is a strongly basic quartenary ammonium styrene-divinylbenzene resin of chloride form. The structural formula is



The solution containing a mixture of phosphates, for example ortho-, pyro-and tripolyphosphate, is introduced into the top of a column containing the above resin, and flows downward. The phosphate ions are retained in a band at the top, exchanging with the chloride ion of the resin. The exchange mechanism may be described by the following equation, written for the orthophosphate ion.

$$3\ (R_4N)^+\ Cl^- \ + \ PO_4^{3-} \rightleftharpoons (R_4N)_3^+\ PO_4^{3-} \ + \ 3Cl^-$$

The phosphate ions are then eluted by passing dilute potassium chloride through the column. The phosphate ions are at first partially replaced and carried downwards. In dilute solutions in general, the ions of higher charge are preferentially retained by the resin. Thus orthophosphate ion has a lower affinity for the resin than the pyro- or tripolyphosphate ion and moves downward at a faster rate. Under proper conditions complete separation of the three ions can be achieved. The column effluent can then be analyzed colorimetrically for the orthophosphate ion, after first converting the condensed phosphates to orthophosphate by a digestion step. Samples can be collected and analyzed fractionally or continuously.

Beukenkamp et al (B-10) were the first to successfully separate a mixture of condensed phosphates in this way. They developed equations for describing the elution graphs of polyprotic acids as functions of the concentration of the eluant, potassium chloride, and the pH. They also developed equations to allow the calculation of the required column height for a given separation. Lindenbaum et al (L-6) have used these equations to set up an experimental apparatus for the separation of mixtures of several condensed phosphates. It is theoretically possible to obtain complete separation of the five condensed phosphate species used in their work, with a single eluant concentration. However, such an elution would necessitate a low eluant concentration and therefore lengthy elutions. For this reason they decided to use discontinuous elution at three different concentrations of potassium chloride. The effluent from the column was sampled at frequent intervals and a manual phosphate analysis made. The result gave Gaussian curves, for each phosphate species. Grande and Beukenkamp (G-4) decided on the use of a continuous elution technique, in which the eluant concentration is increased continuously. They called this "gradient elution". This has the following advantages:

(1) One standard potassium chloride solution, instead of a series, is needed.

(2) A higher flow rate, and thus shorter elution time, is possible.

(3) Tailing of triphosphate curve is eliminated.

Schwab et al (S-11) developed equations to predict the position of the peaks in the graphs of a gradient elution, and then tested these equations with linear and exponential variation in the gradient with satisfactory results. Lundgren and Loeb (L-10) added continuous analysis of the column effluent by means of a Technicon Autoanalyzer, thus making rapid routine analysis of condensed phosphate mixtures in detergent solutions possible. Interferences were eliminated by the use of a dialyzer. Pollard et al (P-1, P-2) modified Lundgren and Loebs method so that analysis of mixtures containing lower phosphorus anions, such as thiophosphates, amido- and imidophosphates, as well as polyphosphates, is made a fully automatic procedure. Czech and Hrycyshyn (C-17) modified Lundgren and Loebs method by substituting filtration prior to chromatography for the dialyzer, using a smaller size resin, which results in faster elutions, and a steeper gradient elution system. The maximum amount of phosphorus fed to the column was 700 μg P_2O_5. The sample concentration used was 5800 mg/l P_2O_5.

Development work on differential analysis of condensed phosphates by ion exchange chromatography is reported in Chapter IV-2.5.

Radioactive Tracers

Van Wazer (V-2) reports:

> "In certain analytical procedures radioactive phosphorus has been used as a tracer. In order to do this properly, it is important that the phosphorus does not exchange between the species to be differentiated. Fortunately, this is the case for the phosphates, which do not exchange with other phosphorus compounds (phosphites, hypophosphites, etc.) in aqueous solution. Moreover, the various condensed phosphates do not exchange with each other nor do orthophosphate esters exchange with the orthophosphate ions. It is probably safe to conclude that, when radioactive phosphorus in a specific phosphate appears in another phosphorus based compound, the second compound must have been formed from the particular phosphate which was radioactive originally."

Campbell and Kilpatrick (C-1) used radioactive pyrophosphate in their studies of the kinetics of the hydrolysis of pyrophosphates. The initial concentrations of pyrophosphate were in the range of 1.9 to 38 mg/l PO_4. Quimby, Mabis and Lampe (Q-3) used an isotope dilution method for the pyrophosphate and tripolyphosphate analysis. It took 4 man-hours per sample, and results were available 1 - 3 days later. The concentrations used were higher than used in this work. Clesceri (C-6) used the method of Lowenstein (L-7) and Campbell and Kilpatrick (C-1) for the preparation of radioactive pyrophosphate and a modification of the Bell (B-7) procedure for the preparation of tripolyphosphate. He used these tagged compounds for the evaluation of a method developed by him using thin layer chromatography.

Rigler (R-3, R-4) used $P^{32}O_4$ as a tracer for radiobiological analysis of inorganic phosphorus in lake water and the determination of the phosphorus fractions and turnover time of inorganic phosphorus in lake waters.

The conclusion was reached that the use of radioactive condensed phosphate compounds in the hydrolysis studies would be possible, but that it required considerable equipment and would likely be a more time-consuming analysis than the use of Ion Exchange Chromatography.

II-4.2 APPLICATION TO WASTEWATER

In view of the importance attributed to phosphorus in the eutrophication of our surface water, it has been suggested by many that phosphorus should be removed from sewage treatment plant effluents. It is therefore most surprising that the current edition of Standard Methods (A-3) does not contain a recommended method for the analysis of phosphorus in wastewaters. Many analysts are in fact using the methods recommended for waters in the absence of gross pollution. A recent research work by Finstein and Hunter (F-3) is an example of this. They carried out a field study at several sewage treatment plants on the hydrolysis of condensed phosphates during aerobic biological treatment. No mention was made of any interferences to the analytical method employed. On the other hand, a very recent publication of Jankovic, Mitchell and Buzzell (J-1) examined this very problem and recommended the use of ascorbic acid, as a reductant. The Standard Methods (A-3), Stannous Chloride Method was shown to give lower values due to some interference. This article was received after all development on experimental methods on this work was completed, and supplied confirmation to this work.

Henricksen (H-15) reports on an automatic method for determining orthophosphate in sewage and highly polluted waters using a modified stannous chloride method. The range of the method is 0 to 6 mg/l P. Iron, copper and silica were found not to interfere below certain concentrations.

The general conclusion can be made that any of the methods for natural waters must be checked out on wastewaters for interferences before being applied on a routine basis. This is discussed in detail for the methods used in this work on wastewaters in Chapter IV-3.

III ANALYSIS OF LITERATURE DATA ON EFFECT OF ENVIRONMENT ON THE RATE OF HYDROLYSIS

The effect of the environment on the rate of hydrolysis of condensed phosphates has been discussed in general form in Chapter II-3 as part of the literature survey. This chapter will deal with the comparison of literature data on the rate of hydrolysis of sodium tripolyphosphate and sodium pyrophosphate. The experimental data were obtained by the investigators under varying environmental conditions, such as temperature, pH, concentration, aqueous medium, presence or absence of organisms, etc. The direct comparison of rates under these varying conditions is not possible. The purpose of the work reported in this chapter is to establish, where sufficient literature were available, the quantitative effect of temperature, pH, concentration, and presence of organisms, on the rate of hydrolysis of sodium tripolyphosphate and sodium pyrophosphate. These quantitative relationships can then be used to recalculate rates at a standard temperature, 20°C, and a standard pH of 7 for direct comparison of rate data. The effect of organisms can best be compared by separating the data on the basis of the aqueous medium employed into distilled water studies, surface water studies, and wastewater and algal culture studies.

III-1 THE EFFECT OF TEMPERATURE ON THE RATE OF HYDROLYSIS

Levenspiel (L-2) discusses the temperature dependence of a reaction from Arrhenius' Law, from thermodynamics, from collision theory and from transition state theory. The following is a brief summary.

"The rate expression can be written as

$$r_i = f_1 \text{ (temperature) } x\ f_2 \text{ (composition)}$$
$$= k\ x\ f_2 \text{ (composition)}$$

Empirically the reaction rate constant k has been found to be well represented by Arrhenius' Law.

$$k = k_o e^{-E/RT}$$

Comparison with the temperature dependence obtained from collision theory and transition-state theory can be made by rewriting the above equation as

$$k = (k_o' \ T^m)\ e^{-E/RT}$$

The exponent m has the following values:

Arrhenius' Law:	$m = 0$
Collision Theory:	$m = 0.5$
Transition-state Theory:	$m = 1$

However since the exponential term is so much more temperature sensitive than the T^m term, the variation of k caused by the latter, is effectively masked, and k_o is generally considered as temperature independent. The temperature dependency from a thermodynamic point can be shown as follows. For an elementary reversible reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R \qquad , \text{ with } \Delta H_r$$

the van't Hoff equation

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{RT^2}$$

states the temperature dependence of the equilibrium constant K.

As $K = k_1/k_2$, the van't Hoff equation can be rewritten as

$$\frac{d(\ln k_1)}{dT} - \frac{d(\ln k_2)}{dT} = \frac{\Delta H_r}{RT^2}$$

The fact that the difference in derivatives is equal to $\frac{\Delta H_r}{RT^2}$ suggests that each derivative alone is equal to a term of that form or

$$\frac{d(\ln k_1)}{dT} = \frac{E_1}{RT^2} \quad \text{and} \quad \frac{d(\ln k_2)}{dT} = \frac{E_2}{RT^2}$$

If the energy terms are assumed to be temperature independent, integration will yield Arrhenius' Law. E_1 and E_2 are the activation energies for the reaction rate going in the forward and backward direction. With these substitutions the van't Hoff equation reduces to

$$E_1 - E_2 = \Delta H_r \text{ "}$$

Katchman (K-4) graphically demonstrates this relationship, in the correct order of magnitude for the hydrolytic scission of P-O-P linkages in polyphosphates. This is shown in Fig. 5

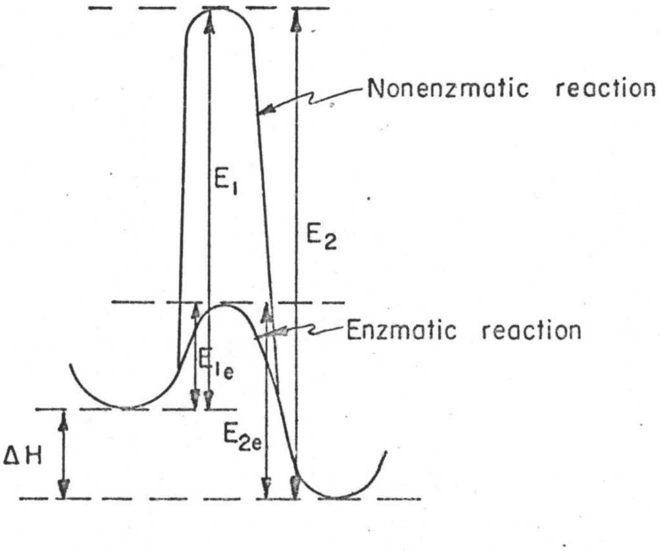


FIGURE 5: RELATIONSHIP BETWEEN ACTIVATION ENERGIES AND ENTHALPIES

(From Katchman (K-4))

The activation energies for the nonenzymatic reaction rates are denoted by E_1 and E_2, and for the enzymatic reaction rate as E_{1_e} and E_{2_e}. The values for the nonenzymatic reaction are higher than for the enzymatic reaction. Therefore, the enzymatic reaction will be less temperature sensitive than the nonenzymatic reaction. The activation energies for the hydrolysis in lake water and wastewater should therefore be considerably lower than the average value of 25 kcal/mole for the reaction in distilled water. It should be noted in Fig. 5 that the catalyst (enzyme) changes the activation energies (and also the frequency factor) but does not affect the enthalpy change, ΔH, of the reaction.

Several experimenters give activation energy values for the hydrolysis of tripolyphosphate and pyrophosphate. These experiments were all carried out in distilled water. Others report reaction rates or present their data in graphical form at different temperatures. The media were distilled water, surface water, wastewater or algal culture. From this information one may calculate activation energies. If at least three different temperatures have been used in a set of experiments, a plot of ln k versus $1/T$ should yield a straight line, whose slope is $-E/R$. When only two temperatures were employed an approximate value of the activation energy can be obtained by the following equation:

$$\frac{k_{T_1}}{k_{T_2}} = \frac{k_o\, e^{-E/RT_1}}{k_o\, e^{-E/RT_2}} \qquad \text{or} \qquad E = \frac{R\, T_1 T_2}{T_1 - T_2} \ln \frac{k_{T_1}}{k_{T_2}}$$

The units of activation energy E are calories (or kilocalories) per mole. The moles referred to are the quantities associated with the molar representation of the rate controlling step of the reaction. Numerically E can be found without knowing what this is; only when it is compared to analogous quantities from thermodynamics must the mechanisms be known and its stoichiometric representation used throughout.

A summary of some of the available data on the activation energy for distilled water samples is given in Table XVIII. Also shown are the few experiments on natural water and wastewater, where at least two temperatures were used, so that activation energies could be estimated. Explanations on how they were calculated from the rate data are given. Data of Karl-Kroupa (K-3), Clesceri (C-6) and Englebrecht and Morgan (E-3) could not be included as a single experimental temperature was used by these investigators.

A study of Table XVIII reveals the following:

	Activation Energy E, kcal/mole	
Aqueous Medium	Range	Avg. Value
Distilled Water	21.2 - 33.6	25 (from Van Wazer (V-2))
Natural Water	5.8 - 18.5	11
Wastewater	8.6 - 11.2	10

This finding is in agreement with the general statement of Katchman (K-4) that the activation energies for the enzymatic reaction, as in natural water and wastewater, are lower than in the nonenzymatic, distilled water reaction. Based on the above average values of the activation energy, a change of +10°C would increase the rate in distilled water by about 4.5 times, and in natural water or wastewater by about 1.8 times. If the practical range of temperature for surface water and wastewater in this area is taken as 4°C to 24°C, it would indicate that the rate of hydrolysis at winter conditions may be one quarter of the summer rate. However, this conclusion is probably quite erroneous, as the changes between summer and winter water are not just in temperature, but in the microbial population due to the temperature change. It is therefore quite likely that the winter rates, with lower microbial activity, are in fact smaller than predicted above.

The data on natural waters and on wastewater are too few to rely on the average activation energy shown with any degree of certainty, but they are useful in relation to the literature values for distilled water. Since the enzymatic activity in lake water may be quite different to that in wastewater, a range of values is to be expected. The concept of using Arrhenius' temperature dependence for a microbiological system is itself questionable, since it does not account for the optimum temperature for growth for different organisms. However, for the purpose of this research the following will be used, in order to be able to compare rates determined at widely differing experimental temperatures to a common temperature of 20°C:

TABLE XVIII: REPORTED OR CALCULATED ACTIVATION ENERGIES FOR THE HYDROLYSIS OF TRIPOLYPHOSPHATE AND PYROPHOSPHATE IN VARIOUS AQUEOUS MEDIA

AUTHOR	REFERENCE NO.	TYPE OF SAMPLE	TPP OR PP	TEMPERATURE °C	pH	ACTIV. ENERGY E k cal/mole	REMARKS
Van Wazer	V-2	Distilled Water	TPP or PP			~25 (reported)	Based on a summary of other authors data, for the splitting of P-O-P linkages in phosphate chains and rings. E from 20-40 k cal/mole.
Van Wazer, Griffith and McCullough	V-5	Distilled Water	TPP	60 and 90	4	27.6(reported)	Other data on 1% tetramethylammonium pyrophosphate and triphosphate showed a variation of E from 23.8 to 39.8
					7	28.0(reported)	
					10	22.8(reported)	
Campbell and Kilpatrick	C-1	Distilled Water	PP	50, 60 and 70	0.8	21.5(reported)	Other data at pH values between 0.8 and 4 lie in between the values shown
					4	27.7-30.1 (reported)	
Friess	F-5	Distilled Water	TPP	40-50	0.8-1.0	22.9	Also gives data on enthalpy, entropy and free energy changes during hydrolysis of PP and TPP.
			PP			22.8	
Green	G-6	Distilled Water	PP	87.8 and 65.5	5	28.0 (calc.)	Calculated from k_{avg}.
					7	29.6 (calc.)	
			TPP	"	5	28.6 (calc.)	
					7	30.9 (calc.)	

TABLE XVIII - Cont'd.

AUTHOR	REFERENCE NO.	TYPE OF SAMPLE	TPP OR PP	TEMPERATURE °C	pH	ACTIV. ENERGY E k cal/mole	REMARKS
Van Wazer, Griffith and McCullough	V-3	Distilled Water	TPP		1-13	approx. ~20-40 (rep.)	In graphical form as E vs. pH. Tetramethylammonium triphosphate.
Shannon	S-12	Distilled Water	PP	20 and 4	6.3	21.2 (calc.)	Calculated from rate data presented as a zero-order reaction (mg P/1-500 hrs) at 20°C and 4°C.
			TPP	"	"	33.6 (calc.)	
Smith, Cohen and Walton	S-17	Ohio River	TPP	5, 20 and 35	7.5	13.2 (calc.)	from 35°/20° — Activation energies were calculated from the reported half-lifes in days at the three temperatures reported
						14.3 "	" 35/5
						14.4 "	" 20/5
		Ohio River	PP	"		11.8 "	" 35/20
						9.1 "	" 35/5
						6.3 "	" 20/5
		Local Stream (Ohio)	PP	"		10.5 "	" 35/20
						8.3 "	" 35/5
						5.8 "	" 20/5
Shannon	S-12	Black Earth Creek	TPP	20 and 4	8.6	12.3 (calc.)	Calculated from rate data presented as a zero-order reaction (mg P/1-500 hrs) at 20° and 4°C. All data presented are based on one experiment at each condition.
		"	PP	"	8.6	8.6 "	
		"	"nat." cond. phosp.	"	7.9	8.5 "	
		Lake Mendota	TPP	"	8.4	15.6 "	
			PP	"	8.4	15.8 "	
		Low Hardness Water	TPP	"	7.4	8.1 "	
			PP	"	7.4	6.6 "	
Sawyer	S-6	Sewage	TPP	20 and 5	not started	8.6 (calc.)	Calculated from rate data presented in graphical form as conc. of orthophosphate vs. time. From this a 1st order k value was calculated at 20°C and 4°C from which activation energy was obtained.
			PP	"	"	11.2 "	

(1) Arrhenius temperature dependence.

(2) When information on activation energy has been provided or can be calculated, its value will be employed.

(3) When no information can be obtained, the average values for distilled water, natural water and wastewater shown above will be employed.

III-2 THE EFFECT OF CONCENTRATION OF CONDENSED PHOSPHATES ON THE RATE OF HYDROLYSIS

Tables XII to XV summarize the hydrolysis studies for tripolyphosphate and pyrophosphate in distilled water, natural water, wastewater and algal cultures. In these tables the initial concentration of condensed phosphates used is shown. It varies as follows:

Distilled Water	1.5 - 77,000	mg/l PO_4
Natural Water	1 - 20	mg/l PO_4
Wastewater and Algal Cultures	1.5 - 30	mg/l PO_4

Rate data are almost exclusively reported as first-order rate constants, with the exception of Shannon (S-12) and Quimby (Q-2) who report zero-order response. As the concentration of importance in natural waters lies at or below the lowest concentrations of previous investigators, and for wastewaters near the low end of the range, a detailed investigation of the literature was made to establish if the first-order response, generally held to be true at higher concentrations, still applies for low levels of concentrations.

Van Wazer (V-2) p. 457 states:

> "The hydrolysis of pyro- and tripolyphosphates appears to truly be a first-order process, so that the rate is exactly proportional to concentration."

He bases this on the work of several authors, among which are:

Van Wazer, Griffith and McCullough (V-3):

> "The degradations from tripoly- to pyro- to ortho- were found to follow a first-order law."

Crowther and Westman (C-12):

> "Our results are in agreement with Muus' theory that the hydrolysis of the pyrophosphate anion is a first-order reaction at constant hydrogen ion concentration."

In contrast to this, Van Wazer (V-2) p. 457 mentions:

> "There are reports in the literature that the rate of hydrolysis of chains increases somewhat less than in proportion to the concentration, and amazingly enough, trimetaphosphate hydrolysis is said to accelerate with decreasing concentration even though the process appears to be first-order. Presumably there are several opposing effects which masquerade under the term concentration."

The above statement is based on the work of Balareff (B-1) in 1911 and Karbe and Jander (K-1) in 1942. Both are published in German. Without providing rate data in the article, Karbe and Jander make the statement that

> "they found very dilute solutions of condensed phosphates less stable than more concentrated ones. This contradicts other literature data, according to which the rate of hydrolysis of metaphosphates in all cases increases with concentration. They felt that while there undoubtedly was a concentration influence, it is overshadowed by the more important phenomenon that in the hydrolysis of one molecule of metaphosphate several moles of orthophosphate are produced. This process is naturally favoured by increasing dilution."

Green (G-6) worked with concentrations of 50 and

5 mg/l PO_4 and various types of condensed phosphates. He was not able to analyze differentially for mixtures of condensed phosphates. Therefore the rate of formation of orthophosphate has been taken as a measure of the stability of the dehydrated phosphate. He found that in distilled water experiments, at pH of 9 and 190°F, the rate of reversion of several condensed phosphates is greater at the lower concentration of 5 mg/l PO_4. He concluded that in view of the influence of concentration on the rate, it is apparent that the reversion process under consideration cannot be regarded as strictly of first-order with respect to the dehydrated phosphate. However, a number of individual experiments were found to conform to such a rate law, and rate constants were evaluated for those which yielded sufficiently accurate data.

Crowther and Westman (C-12) concluded from their own and Green's data that

> "Possibly in very dilute solutions the reaction may not be first-order with respect to the triphosphate concentration, but it certainly appears to be so over the concentration range of 0.005 to 1.17 percent (as PO_4)."

Crowther and Westman (C-12) in another article found that the data for the hydrolysis of tetraphosphate anions do not fit the first-order equation after 85 percent of the tetraphosphate phosphorus is no longer in tetraphosphate form, suggesting that deviations from the first-order behaviour may generally be expected in the final stages of the reaction.

Quimby (Q-2) carried out distilled water experiments over a concentration range of 770 to 77,000 mg/l PO_4. He found that the concentration of condensed phosphate decreased linearly with time, ie. appears to follow a zero-order rate law. However, he did not keep pH constant, which decreased during the experiment. This amounts to a hydrogen ion catalyzed reaction, and can therefore not be used for determining the concentration effect above.

Lundgren and Loeb (L-10) state that

> "at very low concentrations tripolyphosphate appears to degrade spontaneously, possibly from the same enzymatic catalysis as reported by Karl-Kroupa _et al_ (K-3)."

Hydrolysis studies on natural water, wastewater and algal cultures have been summarized in Tables XIV and XV. The concentration of condensed phosphates used in these studies is shown in the tables, and varied from about 1 to 20 mg/l PO_4 in natural waters and from about 1.5 to 30 mg/l PO_4 in wastewater and algal culture studies. Rate data were reported in graphical form, as half-life or first-order rate constants, and in one study (Shannon (S-12)) the rate of hydrolysis was computed from the initial and final concentrations of condensed phosphate assuming linearity over the duration of the study. Shannon does not state it, but this amounts to a zero-order response. It is interesting to note that Shannon used the lowest concentration of condensed phosphates of all the investigators.

In order to be able to explore this question of first-order versus zero-order response at low concentrations of condensed phosphates further, it was decided to examine the experimental data of those authors, where the data could be obtained in reasonably complete form for further analysis.

These are:
Clesceri (C-6)
Shannon (S-12)
Karl-Kroupa *et al* (K-3)
Englebrecht and Morgan (E-3)
Sawyer (S-6)

The details of analysis of data are reported separately under each author.

Clesceri (C-6): Initial concentration of condensed phosphate = 1.5 mg/l PO_4. Work was carried out for tripolyphosphate, pyrophosphate, and mixtures of ortho-, pyro- and tripolyphosphate on Lake Mendota water, and in algal cultures of Chlorella pyrenoidosa in modified Allen and Gorham media. The effect of microorganisms was studied by carrying out experiments in sterile and nonsterile conditions. Unfortunately rate data for nonsterile conditions are given in graphical or tabular form only, whereas first-order rate constants are calculated for the sterile environment. He was not able to analyze condensed phosphate mixtures differentially, but calculated first-order rate constants k_1 for tripolyphosphate from k_{avg} (TPP + PP) and k_2 (PP) on the assumption of independence of the rate of hydrolysis of pyro- and tripolyphosphate in a mixture. No work on distilled water was done by Clesceri, but comparison to other workers data was made.

The following of Clesceri's data were selected for replotting on graphs of concentration of condensed phosphate remaining against time. Where duplicate experimental data were available, the average concentration at each time interval was plotted. For tripolyphosphate experiments the concentration of condensed phosphate remaining was obtained by subtracting the concentration of orthophosphate at any time from the initially measured concentration of tripolyphosphate.

			Data on page number of (C-6)	
Condition	Cond.Ph. added	Lake water	Algal Culture in M.Allen Med.	Algal Culture in M.Gorham Med.
Nonsterile	TPP	98	110 (Mix.Cult.)	116 (Mix.Cult.)
"	PP	98	109 "	115 "
Sterile	TPP	149	166 "	177 "
"	PP	141	163 "	174 "
Nonsterile	TPP		126 (Pure Cult.)	133 (Pure Cult.)
"	PP		125 "	132 "

Lake water data are plotted in Fig. 6.

Algal Culture - M. Allen Med. are plotted in Fig. 7.

Algal Culture - M. Gorham Med. are plotted in Fig. 8.

For tripolyphosphate studies "condensed phosphate remaining" means the sum of TPP and PP. Least square lines were fitted to all data by computer. The rate of hydrolysis, in mg $PO_4/_{1\text{-min}}$, and the correlation coefficient is shown for each set of data on each figure.

The following conclusions can be drawn:

1. Visual as well as the correlation coefficient number evidence indicates that zero-order response is well justified. A lag period of about 100 to 150 hrs. occurred with the pure

culture studies, which was omitted from the least square fit.

2. The rate of hydrolysis in nonsterile algal cultures (mixed) was about three and one-half times the rate in nonsterile lake water, indicating the more intense enzymatic activity in the algal cultures due to the much higher concentration of organisms. The rate of hydrolysis in pure algal cultures was about equal to lake water, after the initial lag period.

3. Sterile conditions reduced the rate of hydrolysis for lake water about 2 to 3 fold and about 20 to 50 fold for mixed algal cultures. If the physical and chemical environment were the same sterile lake water, algal cultures and distilled water rates should be of the same order of magnitude. This is shown by the following comparison.

Sterile Conditions:

	k, $mgPO_4$/l-min	pH
Clesceri (C-6) Lake Mendota + TPP	5.3×10^{-5}	8.3
Clesceri (C-6) Lake Mendota + PP	5.1×10^{-5}	8.3
Clesceri (C-6) Mix.Algal Cult. + TPP	1.9×10^{-5}	8.4
Clesceri (C-6) (Mod. Allen Med.) + PP	1.8×10^{-5}	8.4
Clesceri (C-6) (Mix.Algal Cult.) + TPP	8.8×10^{-6}	8.4
Clesceri (C-6) (Mod.Gorham Med.) + PP	8.6×10^{-6}	8.4
Shannon (S-12)* Distilled water + TPP	1.4×10^{-5}	8.4
Shannon (S-12)* Distilled water + PP	6.1×10^{-6}	8.4

Comparison of the rate data is reasonably good.

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*Shannon's distilled water data were at an experimental pH of 6.3 and were adjusted according to methods in III-3 to a pH of 8.4. The small difference in experimental temperature between Clesceri (23°C) and Shannon (20°C) was neglected.

Distilled Water
+ TPP: = 0.370 mg P/l-500 hrs at pH = 6.3
= $3.8\times10^{-5} mgPO_4$/l-min at pH = 6.3
= $1.4\times10^{-5} mgPO_4$/l-min at pH = 8.4

Distilled Water
+ PP: = 0.163mgP/l-500 hrs at pH = 6.3
= $1.7\times10^{-5} mgPO_4$/l-min at pH = 6.3
= $6.1\times10^{-6} mgPO_4$/l-min at pH = 8.4

Figure 6. Hydrolysis of condensed phosphates in Lake Mendota water - Data of Clesceri (C-6).

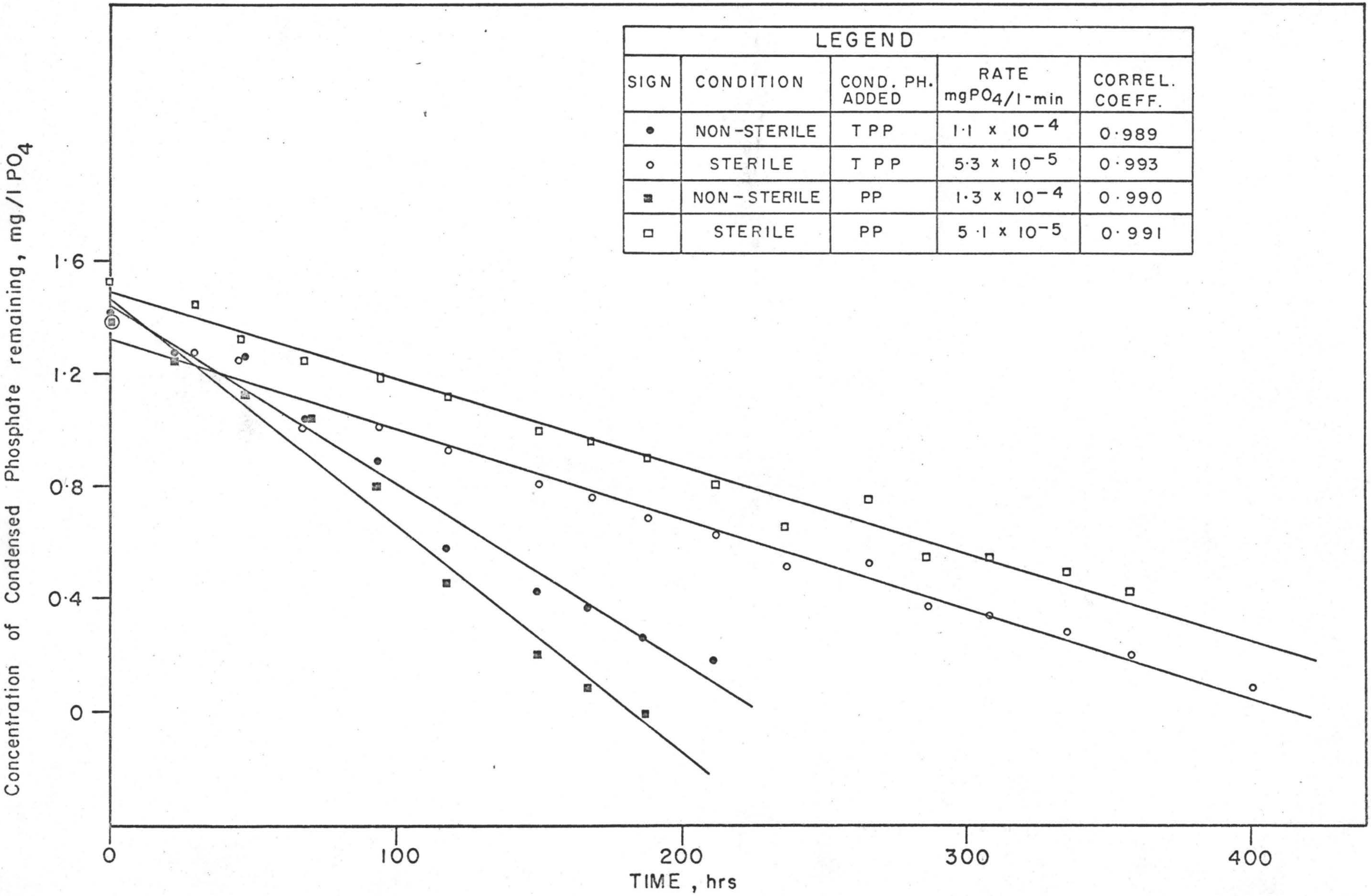
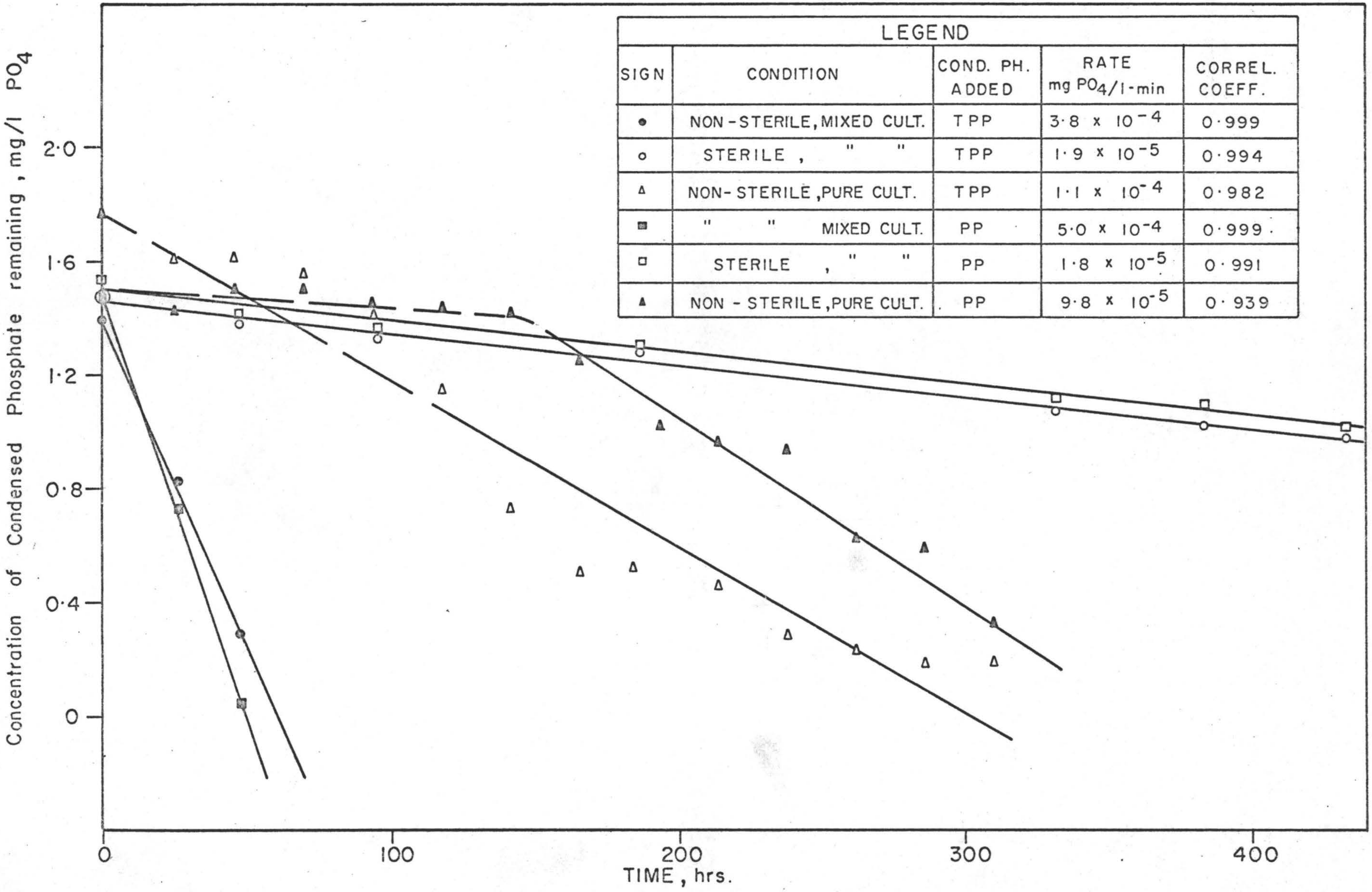


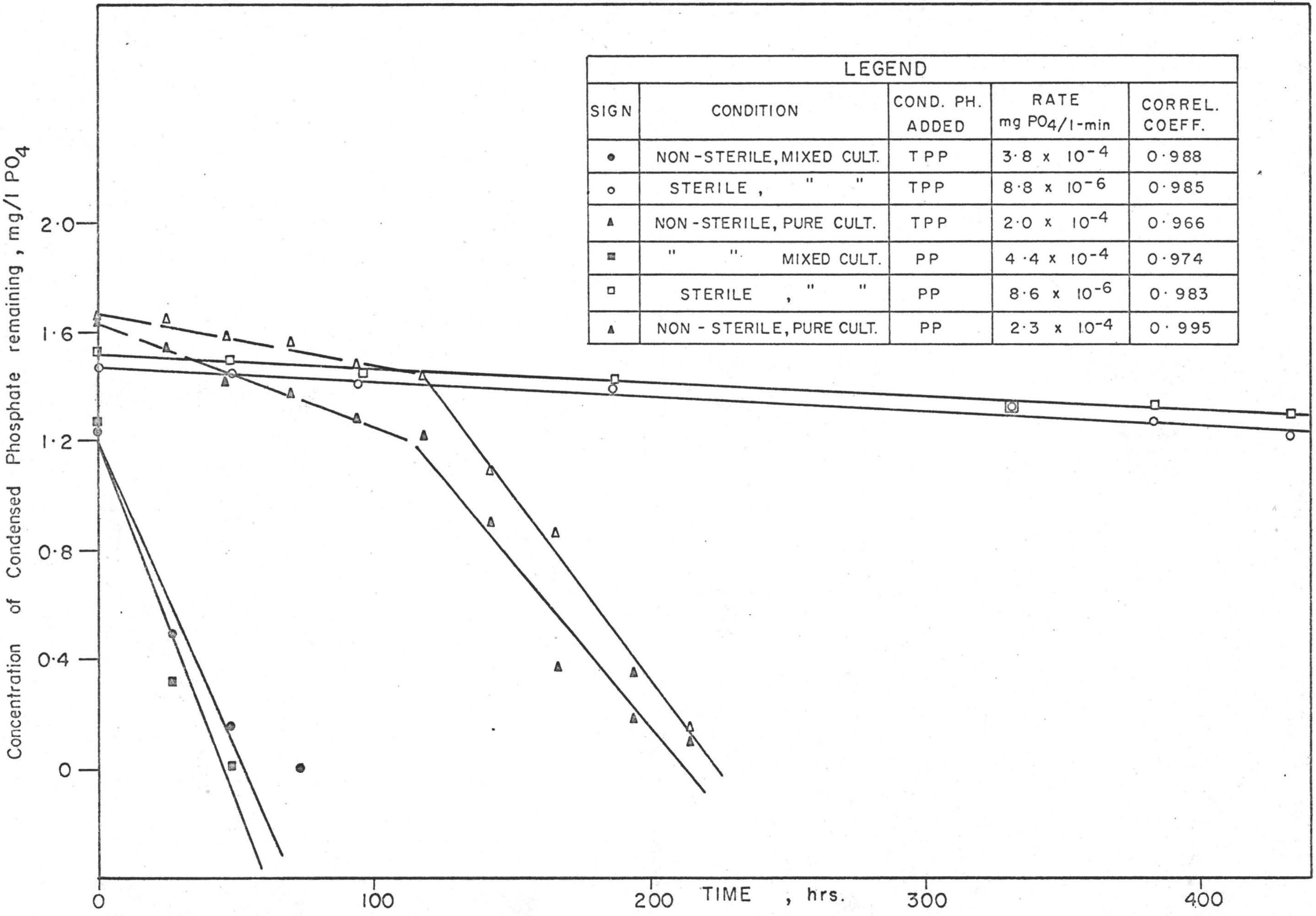
Figure 7. Hydrolysis of condensed phosphates in algal culture (Chlorella pyrenoidosa) in modified Allen Medium - Data of Clesceri (C-6).



LEGEND

SIGN	CONDITION	COND. PH. ADDED	RATE mg PO_4/l-min	CORREL. COEFF.
●	NON-STERILE, MIXED CULT.	TPP	$3 \cdot 8 \times 10^{-4}$	0·999
○	STERILE , " "	TPP	$1 \cdot 9 \times 10^{-5}$	0·994
△	NON-STERILE, PURE CULT.	TPP	$1 \cdot 1 \times 10^{-4}$	0·982
■	" " MIXED CULT.	PP	$5 \cdot 0 \times 10^{-4}$	0·999
□	STERILE , " "	PP	$1 \cdot 8 \times 10^{-5}$	0·991
▲	NON - STERILE, PURE CULT.	PP	$9 \cdot 8 \times 10^{-5}$	0·939

Figure 8. Hydrolysis of condensed phosphates in algal culture (Chlorella pyrenoidosa) in modified Gorham Medium - Data of Clesceri (C-6).



LEGEND

SIGN	CONDITION	COND. PH. ADDED	RATE mg PO_4/l-min	CORREL. COEFF.
●	NON-STERILE, MIXED CULT.	TPP	$3 \cdot 8 \times 10^{-4}$	0·988
○	STERILE, " "	TPP	$8 \cdot 8 \times 10^{-6}$	0·985
▲	NON-STERILE, PURE CULT.	TPP	$2 \cdot 0 \times 10^{-4}$	0·966
■	" " MIXED CULT.	PP	$4 \cdot 4 \times 10^{-4}$	0·974
□	STERILE, " "	PP	$8 \cdot 6 \times 10^{-6}$	0·983
▲	NON-STERILE, PURE CULT.	PP	$2 \cdot 3 \times 10^{-4}$	0·995

Shannon (S-12):

Initial conc. of condensed phosphates = 1.0-2.0mg/1 PO_4. Work was carried out for tripolyphosphate and pyrophosphate on distilled water, Lake Mendota water, Black Earth Creek water, and an artificial low hardness water. The temperature of investigations was either 20° or 4°C. All samples were non-sterile. The rates of hydrolysis given were computed from the initial and final concentrations of condensed phosphates assuming linearity over the duration of the study. The actual data are not always linear throughout, but fit a zero-order plot better than a first-order plot. All of Shannon's data were replotted on a first-order plot as part of the work of this research but are not presented. Shannon's data at 20°C are presented below and certain additions and calculations are made.

Sample	Cond.Ph. added	pH	Rate of Hydrolysis mg P/1-500 hrs	Rate of Hydrolysis mg PO_4/1-min
Distilled water	TPP	6.3	0.370	3.8×10^{-5}
Distilled water	PP	6.3	0.163	1.7×10^{-5}
Lake Mendota	TPP	8.4	0.339	3.5×10^{-5}
Lake Mendota	PP	8.4	0.472	4.8×10^{-5}
Low Hardness water	TPP	7.4	0.500	5.1×10^{-5}
Low Hardness water	PP	7.4	0.407	4.1×10^{-5}
Black Earth Creek	TPP	8.6	0.388	4.0×10^{-5}
Black Earth Creek	PP	8.6	0.232	2.4×10^{-5}

Shannon measured the pH after the addition of the condensed phosphate. He apparently did not measure it during the course of the study. From work done in this research it is reasonable to assume that at this low concentration of condensed phosphates, the pH will remain constant. Shannon compared the above rate data directly. However, in view of the fact that the pH is not the same for the various samples, such a direct comparison should not be made, without prior adjustment of the data to a common pH value.

Comparison between Clesceri and Shannon on Lake Mendota water is good.

Karl-Kroupa *et al* (K-3): Initial concentration of condensed phosphates = 16.8 mg/l PO_4.

Work was carried out for tripolyphosphate hydrolysis in sterile distilled water, and six cultures of bacteria, algae, fungi and higher plants. The temperature of the investigation was 24°C, the pH range is stated as 6.9 to 6.1. Differential analysis of the condensed phosphate mixture was carried out by paper chromatography. The rate of hydrolysis is given as the half-life in hours. An induction or lag period of from 41 to 141 hours occurred with the cultures. Rate data presented are shown below.

Organism added	Dry Weight of Organisms added mg per liter of solution	Approx. Induction period hrs.	Half Life excluding Induction Period hrs.	k_1 24°C Min^{-1}
None- Sterile Distilled water	-	-	10-20,000	$1.2\text{-}6.0 \times 10^{-7}$
Elodea	77.5	26	123	9.4×10^{-5}
Gleocapsa	1.25	55	66	1.8×10^{-4}
Vaucheria	130	26	35	3.3×10^{-4}
Ceratophyllum	159	18	59	2.0×10^{-4}
Allomyces	5	25	19	6.1×10^{-4}
Escherichia coli	.04	65	20	5.8×10^{-4}

The values of k_1 were calculated as part of this work from the given half-lifes. For each hydrolysis experiment four to six data points were presented. As some of these were during the induction period and therefore not useable for establishing the first-order rate, it was questionable how significant the first-order fit really is. Therefore all data were plotted in Fig. 9 as the logarithm of percent tripolyphosphate remaining against time.

The following conclusions can be drawn:

1. All of the many varieties of cellular material tested greatly accelerated the rate of hydrolytic breakdown of tripolyphosphate.
2. There is questionable justification from the given data to report half-lives, since this implies a first-order response, which cannot really be justified by the data. Omitting the induction period, only two data points are

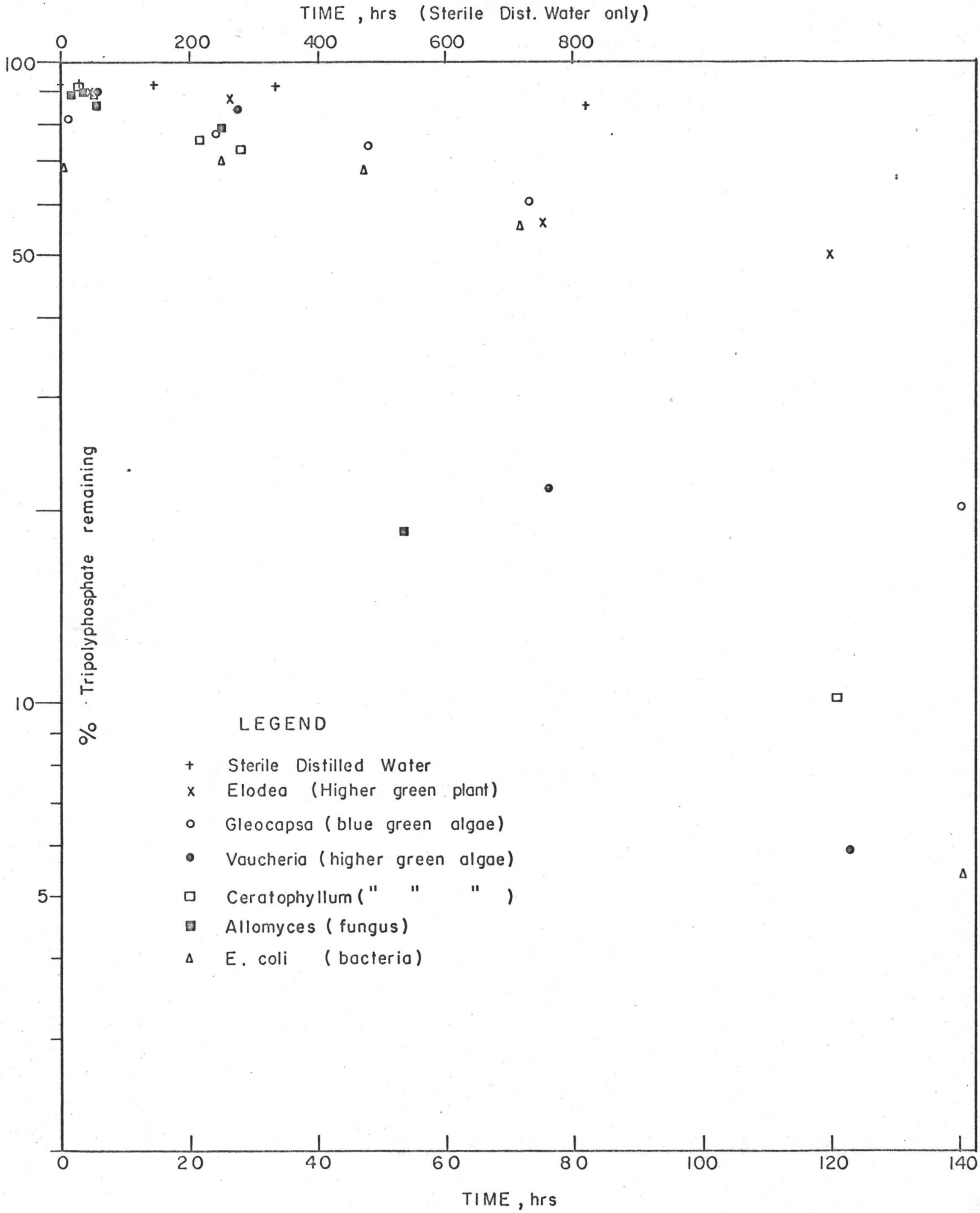


Figure 9. Hydrolysis of tripolyphosphate in various cultures - Data of Karl Kroupa *et al* (K-3).

left for four of the cultures, and three data points for two of the cultures to fit a straight line.

3. On an actual plot of the data, as in Fig. 9, it is difficult to arrive at some of the reported half-lives.
4. Many authors quote the findings of Karl-Kroupa _et al_ as an important reference. It is surprising to find that relatively few actual data were taken.
5. There seems to be no correlation between the amount of organisms added and the rate of hydrolysis. This may be because of the different phosphorus needs of the organisms tested.
6. Escherischia coli caused almost the fastest rate of hydrolysis, even though it has by far the lowest concentration of organisms. The number of cells per ml are in the same order of magnitude as they might occur in sewage. One would therefore expect the rate to be similar to a wastewater sample rate.
7. The lowest rate occurred with Elodea, a higher green plant, which has less need for phosphorus than the algae.
8. Of the three algae tested the rate varies about three-fold, but since only few data support each rate, no further conclusions can be drawn from it.
9. Comparison of the rates in distilled water between Shannon (S-12) and Karl-Kroupa (K-3) is difficult due to
   a) Difference in analytical techniques used (k_{avg} vs k_1)
   b) Difference in reporting rate data as zero- or first-order response.

Shannon (S-12): $k_{avg} = 3.8\text{x}10^{-5}$ mg PO_4/1-min

Karl-Kroupa (K-3): $k_1 = 3.6\text{x}10^{-7}\ \text{min}^{-1}$

C_A = Initial conc. of TPP = 16.8 mg PO_4/1

$\therefore (k_1 C_A) = 6.1\text{x}10^{-6}$ mg PO_4/1-min

This shows that Karl-Kroupa's rate is about six times lower than Shannons. This will be due partly to the fact that Karl-Kroupa used sterile distilled water. The rates are at least in the same order of magnitude.

10. Direct comparison of culture study rates between Karl-Kroupa (K-3) and Clesceri (C-6) is not possible because of the pH difference (8.4 vs about 6.5), and the different type and concentration of organisms used.

Englebrecht and Morgan (E-3): Initial concentration of condensed phosphates

= 2.95 to 12.3 mg/1 PO_4

Work was carried out for tripolyphosphate and pyrophosphate in Illinois river and reservoir waters at 29°C. A variety of storage and pretreatment conditions were used. The pH range of the water samples varied from 7.3 to 8.6. No information on pH measurement during the experiments is given, but it is stated that a change occurred in several of the stored samples. Differential analysis of condensed phosphate mixtures was not possible. The rate data are presented as half-life in days. For one experiment only, at a concentration of 12.3 mg/1 PO_4, a semilog plot of the logarithm of percent of condensed phosphate remaining against time is presented. The fit of straight lines, indicative of first-order response, appeared to be reasonable. No data were presented at the lower concentrations, so the first-order fit at that level could not be checked.

<u>Sawyer (S-6)</u>: Initial concentration of condensed phosphates = 30 mg/l PO_4.

Work was carried out for tripolyphosphate and pyrophosphate in domestic sewage at 20°C and 5°C. No information on the pH value is given. Differential analysis of the condensed phosphate mixture was not possible, the rate data were presented in graphical form only, as orthophosphate appearance against time. These data were replotted on a graph of logarithm of percent condensed phosphate remaining against time. This is presented in Fig. 10.

The following conclusions can be drawn:

1. The data fit a straight line much better on the semilog graph than on the original graph. Therefore a first-order response may be indicated.
2. Rate constant, as k_{avg}, were calculated as follows:

   Wastewater + TPP 20°C $k_{avg} = 1.3 \times 10^{-4}\ min^{-1}$
   Wastewater + TPP 5°C $= 5.6 \times 10^{-5}\ min^{-1}$
   Wastewater + PP 20°C $= 7.5 \times 10^{-4}\ min^{-1}$
   Wastewater + PP 5°C $= 2.5 \times 10^{-4}\ min^{-1}$

   Comparison of these rate constants at 20°C with Karl-Kroupas <u>et al</u> (K-3) culture study rate constants at 24°C

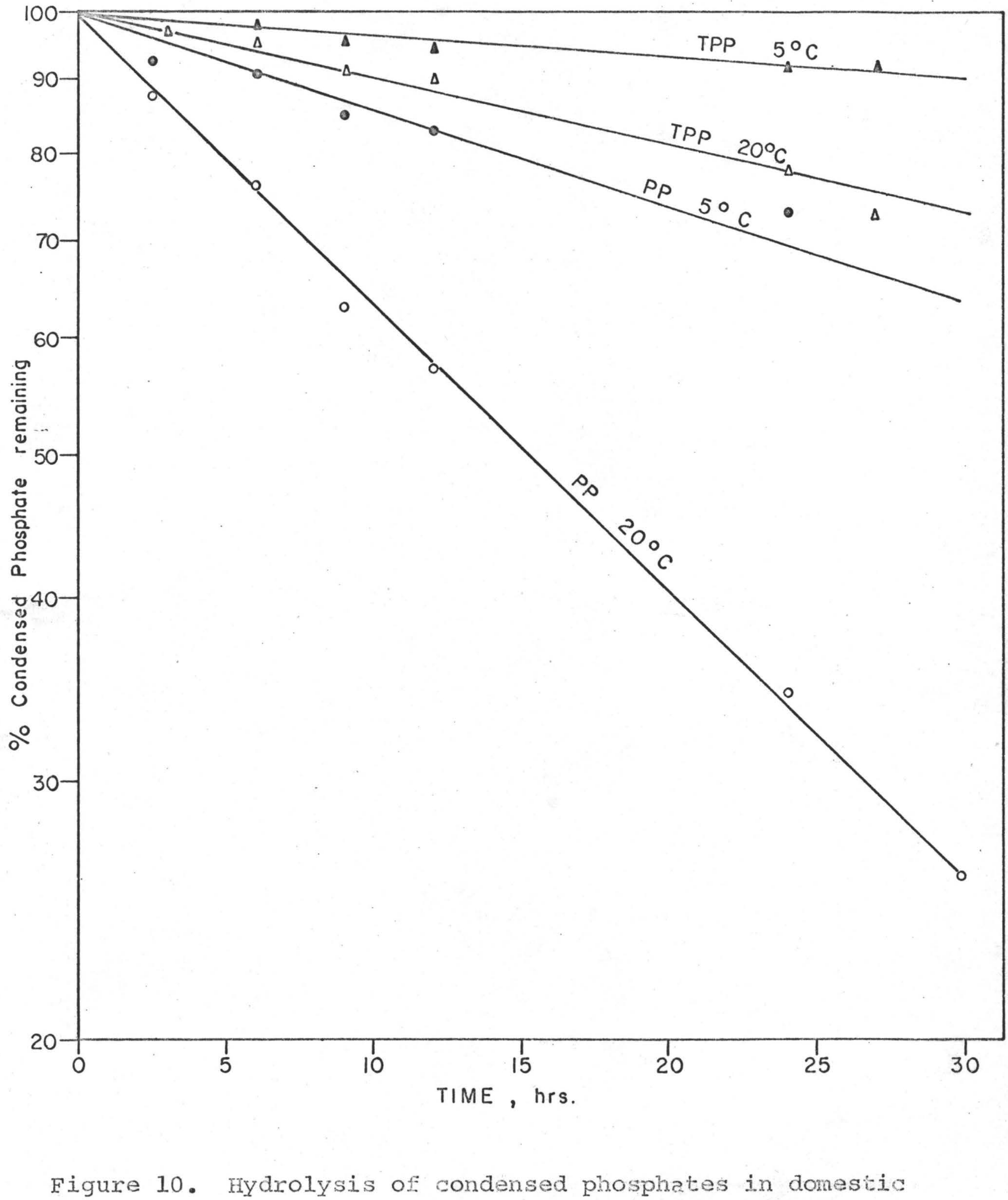


Figure 10. Hydrolysis of condensed phosphates in domestic waste water - Data of Sawyer (S-6).

is reasonable, as suggested before.

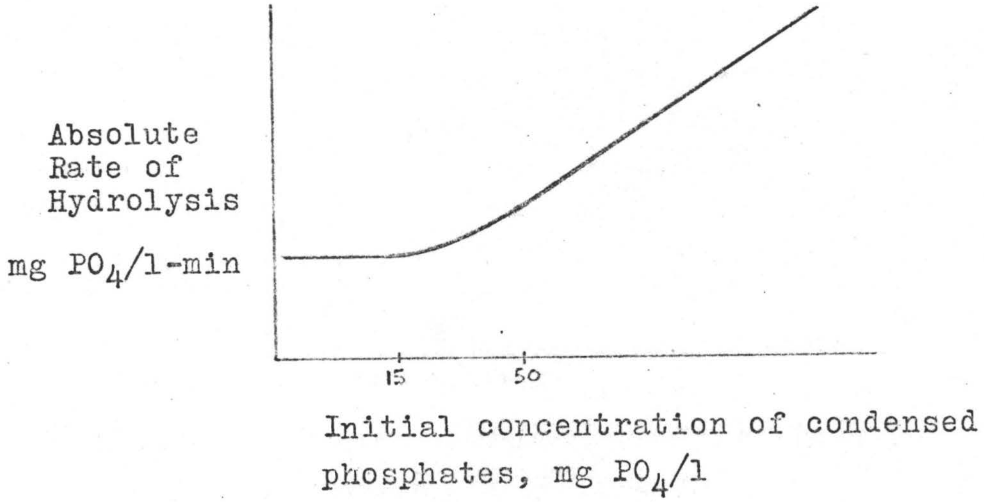
3. It is surprising that the rate of hydrolysis for pyrophosphate is 5 to 6 times as fast as for tripolyphosphate. In distilled water pyrophosphate hydrolyzes slower. In Clesceri's and Shannon's work rates were about equal for pyro- and tripolyphosphate. Davis and Wilcomb (D-1) showed that tripolyphosphate and pyrophosphate hydrolyzed at about the same rate in synthetic sewage and slower than hexametaphosphate. He did not give rate constants but stated that the rate of hydrolysis was faster than found by Sawyer (S-8).
4. Data presented by Sawyer (S-8) on the hydrolysis of tripolyphosphate in domestic sewage were analyzed in the same way as the data of (S-6) and gave rate constants comparable to the results of (S-6).

In summary of the literature survey and detailed analysis of certain low level data on the effect of concentration on the rate of hydrolysis it can be stated:

1. A first-order rate law appears to be followed for concentration of condensed phosphates higher than about 50 mg/l PO_4 in numerous distilled water studies.
2. Work of Shannon (S-12) and the work of Clesceri (C-6), after reanalysis of his data, indicates that a zero-order rate law may be followed at concentrations of about 1-2 mg/l PO_4, regardless of the medium.

3. The work of Karl-Kroupa (K-3) et al reported first-order response at concentrations of 16.8 mg/l PO_4. However, the data were shown to be insufficient to support this conclusion adequately.
4. The work of Sawyer (S-6) at concentrations of 30 mg/l PO_4 in wastewater indicates a first-order response.

If a first-order behaviour is characteristic of concentrations higher than about 15 to 50 mg/l PO_4, and zero-order behaviour at lower concentrations, then a graph of absolute rate, in mg PO_4/l-min, against initial concentration, in mg PO_4/l, should be of the following general form.



The aqueous media such as distilled water, natural water, wastewater or algal culture would be parameters of this graph. In order to be able to plot rate data on this graph it is necessary that they are adjusted to a common temperature and pH, for convenience at 20°C and pH = 7.

Temperature conversion can be carried out according to methods discussed in III-1. Variation with pH will be discussed in III-3 and has been applied in the following work.

Tables XIX and XX are summaries of calculations on hydrolysis studies on tripolyphosphate and pyrophosphate respectively. These tables have been prepared from data contained in Tables XXI and XXIII for tripolyphosphate and Tables XXII and XXIV for pyrophosphate. The rate constants for distilled water in these four tables were adjusted for pH according to Griffith's (G-7) nomograph line (see Fig. 13 and 14) to a pH of 7. River, lake, algal culture and wastewater studies varied from pH = 6.1 to pH = 8.6, relatively close to pH = 7. As shown in III-3 there is no information on the dependence of the rate constant on pH for these type of media. The choice then is to either show rates for these media at the experimental pH value, or to use the distilled water pH dependency for adjusting. Fig. 13 and 14 show that the rate constant for distilled water is about two to three times larger at pH of 6.1 then at pH of 8.6, a relatively small change compared to the increase in rate due to organisms. The decision was made to use distilled water pH dependency for other aqueous media, realizing that the actual adjustment would probably be somewhat smaller.

The data of Tables XIX and XX are plotted in Fig. 11 and 12, as rate of hydrolysis in mg PO_4/l-min against initial concentration of tripolyphosphate and pyrophosphate, in mg PO_4/l,

TABLE XIX: SUMMARY OF CALCULATIONS ON HYDROLYSIS STUDIES ON TRIPOLYPHOSPHATE (TPP) FOR RATE CONSTANTS AT 20°C AND pH = 7

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	INITIAL CONC. OF TPP C_o,mg/l PO_4	RATE CONSTANT k, at 20° and pH=7		RATE OF HYDROLYSIS AT 20°C and pH=7: =(k C_o)for first-order, = k for zero-order, mg PO_4/l-min.	REMARKS
				Zero-order: mg PO_4/l-min	First-order: min^{-1}		
Karl-Kroupa et al	K-3	Distilled (sterile)	16.8		$k_1=3.6x10^{-7}$	$6.0x10^{-6}$	
Friess	F-5	Distilled	6200		$k_1=2.6x10^{-7}$	$1.6x10^{-3}$	Average of several results.
Van Wazer, Griffith and McCullough	V-5	Distilled	5200		$k_1=2.3x10^{-7}$	$1.2x10^{-3}$	
Smith	S-16	Distilled	4700		$k_1=7.0x10^{-7}$	$3.3x10^{-3}$	
Shannon	S-12	Distilled	1.6	$k_{avg}=2.7x10^{-5}$		$2.7x10^{-5}$	No differential condensed phosphate analysis
Quimby	Q-2	Distilled	40,000		$k_1=1.8x10^{-7}$	$7.2x10^{-3}$	Rate and concentration used are at pH=7.5, and adjusted to pH=7.
Green	G-6	Distilled	50		$k_{avg}=5.2x10^{-8}$	$2.6x10^{-6}$	No differential condensed phosphate analysis.

TABLE XIX - Cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	INITIAL CONC. OF TPP C_o, mg/l PO_4	RATE CONSTANT k, AT 20° AND pH=7		RATE OF HYDROLYSIS AT 20°C and pH=7: =($k\ C_o$) for first-order, = k for zero-order, mg PO_4/l-min.	REMARKS
				Zero-order: mg PO_4/l-min	First-order: min^{-1}		
Crowther & Westman	C-12	Distilled	9000		$k_1=2.35x10^{-7}$	$2.1x10^{-3}$	
Van Wazer, Griffith & McCullough	V-3	Distilled	10,000		$k_1=5.4x10^{-7}$	$5.4x10^{-3}$	
Clesceri	C-6	L.Mendota (nonsterile)	1.53	$k_{avg}=1.3x10^{-4}$		$1.3x10^{-4}$	No differential condensed phosphate analysis. Constants based on zero-order response are used.
		L.Mendota (sterile)	"	$=4.7x10^{-5}$		$4.7x10^{-5}$	
		Algal Cult. (nonst.) (mixed) in M.Allen	"	$=6.0x10^{-4}$		$6.0x10^{-4}$	
		" (sterile)	"	$=2.1x10^{-5}$		$2.1x10^{-5}$	
		Algal Cult. (nonst.) (mixed) in M.Gorham	"	$=6.0x10^{-4}$		$6.0x10^{-4}$	
		" (sterile)	"	$=1.0x10^{-5}$		$1.0x10^{-5}$	
		Algal Cult. (nonst.) (Pure) in M.Allen	"	$=1.7x10^{-4}$		$1.7x10^{-4}$	
		"	"	$=3.1x10^{-4}$		$3.1x10^{-4}$	

TABLE XIX - Cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	INITIAL CONC. OF TPP C_o, mg/l PO_4	RATE CONSTANT k, AT 20° AND pH=7		RATE OF HYDROLYSIS AT 20°C and pH=7: $=(k\ C_o)$ for first-order, = k for zero-order, mg PO_4/l-min.	REMARKS
				Zero-order: mg PO_4/l-min	First-order: min^{-1}		
Englebrecht and Morgan	E-3	Illinois Wat. Reservoir, (Unfilt.)	2.95-12.3		$k_{avg}=2.9x10^{-5}$	$8.5x10^{-5}$ to $3.6x10^{-4}$	Since pH range of 7.3 to 8.6 was given only, the avg. value of 8.0 was used in adjusting rate constants. No differential condensed phosphate analysis.
		" (membr. filt)	"		$=1.3x10^{-5}$	$3.8x10^{-5}$ to $1.6x10^{-4}$	
		River (Unfilt.)	2.95		$=1.8x10^{-4}$	$5.3x10^{-4}$	
Smith, Cohen and Walton	S-17	Ohio River (settled)	20.0		$k_{avg}=1.0x10^{-5}$	$2.0x10^{-4}$	No differential condensed phosphate analysis.
Shannon	S-12	L.Mendota (nonsterile)	1.65	$k_{avg}=6.7x10^{-5}$		$6.7x10^{-5}$	No differential condensed phosphate analysis.
		Black Earth Creek	1.6	$=8.6x10^{-5}$		$8.6x10^{-5}$	
Sawyer	S-6	Domestic Wastewater	30.6		$k_{avg}=1.3x10^{-4}$	$4.0x10^{-3}$	No differential condensed phosphate analysis. pH of 7.0 was assumed.
Karl-Kroupa et al	K-3	Cultures of Elodea	16.8		$k_1=5.7x10^{-5}$	$9.6x10^{-4}$	Since pH range of 6.1 to 6.9 was given only, the average value of 6.5 was used in adjusting the data.
		Gleocapsa	"		$=1.1x10^{-4}$	$1.9x10^{-3}$	
		Vaucheria	"		$=2.0x10^{-4}$	$3.4x10^{-3}$	
		Ceratophyllum	"		$=1.2x10^{-4}$	$2.0x10^{-3}$	
		Allomyces	"		$=3.7x10^{-4}$	$6.2x10^{-3}$	
		Escherichia coli	"		$=3.5x10^{-4}$	$5.9x10^{-3}$	

TABLE XX: SUMMARY OF CALCULATIONS ON HYDROLYSIS STUDIES ON PYROPHOSPHATE (PP) FOR RATE CONSTANT AT 20°C AND pH = 7

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	INITIAL CONC.OF PP C_o, mg/l PO_4	RATE CONSTANT, k_2, AT 20°C and pH = 7		RATE OF HYDROLYSIS AT 20°C AND pH=7 =(k C_o) for first-order, =k for zero-order, mg PO_4/l-min	REMARKS
				Zero-order mg PO_4/l-min	First-order min^{-1}		
Campbell and Kilpatrick	C-1	Distilled	38		$5.6x10^{-8}$	$2.1x10^{-6}$	Rate constants at pH values near 1.0 cannot be adjusted to pH=7 due to unreliability of Fig.12 in this region
Friess	F-5	Distilled	6200				"
Van Wazer, Griffith & McCullough	V-5	Distilled	5200		$7.6x10^{-8}$	$4.0x10^{-4}$	
Smith	S-16	Distilled	4730		$9.3x10^{-8}$ $2.9x10^{-7}$ $3.1x10^{-7}$	$4.4x10^{-4}$ $1.4x10^{-3}$ $1.5x10^{-3}$	
Shannon	S-12	Distilled	1.39	$1.2x10^{-5}$		$1.2x10^{-5}$	
Green	G-6	Distilled	50		$7.6x10^{-8}$	$3.8x10^{-6}$	
Crowther & Westman	C-12	Distilled	7760 11650 23200		$8.0x10^{-8}$ $8.0x10^{-8}$ $9.5x10^{-8}$	$6.2x10^{-4}$ $9.3x10^{-4}$ $2.2x10^{-3}$	
Clesceri	C-6	L.Mendota (nonsterile)	1.53	$1.4x10^{-4}$		$1.4x10^{-4}$	Constants based on zero-order response are used.
		L.Mendota (sterile)	"	$4.4x10^{-5}$		$4.4x10^{-5}$	

TABLE XX - Cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	INITIAL CONC. OF PP C_o, mg/l PO_4	RATE CONSTANT, k_2, AT 20°C and pH =7		RATE OF HYDROLYSIS AT 20°C AND pH=7 =(k C_o) for first-order, =k for zero-order, mg PO_4/l-min	REMARKS
				Zero-order mg PO_4/l-min	First-order min^{-1}		
Clesceri (cont'd.)	C-6	Algal C. (Mixed) in M. Allen (nonsterile)	1.53	7.9×10^{-4}		7.9×10^{-4}	Constants based on zero-order response are used.
		" (sterile)	"	2.1×10^{-5}		2.1×10^{-5}	
		Algal C. (Mixed) in M. Gorham (nonsterile)	"	6.9×10^{-4}		6.9×10^{-4}	
		" (sterile)	"	1.0×10^{-5}		1.0×10^{-5}	
		Algal C. (Pure) in M. Allen (nonsterile)	"	1.5×10^{-4}		1.5×10^{-4}	
		Algal C. (Pure) in M. Gorham (nonsterile)	"	3.6×10^{-4}		3.6×10^{-4}	
Englebrecht and Morgan	E-3	Illinois Rivers NFSQ	2.95		1.8×10^{-4}	5.3×10^{-4}	NFSQ-nonfiltered semi-quiescent storage condition. Avg. value of pH=8.0 was used in adjusting rate constant
			2.95		4.3×10^{-4}	1.3×10^{-3}	
			7.36		5.9×10^{-5}	4.3×10^{-4}	

TABLE XX - Cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	INITIAL CONC. OF PP C_o, mg/l PO_4	RATE CONSTANT, k_2, AT 20^oC and pH = 7		RATE OF HYDROLYSIS AT 20^oC AND pH=7 $=(k\ C_o)$ for first-order, = k for zero-order, mg PO_4/l-min	REMARKS
				Zero-order mg PO_4/l-min	First-order min^{-1}		
Smith, Cohen and Walton	S-17	Ohio River (settled)	20.0		$5.1x10^{-6}$	$1.0x10^{-4}$	
		Local Ohio Stream	20.0		$4.6x10^{-6}$	$9.2x10^{-5}$	
Shannon	S-12	L.Mendota (nonsterile)	1.1	$9.2x10^{-5}$		$9.2x10^{-5}$	
		Black Earth Creek	1.0	$4.6x10^{-5}$		$4.6x10^{-5}$	
Sawyer	S-6	Domestic Wastewater	30.6		$7.5x10^{-4}$	$2.3x10^{-2}$	pH = 7.0 was assumed.

Figure 11. Concentration dependence of the rate of hydrolysis of tripolyphosphate at 20°C and pH = 7.

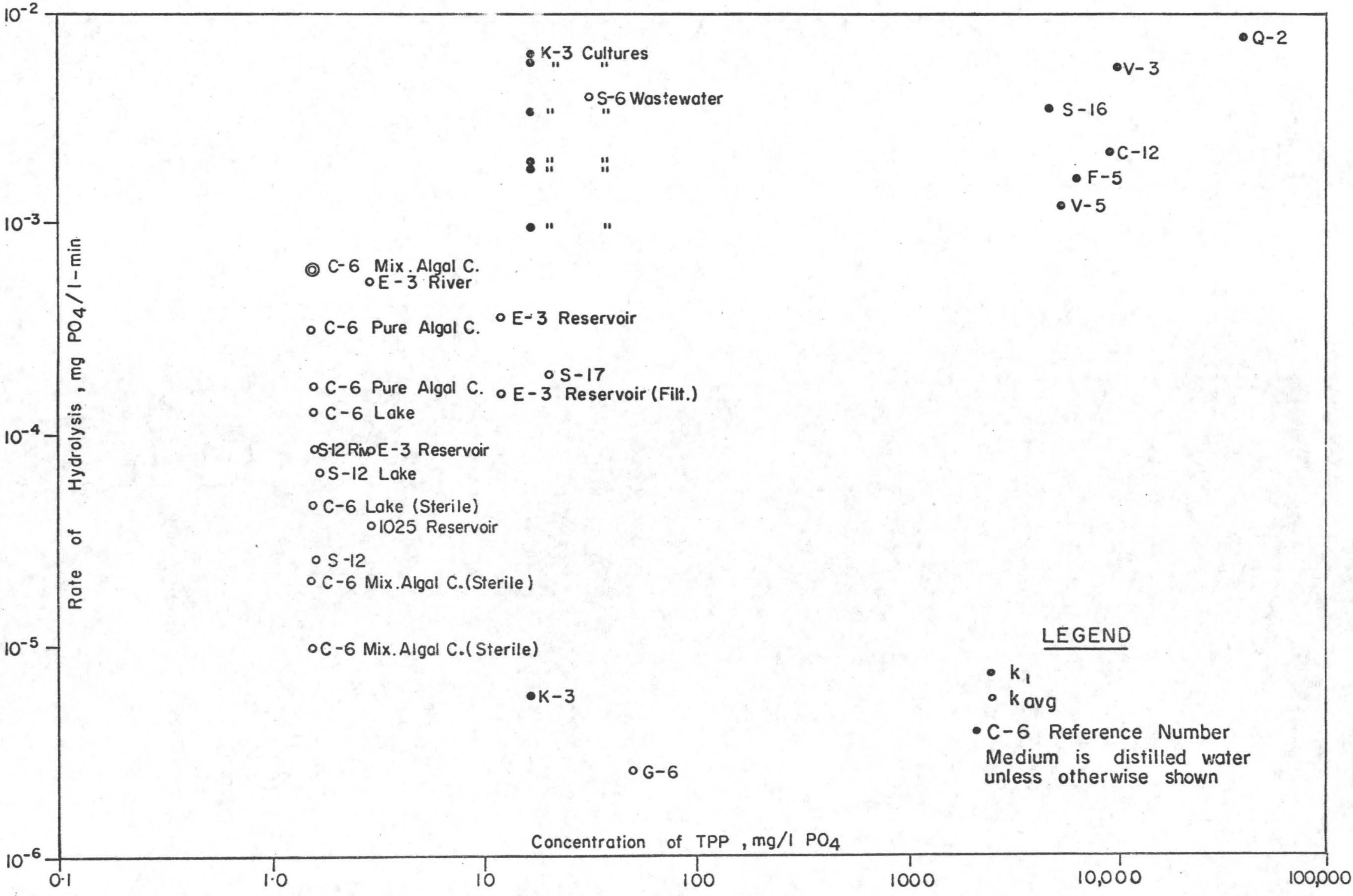
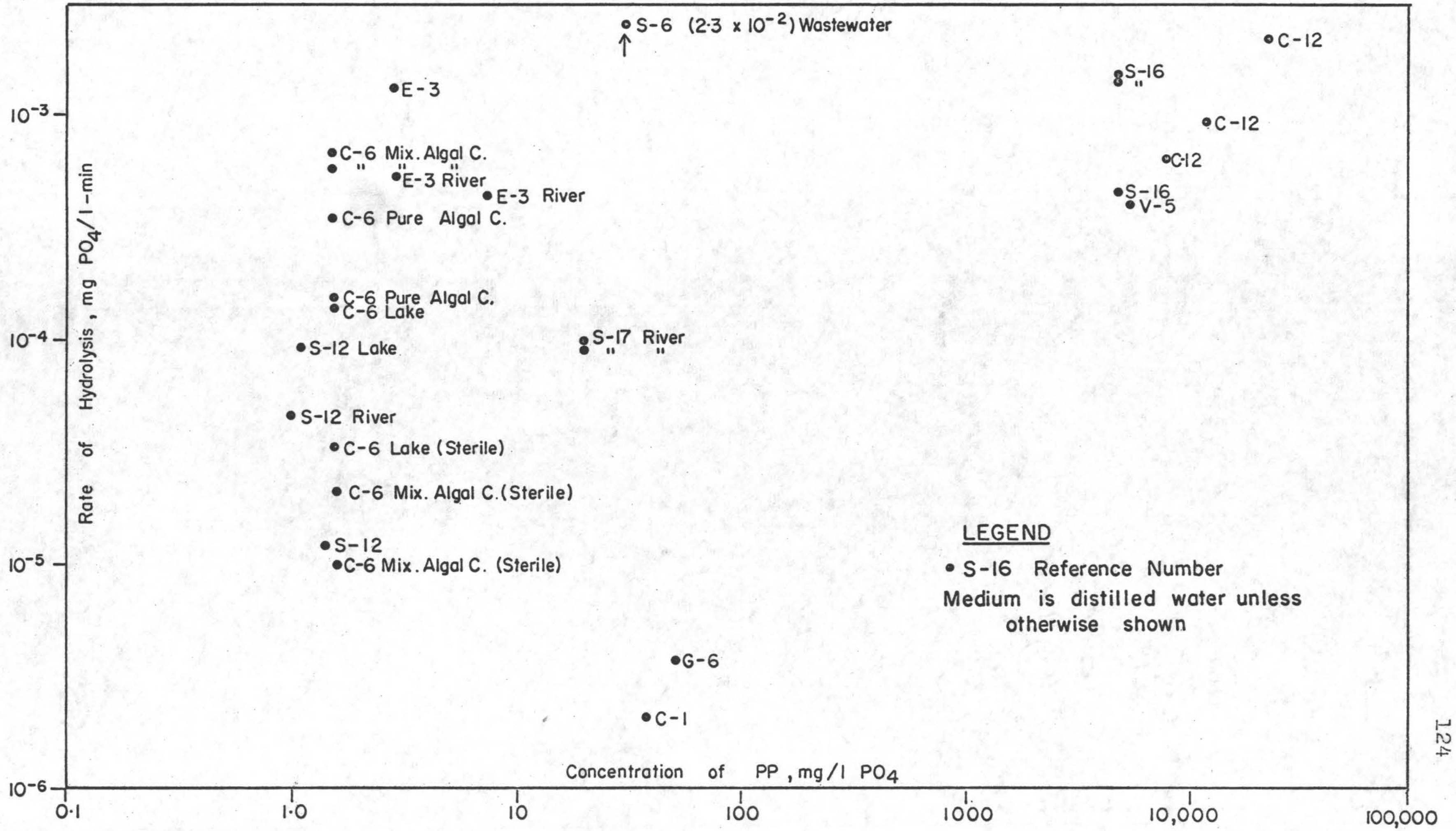


Figure 12. Concentration dependence of the rate of hydrolysis of pyrophosphate at 20° and pH = 7.



respectively. The aqueous medium is shown as a parameter. As the concentration and rate range over several orders of magnitude, a log-log plot is employed.

A discussion of Figs. 11 and 12 follows. As several of the points apply to both figures, they are discussed jointly.

1. Distilled water studies are mainly at high concentrations of 4000 to 40,000 mg/l PO_4. Very few studies are at low concentrations of 1 to 50 mg/l PO_4. No studies were carried out in the intermediate concentration range. This makes it difficult to connect these two areas. Natural water, algal cultures and wastewater hydrolysis studies were carried out only at low concentrations.

2. At high concentration distilled water studies indicate, with some degree of variation, the first-order dependence of the rate of hydrolysis on concentration. On tripolyphosphate studies (Fig. 11) Greens (G-6) rate is based on k_{avg} and is therefore lower than Karl-Kroupa's (K-3) rate. Shannon's (S-12) rate, reported as zero-order is about five times faster. On pyrophosphate studies the linear extension of high concentration-rates agrees well with the two rates at concentrations of 38 (Campbell and Kilpatrick (C-1)) and 50 mg/l PO_4 (Green (G-6)). The rate of Shannon (S-12) at 1.39 mg/l PO_4, reported as zero-order, is about four times faster. On the question of first-order versus zero-order at low concentration the literature is not conclusive, but indicates that behaviour other

than first-order may occur at low concentrations.

3. The rates in sterile samples of Clesceri (C-6) agree reasonably well with the distilled water rate of Shannon (S-12) and thus add support to it.

4. Natural water samples of lakes, reservoirs and rivers show a range in rate of up to about 1 to 2 orders of magnitude. The rate of Shannon (S-12) and Clesceri (C-6) on Lake Mendota water agree reasonably well, Shannon being lower, possibly due to the fact that the sample was incubated in darkness, whereas Clesceri's was illuminated. All natural water samples have higher rates than the distilled water or sterile samples at the same level of concentration.

5. Algal cultures of Clesceri (C-6) have generally higher rates than most of the natural water samples. This would be due to the higher concentration of organisms. The culture studies of Karl-Kroupa (K-3) (Fig. 11) exhibited a rate of the same order of magnitude as the wastewater sample of Sawyer (S-6).

6. Comparing the rate of hydrolysis of tripolyphosphate (Fig. 11) with the rate of hydrolysis of pyrophosphate (Fig. 12) it appears that pyrophosphate hydrolysis is slower in distilled water. As all of the nondistilled water studies on tripolyphosphate, on which data for both tripoly- and pyro- are available, were carried out without

differential condensed phosphate analysis, a comparison is really not possible. However, if rates are compared as shown, there appears no marked difference in the rate between pyrophosphate and tripolyphosphate.

III-3 THE EFFECT OF pH ON THE RATE OF HYDROLYSIS

Van Wazer (V-2) p. 455 states the following:

> "The hydrolytic degradation of all chain and ring phosphates is strongly catalyzed by hydrogen ions. Therefore the rates in acidic media are orders of magnitude faster than in neutral solution. A logarthimic dependence of the rate on pH appears to be a rather general phenomenon in the acidic region."

In order to be able to compare rate data of various authors it is therefore necessary, just as it was for temperature, to have a method of converting from one pH to another. This can be done by constructing an empirical graph of rate against pH or by a nomograph. Griffith (G-7) has constructed such a nomograph for pyrophosphate and tripolyphosphate in distilled water based on the data of Van Wazer, Griffith and McCullough (V-5). Temperature and pH are parameters on this nomograph, with the rate given as the half-life in hours. This nomograph could be used for the conversion in distilled water studies. However since it was based on the work of one group, it was decided to construct a graph of the logarithm of the rate constant against pH and show all pertinent data on it. This would show the reliability of Griffith nomograph. Rate data in other media, such as natural waters, wastewater and algal cultures are shown on this graph as a parameter. A common temperature of 20°C is used. All pertinent rate constants are shown in Table XXI and Table XXIII for distilled water, for tripolyphosphate and pyrophosphate respectively, and Table XXII and XXIV for natural water, wastewater and algal cultures, for tripolyphosphate and pyrophosphate respectively.

The rate constants are plotted against pH in Fig. 13 for tripolyphosphate and Fig. 14 for pyrophosphate, with the reference number shown next to the data. Griffith (G-7) nomograph results are shown in a solid line. A different symbol, as shown in the legend, was used, where no differential analysis was done, and where the data were represented by a zero-order response, rather than a first-order response.

The following conclusions can be drawn:

Tripolyphosphate pH dependence, Fig. 13

1. The dependence of the first-order rate constant for the hydrolysis of tripolyphosphate in distilled water is well represented by the nomograph of Griffith (G-7). Data of six other workers agree reasonably well, considering the assumptions that had to be made, in some cases, on activation energy values, and variations in experimental conditions other than temperature and pH. The rate constants are about two orders of magnitude higher in acidic conditions (pH = 1) than at neutral conditions. The range of concentration of these data varied from 16.8 to 77,000 mg/l PO_4 and from 24° to 90°C as a temperature range.

TABLE XXI: SUMMARY OF CALCULATIONS ON HYDROLYSIS STUDIES ON TRIPOLYPHOSPHATE (TPP) IN DISTILLED WATER FOR RATE CONSTANTS AT 20°C

AUTHOR	REFERENCE NO.	pH	TEMP. °C	E k cal/ mole	INITIAL CONC. OF TPP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA $k^{20^\circ C}$, min^{-1}	REMARKS
Karl-Kroupa et al	K-3	6.1-6.9	24	25.0	16.8	$t_{\frac{1}{2}}$=10,000-20,000 hrs.	$k_1=4.6x10^{-7}$	
Friess	F-5		42	22.9	6200			Extensive data, only some used.
		0.9				$k_1=1.3x10^{-5}$ sec^{-1}	$k_1=4.9x10^{-5}$	No catylyst added.
		0.9				$=1.73x10^{-5} sec^{-1}$	$6.6x10^{-5}$	NaCl " "
		0.8				$=2.04x10^{-5} sec^{-1}$	$7.7x10^{-5}$	" " "
		1.0				$=8.7x10^{-6}$ sec^{-1}	$3.3x10^{-5}$	" " "
Van Wazer, Griffith & McCullough	V-5				5200			
		4	60	27.6		$k_1=2.39x10^{-2}$ hrs^{-1})	$k_1=1.4x10^{-6}$	
			90	"		$=7.66x10^{-1}$ hrs^{-1})		
		7	60	28.0		$=4.51x10^{-3}$ hrs^{-1})	$=2.3x10^{-7}$	
			90	"		$=1.52x10^{-1}$ hrs^{-1})		
		10	60	22.8		$=1.23x10^{-3}$ hrs^{-1})	$=1.8x10^{-7}$	
			90	"		$=2.14x10^{-2}$ hrs^{-1})		
Smith	S-16		65.5	25.0	4700			
		1.4				$k_1=86.4x10^{-4}$ min^{-1}	$k_1=2.7x10^{-5}$	
		3.0				$=16.2x10^{-4}$ min^{-1}	$=5.0x10^{-6}$	
		4.3				$=6.28x10^{-4}$ min^{-1}	$=2.0x10^{-6}$	
		4.4				$=8.4$ $x10^{-4}$ min^{-1}	$=2.3x10^{-6}$	
		4.7				$=7.55x10^{-4}$ min^{-1}	$=2.6x10^{-6}$	
		5.0				$=6.7$ $x10^{-4}$ min^{-1}	$=1.9x10^{-6}$	

TABLE XXI - Cont'd.

AUTHOR	REFERENCE NO.	pH	TEMP. °C	E k cal/ mole	INITIAL CONC. OF TPP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA $k^{20°C}$, min^{-1}	REMARKS
Shannon	S-12	6.3		33.6	~1.6			Reports data as zero-order response. On replot of data on semilog paper (1st order) poor straight line fit was obtained. No differential analysis for condensed phosphates was used.
			20			0.370 mg P/l-500 hrs.	$k_{avg}=3.8 \times 10^{-5}$ mg PO_4/l-min	
			4			0.013 "		
Quimby	Q-2	10.0 down	82	25.0	77,000			Reported zero-order response. But since pH changed continuously, this amounts to an H+ catalyzed reaction with increasing rate. From his data at points of known pH rates were determined as shown.
		7.5				$k_1=2.36 \times 10^{-4} hr^{-1}$	$k_1=1.4 \times 10^{-7}$	
		10.0				$=1.42 \times 10^{-4} hr^{-1}$	$=8.5 \times 10^{-8}$	
Green	G-6	5	65.5	28.6	50	$k_{avg}=0.0150\ hr^{-1}$)	$k_{avg}=3.7 \times 10^{-7}$	No differential condensed phosphate analysis. Therefore rate data are as $k_{avg.}$, which cannot be compared directly with k_1.
			87.8			$=0.202\ hr^{-1}$)		
		7	65.5	30.9		$=0.00357\ hr^{-1}$)	$=5.2 \times 10^{-8}$	
			87.8			$=0.0591\ hr^{-1}$)		
		9	65.5	30.9		$=0.00099\ hr^{-1}$	$=1.5 \times 10^{-8}$	

TABLE XXI - Cont'd.

AUTHOR	REFERENCE NO.	pH	TEMP. °C	E k cal/mole	INITIAL CONC. OF TPP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA $k^{20°C}$, min^{-1}	REMARKS
Crowther and Westman	C-12	2.0	65.5	25.0	9,000	$k_1=2.19 x 10^{-3} min^{-1}$	$k_1=7.6 x 10^{-6}$	
		2.0			18,000	$=2.05 x 10^{-3} min^{-1}$	$=7.1 x 10^{-6}$	
		3.0			9,000	$=9.4 x 10^{-4} min^{-1}$	$=3.2 x 10^{-6}$	
		5.0			9,000	$=2.89 x 10^{-4} min^{-1}$	$=1.0 x 10^{-6}$	
		9.3			9,000	$=1.5 x 10^{-5} min^{-1}$	$=5.2 x 10^{-8}$	
		12.0			9,000	$=1.41 x 10^{-4} min^{-1}$	$=4.9 x 10^{-7}$	
Van Wazer, Griffith and McCullough	V-3	7.0	90	26	10,000	$k_1=0.152 hr^{-1}$	$k_1=5.4 x 10^{-7}$	No catalyst added.

TABLE XXII: SUMMARY OF CALCULATIONS ON HYDROLYSIS STUDIES ON TRIPOLYPHOSPHATE (TPP) IN NATURAL WATERS, WASTEWATERS AND ALGAL CULTURES FOR RATE CONSTANTS AT 20°C

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	pH	TEMP. °C	E k cal/ mole	INITIAL CONC.OF TPP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA AT 20°C	REMARKS
Clesceri	C-6	L.Mendota (nonster.)	8.3	25	15.6	1.53	graphical form only or from Fig. 6 $1.1x10^{-4}$mg PO_4/l-min	-- $7.0x10^{-5}$mg PO_4/l-min	No differential condensed phosphate analysis. Rate data, for sterile media only, obtained as k_{avg} and k_2, from which k_1 was calculated. These k_1 values based on a first order response are shown. For nonsterile media rate data were presented in graphical form only. All rate data, calculated as part of this work in Fig.6,7 and 8, based on a zero-order response, are also shown. For comparison purposes with other authors k_{avg} values from Fig. 6, 7 and 8 are plotted in Fig. 11.
		L.Mendota (sterile)	8.3	25	25	1.53	$k_1=1.4x10^{-4}$ min^{-1} or from Fig.6 $5.3x10^{-5}$mg PO_4/l-min	$6.6x10^{-5}min^{-1}$ $2.5x10^{-5}$mg PO_4/l-min	
		Algal Cult. (Mixed) in M.Allen (nonster.)	8.4	23	10	1.53	graphical form only or from Fig.7 $3.8x10^{-4}$mg PO_4/l-min	-- $3.1x10^{-4}$mg PO_4/l-min	
		" (sterile)	8.4	23	25	1.53	$k_1=5.5x10^{-5}min^{-1}$ or from Fig. 7 $1.9x10^{-5}$mg PO_4/l-min	$3.3x10^{-5}min^{-1}$ $1.1x10^{-5}$mg PO_4/l-min	
		Algal Cult. (Mixed) in M.Gorham (nonster.)	8.4	23	10	1.53	graphical form only or from Fig. 8 $3.8x10^{-4}$mg PO_4/l-min	-- $3.1x10^{-4}$mg PO_4/l-min	
		" (sterile)	8.4	23	25	1.53	$k_1=1.9x10^{-5}min^{-1}$ or from Fig. 8 $8.8x10^{-6}$mg PO_4/l-min	$1.1x10^{-5}min^{-1}$ $5.3x10^{-6}$mg PO_4/l-min	

TABLE XXII - Cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	pH	TEMP. °C	E k cal/ mole	INITIAL CONC. OF TPP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA AT 20°C	REMARKS
Clesceri (cont'd.)	C-6	Algal Cult. (Pure) in M.Allen (nonsterile)	8.4	23	10	1.53	graphical form only or from Fig. 7 $1.1x10^{-4}$mg PO_4/l-min	-- $9.0x10^{-5}$mg PO_4/l-min	
		Algal Cult. (Pure) in M.Gorham (nonsterile)	8.4	23	10	1.53	graphical form only or from Fig. 8 $2.0x10^{-4}$mg PO_4/l-min	-- $1.6x10^{-4}$mg PO_4/l-min	
Englebrecht and Morgan	E-3	Illinois Waters	7.3-8.6	29	11		Halflife, days		No differential condensed phosphate analysis. Large amount of data on river and reservoir water, average values are presented only.
		Reservoir, nonfilt.				2.95-12.3	15.2	$1.8x10^{-5}min^{-1}$	
		Reservoir, membrane filtered				"	34.1	$8.0x10^{-6}$ "	
		River, nonfiltered				2.95	2.4	$1.1x10^{-4}$ "	
Smith, Cohen and Walton	S-17	Ohio River (settled)	7.5	5,20, 35	13.2 - 14.4	20	Halflife, days, of 240, 60 and 20	$8.0x10^{-6}min^{-1}$	No differential condensed phosphate analysis.
Shannon	S-12	L.Mendota (nonster.)	8.4	20 4	15.6	1.65	0.339 mg P/l-500 hrs.) 0.072 ")	$3.5x10^{-5}$mg PO_4/l-min	No differential condensed phosphate analysis
		Black Earth Creek	8.6	20 4	8.6	1.6	0.388 ") 0.114 ")	$4.0x10^{-5}$mg PO_4/l-min	

TABLE XXII - cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	pH	TEMP. °C	E k cal/mole	INITIAL CONC.OF TPP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA AT 20°C	REMARKS
Sawyer	S-6	Domestic Wastewater	?	20,5	8.6	30.6	graphical form only	from Fig.10 $1.3 \times 10^{-4} min^{-1}$	No differential analysis
Karl-Kroupa et al	K-3	Cultures of	6.9-6.1	24	10	16.8	Halflife, excluding induction period,hrs		Differential analysis of condensed phosphate mixture. Validity of first-order response is questionable. (See Fig. 9).
		Elodea					123	$7.3 \times 10^{-5} min^{-1}$	
		Gleocapsa					66	1.4×10^{-4} "	
		Vaucheria					35	2.6×10^{-4} "	
		Ceratophyllum					59	1.6×10^{-4} "	
		Allomyces					19	4.8×10^{-4} "	
		Escherischia coli					20	4.5×10^{-4} "	

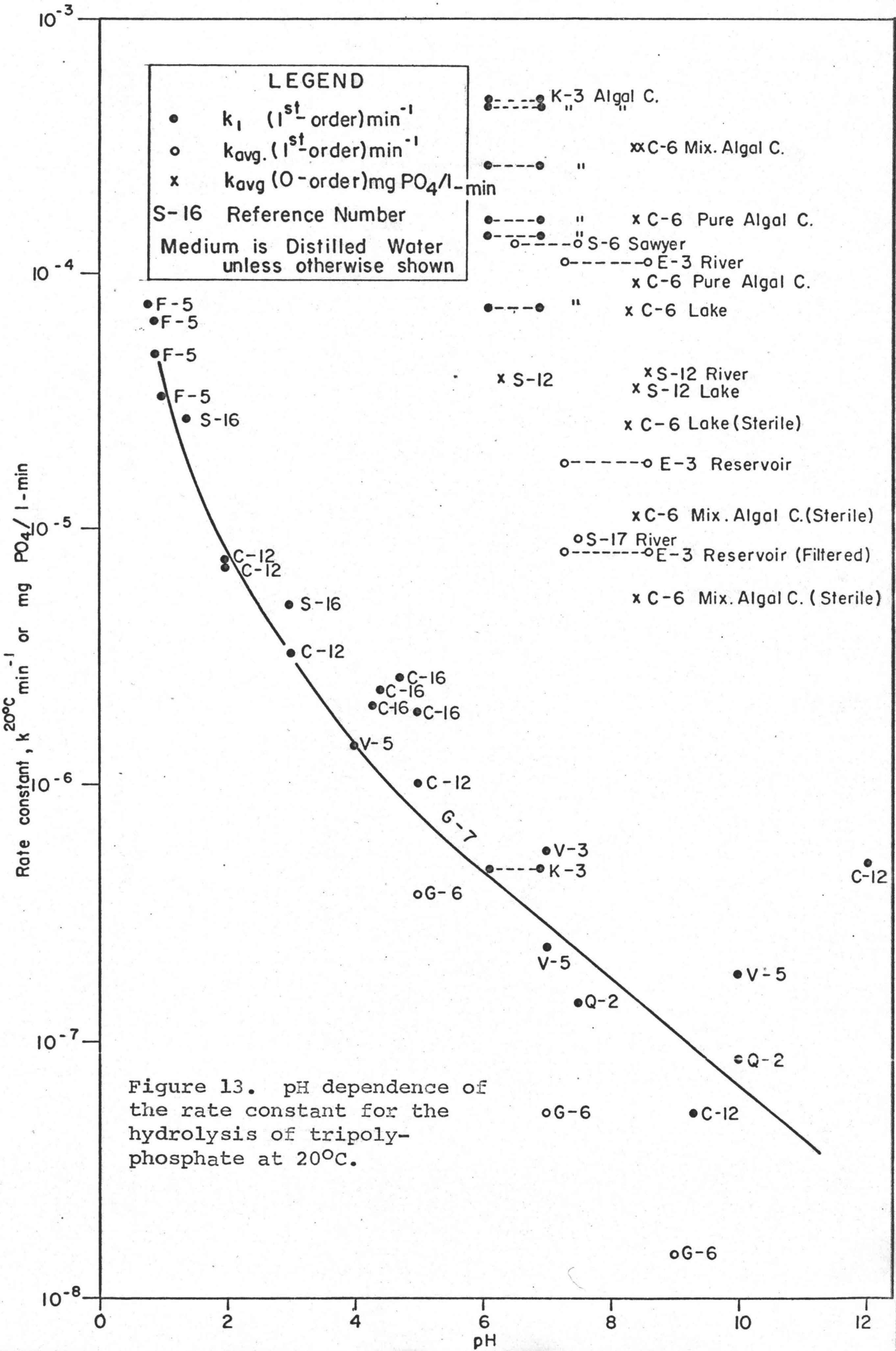


Figure 13. pH dependence of the rate constant for the hydrolysis of tripolyphosphate at 20°C.

TABLE XXIII: SUMMARY OF CALCULATIONS ON HYDROLYSIS STUDIES ON PYROPHOSPHATE IN DISTILLED WATER FOR RATE CONSTANTS AT 20°C

AUTHOR	REFERENCE NO.	pH	TEMP. °C	E k cal/mole	INITIAL CONC. OF PP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA k_2 20°C, min^{-1}	REMARKS
Campbell and Kilpatrick	C-1	0.7	49.83	21.7	1.9	$k_2=0.233$ hr^{-1}	$k_2=1.3x10^{-4}$	Extensive data, only some used
		0.7		21.7	19	$=0.216$ hr^{-1}	$= 1.2x10^{-4}$	
		1.1		27.5	3.8	$=0.0319$ hr^{-1}	$= 7.2x10^{-6}$	
		1.1		27.5	38	$=0.0318$ hr^{-1}	$= 7.2x10^{-6}$	
		1.3		28.3	38	$=0.0181$ hr^{-1}	$= 3.7x10^{-6}$	
		3.3		29.0	38	$=0.00272$ hr^{-1}	$= 5.0x10^{-7}$	
Friess	F-5	0.9	49.75	22.8	6200	$k_2=5.4x10^{-6}$ sec^{-1}	$k_2=8.7x10^{-6}$	
		0.85				$=6.94x10^{-6}$ sec^{-1}	$=1.1x10^{-5}$	
		0.8				$=9.15x10^{-6}$ sec^{-1}	$=1.5x10^{-5}$	
Van Wazer, Griffith and McCullough	V-5	1	60	22.7	5200	$k_2=6.39x10^{-2}$ hrs^{-1}	$k_2=1.0x10^{-5}$	
		4		27.6		$=7.38x10^{-3}$ "	$=4.2x10^{-7}$	
Smith	S-16	2.8	65.5	25.0	4730	$k_2=4.04x10^{-4}$ min^{-1}	$k_2=1.2x10^{-6}$	
		4.9				$=2.99x10^{-4}$ min^{-1}	$=9.2x10^{-7}$	
		5.0				$=2.90x10^{-4}$ min^{-1}	$=9.0x10^{-7}$	
Shannon	S-12	6.3	20	21.2	1.39	$0.163 \frac{mg\ P}{l\text{-}500\ hrs}$	$=1.7x10^{-5} \frac{mg\ PO_4}{l\text{-}min}$	Reports data as zero-order response.
			4		2.15	0.020 "		

TABLE XXIII - Cont'd.

AUTHOR	REFERENCE NO.	pH	TEMP. °C	E k cal/ mole	INITIAL CONC. OF PP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA k_2 20°C, min^{-1}	REMARKS
Green	G-6	5	65.5	28.0	50	$k_2=0.0168\ hr^{-1}$)	$k_2=4.6x10^{-7}$	
			87.8			$=0.215\ hr^{-1}$)		
		7	65.5	29.6		$=0.00404\ hr^{-1}$)	$=7.6x10^{-8}$	
			87.8			$=0.0595\ hr^{-1}$)		
Crowther and Westman	C-12	2.0	65.5	25.0	23,200	$k_2=5.53x10^{-4} min^{-1}$	$k_2=1.9x10^{-6}$	
		2.0			11,650	$=5.36x10^{-4} min^{-1}$	$=1.85x10^{-6}$	
		2.0			7,760	$=5.36x10^{-4} min^{-1}$	$=1.85x10^{-6}$	
		3.0			23,200	$=3.31x10^{-4} min^{-1}$	$=1.1x10^{-6}$	
		6.0			23,200	$=1.25x10^{-4} min^{-1}$	$=4.3x10^{-7}$	
		9.3			23,200	$=1.0x10^{-5}\ min^{-1}$	$=3.4x10^{-8}$	
		10.9			23,200	$=4.8x10^{-6}\ min^{-1}$	$=1.6x10^{-8}$	

TABLE XXIV: SUMMARY OF CALCULATIONS ON HYDROLYSIS STUDIES ON PYROPHOSPHATE (PP) IN NATURAL WATERS, WASTEWATERS AND ALGAL CULTURES FOR RATE CONSTANTS AT 20°C

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	pH	TEMP. °C	E k cal/mole	INITIAL CONC.OF PP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA AT 20°C	REMARKS
Clesceri	C-6	L.Mendota (nonsterile)	8.3	25	18.5	1.53	graphical form only or from Fig. 6 1.3x10^{-4} mg PO_4/l-min	-- 7.4x10^{-5} mg PO_4/l-min	No differential condensed phosphate analysis. Rate data presented as k_2 for sterile conditions and in graphical form for nonsterile conditions. Clesceri's k_2 values, based on a first-order response are shown. All rate data, calculated as part of this work in Fig. 6,7 and 8, based on a zero-order response are also shown. For comparison purposes with other authors k_{avg} values from Fig.6,7 and 8 are plotted in Fig.11.
		L.Mendota (sterile)	8.3	25	25	1.53	6.1x10^{-5} min^{-1} or from Fig. 6 5.1x10^{-5} mg PO_4/l-min	2.9x$10^{-5}$$min^{-1}$ 2.4x10^{-5}mg PO_4/l-min	
		Algal Cult. (Mixed) in M.Allen (nonsterile)	8.4	23	10	1.53	graphical form only or from Fig. 7 5.0x10^{-4} mg PO4/l-min	-- 4.1x10^{-4}mg PO4/l-min	
		" (sterile)	8.4	23	25	1.53	7.4x10^{-6} min^{-1} or from Fig. 7 1.8x10^{-5} mg PO_4/l-min	4.5x$10^{-6}$$min^{-1}$ 1.1x10^{-5}mg PO_4/l-min	
		Algal Cult. (Mixed) in M.Gorham (nonsterile)	8.4	23	10	1.53	graphical form only or from Fig. 8 4.4x10^{-4} mg PO_4/l-min	-- 3.6x10^{-4}mg PO_4/l-min	
		" (sterile)	8.4	23	25	1.53	6.1x10^{-6} min^{-1} or from Fig. 8 8.6x10^{-6} mg PO_4/l-min	3.7x$10^{-6}$$min^{-1}$ 5.2x10^{-6}mg PO_4/l-min	
		Algal Cult. (Pure) in M.Allen (nonsterile)	8.4	23	10	1.53	graphical form only or from Fig. 7 9.8x10^{-5} mg PO_4/l-min	-- 8.0x10^{-5}mg PO_4/l-min	
		Algal Cult (Pure) in M.Gorham(nonst)	8.4	23	10	1.53	graphical form only or from Fig. 8 2.3x10^{-4} mg PO_4/l-min	-- 1.9x10^{-4}mg PO_4/l-min	

TABLE XXIV - Cont'd.

AUTHOR	REFERENCE NO.	AQUEOUS MEDIUM	pH	TEMP. °C	E k cal/mole	INITIAL CONC. OF PP mg/l PO_4	RATE DATA AT EXPT. TEMP. AND IN AUTHORS UNITS	RATE DATA AT 20°C	REMARKS
Englebrecht and Morgan	E-3	Illinois Rivers	7.3-8.6	29	11		Half-life, days		No differential condensed phosphate analysis. NFSQ-non-filtered, semi-quiescent storage conditions
		NFSQ				2.95	2.5	$1.1x10^{-4}min^{-1}$	
						2.95	1.0	$2.7x10^{-4}min^{-1}$	
						7.36	7.5	$3.7x10^{-5}min^{-1}$	
Smith, Cohen and Walton	S-17	Ohio River (settled)	7.5	5,20, 35	6.3-11.8	20	Half-life, days, of 220, 120, 45	$4.0x10^{-6}min^{-1}$	No differential phosphate analysis
		Local Ohio Stream	8.1	5,20, 35	5.8-10.5	20	Half-life, days, of 310, 180, 75	$2.7x10^{-6}min^{-1}$	
Shannon	S-12	L.Mendota (nonster.)	8.4	20 4	18.5	1.1 2.08	0.472mg P/l-500hrs 0.075 "	$4.8x10^{-5}$mg PO_4/l-min	No differential condensed phosphate analysis
	S-12	Black Earth Creek	8.6	20 4	8.6	1.0	0.232 " 0.099 "	$2.4x10^{-5}$mg PO_4/l-min	
Sawyer	S-6	Domestic Wastewater	?	20,5	11.2	30.6	graphical form only	from Fig.10 $7.5x10^{-4}min^{-1}$	No differential condensed phosphate analysis.

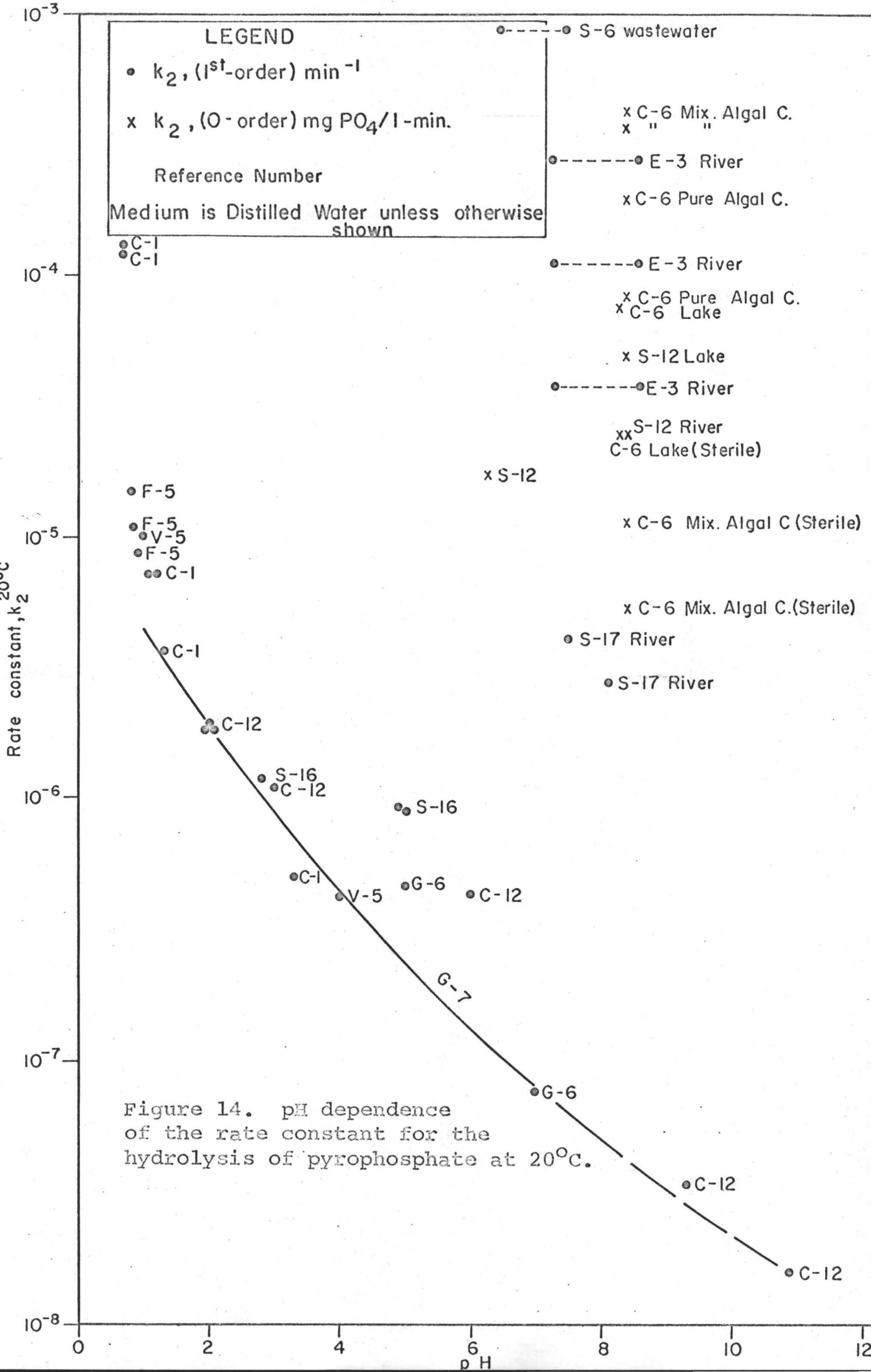


Figure 14. pH dependence of the rate constant for the hydrolysis of pyrophosphate at 20°C.

2. The data of Green (G-6) on distilled water are low due to the fact that they are k_{avg} values which are of necessity lower than k_1. The data of Crowther and Westman (C-12), at pH of 12, are high and would indicate a base catalysis. Van Wazer, Griffith and McCullough (V-3) have suggested that this apparent base catalysis is caused by formation of complexes with sodium ion.

3. The data of Shannon (S-12) on distilled water are at the lowest concentration of tripolyphosphate, 1.6 mg/l PO_4, and are the only ones reported as a zero-order response. Nondifferential condensed phosphate analysis was used. A direct comparison with other workers on distilled water is therefore difficult, but it is evident that Shannon's rate constant is at least one magnitude higher than others. Further discussion on this point is given in III-2, under concentration effect on rate of hydrolysis.

4. All data on river, lake, algal cultures and wastewater are about two to three magnitudes faster than predicted by Griffith nomograph for distilled water. Algal cultures and wastewater, having the highest concentration of organisms show the fastest rate of hydrolysis. Sterile samples show the slowest rate, of about the same order of magnitude or lower than Shannon's distilled water rate. Direct numerical comparison is not possible due to the different analytical techniques used, different order of response of reporting rate data, and the differences in

media and environmental conditions.

5. The pH value of river, lake, algal cultures and wastewater samples varied from 6.1 to 8.6. No single experiment was carried out at several different pH values. The pH dependence of the rate is therefore unknown. As the relatively fast rate of hydrolysis in these samples is due primarily to the presence of some organisms, one would expect the fastest rate of hydrolysis at the optimum pH for growth of the organisms.

<u>Pyrophosphate pH dependence, Fig. 14</u>

1. The dependence of the first-order rate constant for the hydrolysis of pyrophosphate in distilled water is well represented by Griffith's (G-7) nomograph. Data of six other workers agree reasonably well, considering the assumptions that had to be made, in some cases on activation energy values, and variations in experimental conditions other than temperature and pH. The rate constants are about two to three orders of magnitude higher in acidic conditions (pH = 1) than at neutral conditions. The range of concentration of these data is from 1.9 to 23,200 mg/l PO_4, the low concentration having a very low pH value of 0.7. The range of temperature is from 49.75 to 87.8°C.

2. The data of Shannon (S-12) on distilled water are at the lowest concentration of pyrophosphate, 1.39 mg/l PO_4,

and are the only ones reported as a zero-order response. As with tripolyphosphate, it is evident that Shannon's rate constant is at least one magnitude higher than others. Further discussion on this point is given in III-2, under concentration effect on rate of hydrolysis.

3. The rate of hydrolysis of pyrophosphate in distilled water is about two to four times slower than for tripolyphosphate.

4. Conclusions 4 and 5 on tripolyphosphate hydrolysis in river, lake, algal culture and wastewater apply as well for pyrophosphate. No general conclusion can be made on the relative rate of tripolyphosphate versus pyrophosphate in these type of media.

McGilvery and Crowther (M-8) examined the role of the hydrogen ion in the hydrolysis of sodium pyrophosphate in some detail. They found that experimental data were well represented by an expression

$$\frac{dC}{dt} = - k\ (H^{+})^{0.25} \times C$$

where C is the concentration of pyrophosphate at any time t. Since it was difficult to conceive of any mechanism which would satisfactorily explain the fractional power of the hydrogen ion concentration, they proposed a different rate equation.

$$-\frac{dC}{dt} = k_o\ (H_o) + k_1\ (H_1) + k_2\ (H_2) + k_3\ (H_3) + k_4\ (H_4)$$

where (H_o), (H_1), (H_2), (H_3) and (H_4) are the concentrations of $P_2O_7^{\ 4-}$, $HP_2O_7^{\ 3-}$, $H_2P_2O_7^{\ 2-}$, $H_3P_2O_7^{\ 1-}$ and $H_4P_2O_7$ respectively and k_o, k_1, k_2, k_3 and k_4 are the first-order hydrolysis rate constants associated with the various anionic species. The role of the hydrogen ion is to determine the proportion of each species present in the pyrophosphate solution. The above equation was solved and the following values were obtained

$$k_o = 4.7 \times 10^{-6} \text{ min}^{-1}$$

$$k_1 = 5.25 \times 10^{-5} \text{ min}^{-1}$$

$$k_2 = 2.8 \times 10^{-4} \text{ min}^{-1}$$

$$k_3 = 7.3 \times 10^{-4} \text{ min}^{-1}$$

$$k_4 = 3.9 \times 10^{-3} \text{ min}^{-1}$$

A possible mechanism of hydrolysis that could explain the profound differences in the rates of the various species is discussed at length.

IV DEVELOPMENT OF ANALYTICAL TECHNIQUES

The literature survey revealed a number of possible methods that might be modified in order to suit the needs of this work. These needs are:

1. A method for the analysis of distilled water and lake water; concentration range: 0.010 - 1.0 mg/l PO_4. Manual and automatic analysis for orthophosphate, condensed phosphates and total phosphorus.
2. A method for the analysis of distilled water and wastewater.

   Concentration range: 1 - 100 mg/l PO_4. Manual and automatic analysis for orthophosphate, condensed phosphates and total phosphorus.
3. A method for the differential analysis of a mixture of condensed phosphates.

   Concentration range: lake water and wastewater levels.

   Medium: Distilled water, lake water and wastewater.

   Mixture: Orthophosphate, pyrophosphate and tripolyphosphate.

The development work first concentrated on 1 and 2. The early literature survey on 3 did not reveal methods that appeared likely to give reliable quantitative results, particularly at the low concentrations used in lake water work. Only later literature surveys suggested that the use of ion exchange chromatography might be both feasible and possible without the purchase of extra equipment. Development work on 3. was therefore not done until several months of experimental work had been completed.

The methods as finally used are written up in detail in Appendix A. This chapter describes some of the trials and tribulations experienced.

IV-1 DEFINITION OF TERMS AND UNITS OF MEASUREMENT

Definition of Terms:

The samples to be analyzed throughout this work are distilled water, lake water and wastewater as media, with added tripolyphosphate or pyrophosphate. For the distilled water and in fact also for lake water with added condensed phosphates the particulate phosphorus fraction is either nonexistent or negligibly small, so that only soluble phosphorus is of importance. For the wastewater samples on the other hand both the particulate and the soluble phosphorus fractions must be measured. For the purpose of this work the following definitions and methods of determination are made.

Filter: means a Millipore filter, 0.45 micron HA, 47 mm dia, (unless otherwise stated under each experiment).

Extraction: solvent extraction with isobutyl alcohol.

The following determinations are done:

On Unfiltered Sample

Det. 1: Total Phosphorus (UTP) - see Appendix A, 3.

Det. 3: Reactive Phosphate (Orthophosphate) (UOP) - see Appendix A, 1 or 2.

On Filtered Sample

Det. 2: Total Phosphorus (FTP) - see Appendix A, 3.

Det. 4: Reactive Phosphate (orthophosphate) (OP) - see Appendix A, 1 or 2.

Total Phosphorus (UTP): Determination 1

Filtered Total Phosphorus (FTP): Determination 2

Filtered Reactive (Orthophosphate) (OP): Determination 4

Filtered Unreactive (Condensed Phosphate) (CP): Determination 2 - Determination 4

Particulate Phosphorus (PAP): Determination 1 - Determination 2.

For wastewater samples all four determinations are normally made. For distilled water samples and lake water samples with added condensed phosphates results of Determination 1 and 2, and 3 and 4, respectively, were shown to be the same, as expected, and therefore, only Determination 1 and Determination 3 were carried out in general.

The results of Determination 4, Reactive Phosphate (Orthophosphate), could include some portion of any condensed phosphates, and soluble organic phosphorus which might be hydrolyzed during the test procedure. Tests on prepared samples showed that for the procedures used this was not detectable. Therefore the term Reactive Phosphate is synonymous with orthophosphate in this work. For the same reason Filtered Unreactive Phosphates are equated to Condensed Phosphates, for distilled water and lake water samples. In some of the wastewater samples soluble organic phosphorus compounds may have been present and in this case filtered unreactive phosphate is the sum of condensed phosphates, naturally present or added, and any soluble organic phosphorus naturally present.

Units of Measurement

In looking through the literature of methods of measurements and actual data on phosphorus levels in wastewater, streams, lakes and oceans it is difficult to compare numbers since several units are used and often it is not clear in which units the particular author reports his data. The following units are used as shown in Table XXV and conversion figures are given in Table XXVI.

TABLE XXV: UNITS OF MEASUREMENT OF PHOSPHORUS

UNIT OF MEASUREMENT	REFERENCES
μg/l P (or PO_4 -P)	C-2, E-1, F-4, H-9, K-8, M-10, M-15, S-7, V-6, B-4.
μg/l PO_4	A-3, G-1, G-2, H-8, V-1
μg/l P_2O_5	A-9, E-3, L-9, L-10
μg-at/l P	S-19, S-20
μ M (micro molar) PO_4	P-3

For higher concentrations mg/l is used for 1000 μg/l.

TABLE XXVI: CONVERSION FOR UNITS OF MEASUREMENT OF PHOSPHORUS

Given Unit / Desired Unit	µg/l P (or PO_4-P)	µg/l PO_4	µg/l P_2O_5	µg-at/lP
µg/l P (or PO_4-P)	1	3.06	2.29	0.032
µg/l PO_4	0.33	1	0.75	0.010
µg/l P_2O_5	0.43	1.34	1	0.014
µg-at/l P	30.97	94.8	70.9	1

The most commonly used unit is µg/l P. Oceanographers seem to prefer µg-at/l P, the soap industry uses mg/l P_2O_5. Standard Methods (A-3) uses mg/l PO_4. All measurements in this work are reported as mg/l PO_4. The conversion numbers given in Table XXVI are used to convert other authors data to mg/l PO_4.

IV-2 LAKE WATER APPLICATION

IV-2.1 MANUAL ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE)

As the equipment to carry out automatic analysis for phosphorus was available from the beginning of this work, the need for a manual analysis was caused by the desirability of checking the automatic analyses at times. Based on the literature survey the decision was made to try the Stannous Chloride Method as recommended by Association of American Soap and Glycerine Producers Committee Report (A-11) and the Ascorbic

Acid Method, Murphy and Riley (M-16) and modified by Stephens (S-19) and Kramer (K-9). Both methods need to be used with and without extraction to cover the range of phosphates in lake water, ie.

Unpolluted Lake waters:	0.0-0.1 mg/1 PO_4	Extraction required.
Polluted Lake waters:	0.1-1.0 mg/1 PO_4	No extraction required.

The Stannous Chloride Method (A-11) which is a modification of Standard Methods (A-3) Method B, was first tried in the range of 0.025 - .125 mg/1 PO_4. Extraction was used. The reproducibility at the higher level of 0.125 mg/1 PO_4 was reasonable, but poor at lower levels of concentration. Further work on this method was discontinued.

The Ascorbic Acid Method with extraction employs a mixed reagent, containing ammonium molybdate, sulfuric acid, potassium antimony tartrate and ascorbic acid. A blue colour results in the presence of orthophosphates, which is extracted with isobutanol and the optical density is measured at 690 millimicron. Approximately 100 determinations of standards were made in the range of 0.005 to 0.100 mg/1 PO_4. A least square line through the origin was fitted to these data with the following results:

with extraction:

Equation of line: mg/1 PO_4 = 0.285 x optical density

Correlation coefficient: $r = 0.985$

Precision at .020 mg/1 PO_4: ± .004 at 95 percent confidence

Precision at .080 mg/l PO_4: ± .005 at 95 percent confidence

Reagent blank (double distilled water): O.D.= 0.015 ± 0.012

If a sample exceeds 0.1 mg/l PO_4 it can be brought into the range of the extraction method by dilution with double distilled water. This procedure was used only for the occasional high sample. For samples from polluted lake water areas or for artificial samples in the range of 0.1 - 1.0 mg/l PO_4 the extraction step was omitted. A different calibration curve is needed, the optimum wavelength is 880 millimicron. Approximately fifty determinations in the range of 0.1 - 1.0 mg/l PO_4 were made. A least square line through the origin was fitted to the data with the following results.

<u>without extraction</u>:

Equation of line: mg/l PO_4 = 2.10 x optical density.

Correlation coefficient: $r = 0.995$

Precision at 0.2 mg/l PO_4: ± .025 at 95 percent confidence

Precision at 1.0 mg/l PO_4: ± .035 at 95 percent confidence

To improve the precision of the method, a spectrophotometer of 10 cm cell length should be used, rather than the cell length of 1 inch (2.54 cm) of the Bausch and Lomb Spectronic 20. Such an instrument was not available. However, since the data were mainly obtained by the automatic method, this was not a serious disadvantage.

Determination of Optimum Wavelength and Stability with Extraction: Stephens (S-19) reported two absorption peaks for the extract at 690 and 810 millimicron of similar magnitude. Fig. 15 shows data for a .01 and .03 mg/l PO_4 sample, run in this work. These results agree with Stephens' work. 690 millimicron was selected as the optimum wavelength for the extraction method.

Influence of time on optical density was investigated at several levels of concentration. The initial reading is taken about 15 minutes after contacting with mixed reagents. A typical result is given.

Time	Optical Density Reading
Initial Reading	0.115
1/2 hour	0.118
1 hour	0.120

Without Extraction: Absorption peaks for the method without extraction are reported by Murphy and Riley (M-16) at 710 and 882 millimicron, the latter being considerably higher. Results of this work are shown in Fig. 16. These results agree with Murphy and Riley. An optimum wavelength of 880 millimicron was selected.

Influence of time on optical density was investigated at several levels of concentration. The initial reading is taken at about 15 minutes after contact with mixed reagent. A typical result is given.

Figure 15. Spectral transmission curve for ascorbic acid method with extraction.

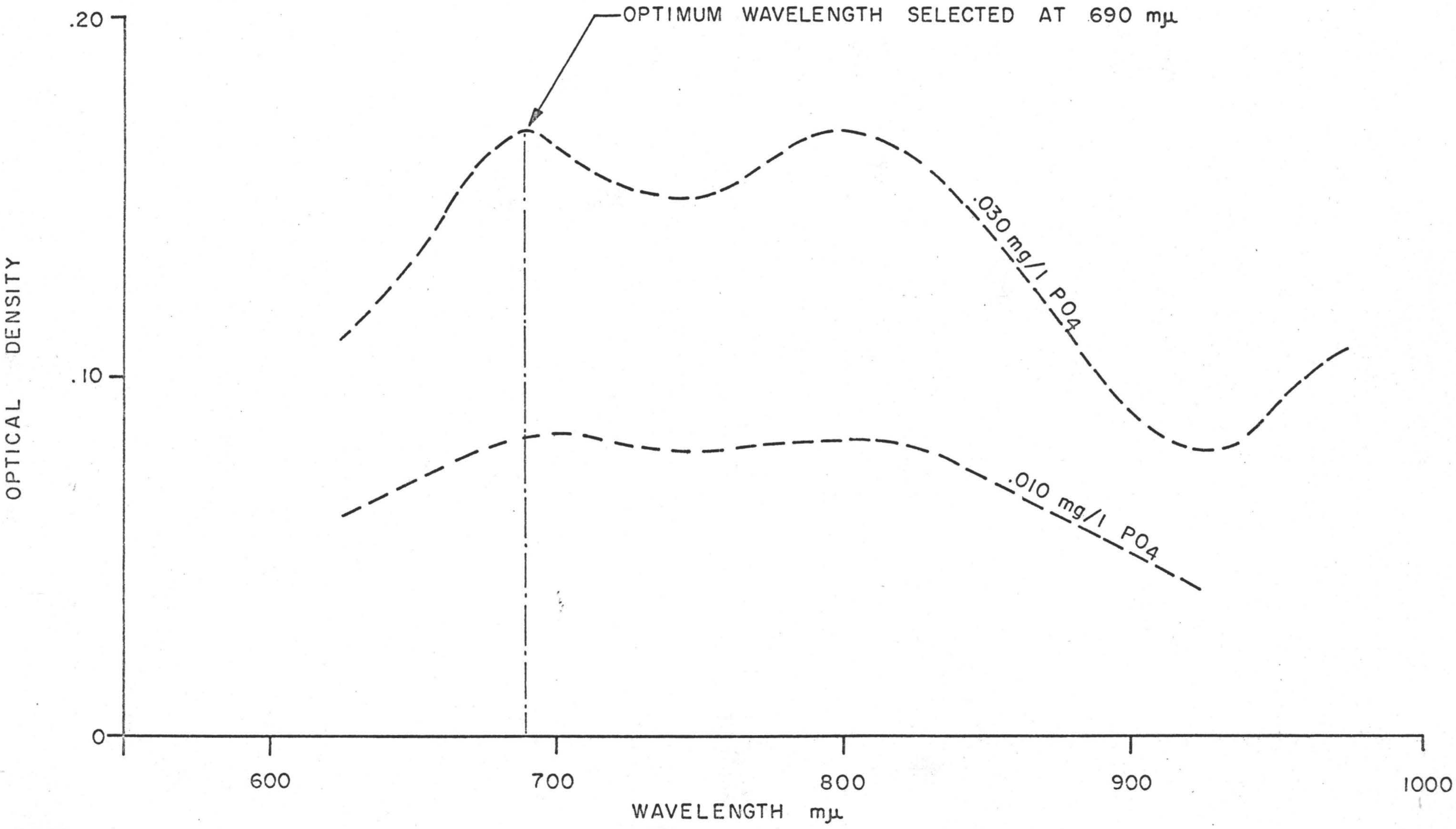
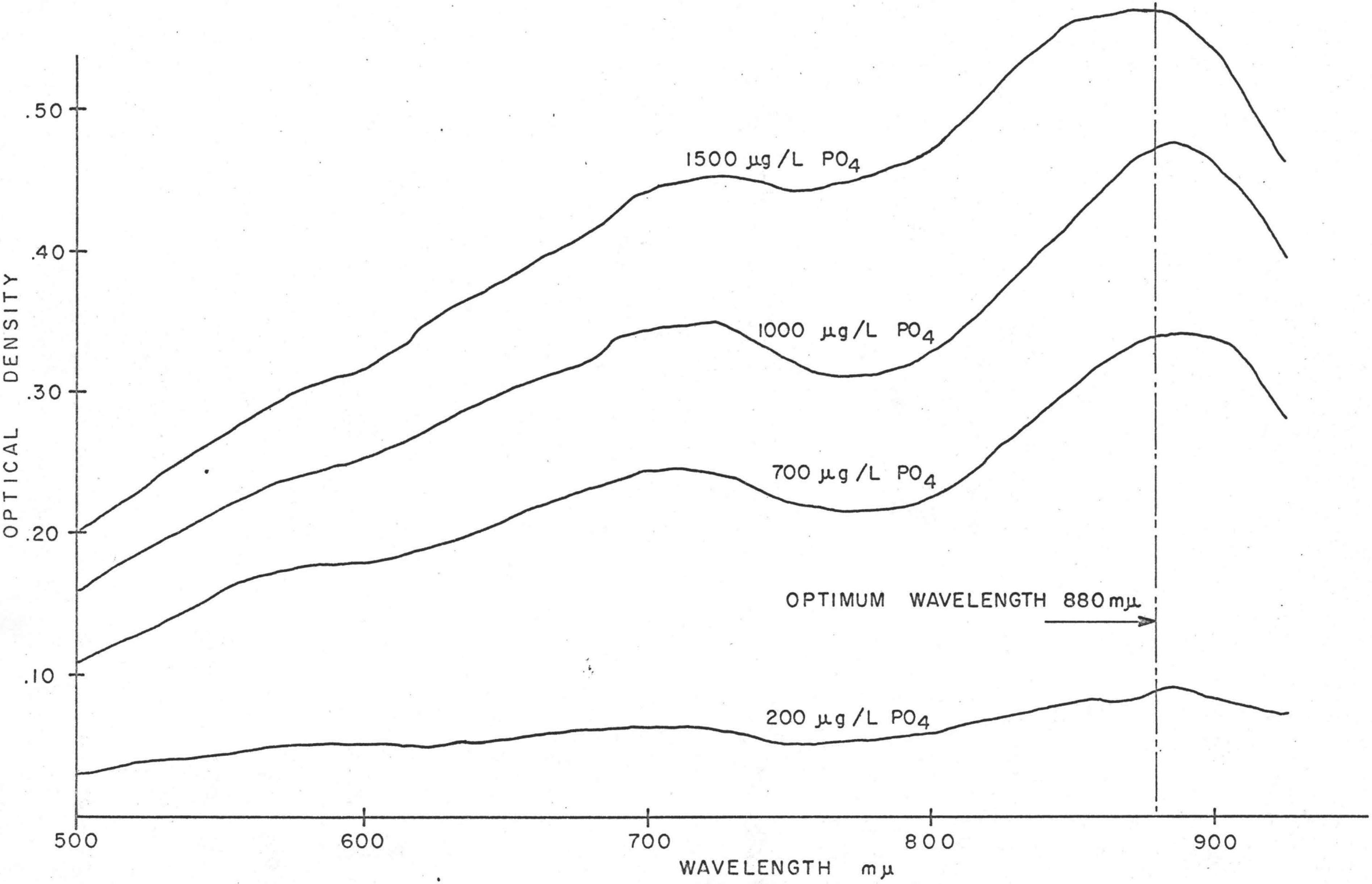


Figure 16. Spectral transmission curve for ascorbic acid method without extraction.



Time	Optical Density Reading
Initial Reading	0.120
½ hour	0.120
1 hour	0.115
6 hours	0.118

Influence of Temperature

Stephens (S-19) reports that the method is independent of temperature but gives no data. Strickland and Parsons (S-20) state

> "The method appears to have no significant temperature coefficient (less than 0.2 percent per °C) between 15°C and 30°C but it is probably wisest to have samples at a temperature within this range."

Temperature influence was investigated in this work and the results are shown below.

Temperature °C	Optical Density Readings	
	Sample #1	Sample #2
5°	0.300	0.280
	0.290	0.275
15°	0.310	0.295
	0.295	0.290
25°	0.300	0.290
	0.285	0.280

The readings at 15°C are a little higher than at 5° or 25°C, but the variation is no larger than the variation at a fixed temperature. Some difficulty was experienced with the extraction at 5°C. The procedure used for routine work is to let all samples come to room temperature (15-25°C) before analysis.

Influence of Filtering

For certain samples containing sufficient turbidity filtering before orthophosphate analysis is necessary. Strickland and Parsons (S-20) suggest to filter when the turbidity gives an extinction exceeding 0.05. The filter used is a Millipore Filter, 47 mm dia.; 0.45 micron Grade HA. A 0.05 mg/1 PO_4 standard solution as well as lake water samples were compared for the effect of filtering. 50 ml of sample was filtered each time. The results are given below. (All figures given are means of triplicates.)

	Optical Density		
	Analysis 1	Analysis 2	Analysis 3
Unfiltered:	0.275	0.280	0.290
Filtered:	0.390	0.300	0.275

Note: For Analysis 1 a new filter was used, and the same filter was used for Analysis 2 and 3.

For this standard solution one would expect no difference between the filtered and unfiltered sample. However, Analysis 1 clearly shows that some material must be picked up by the sample in filtering, which increases the optical density reading and would therefore be interpreted as phosphates. Analysis 1 represents a pickup of 2.6 µg PO_4 from the filter.

After three filtrations this does not occur any longer. The procedure adopted is to filter approximately 100 ml of distilled water through the filter paper before filtering the sample. Rigler (R-3) and Jenkins (J-2) found that membrane filters contain about 1 μg P (or about 3 μg PO_4). They recommended that membrane filters be soaked in distilled water before use or be washed by filtering sufficient distilled water prior to sample application.

With lake water samples taken on a winter cruise, the same phenomenon was observed, that is, filtered samples gave higher orthophosphate results than unfiltered samples, unless the filter paper first had been washed. If this was done then results of filtered and unfiltered samples were the same, showing that for these lake water samples filtering was not necessary. However, with higher turbidities there may be an interference. For this reason all samples are filtered through prewashed filters.

Interferences

Murphy and Riley (M-15) provided information on interferences of several ions with their non-extraction method. Ions investigated were copper, iron, arsenic, silicon, vanadium, and germanium. Only arsenic interfered appreciably when present in concentration of 1.0 mg/l. At the concentrations normally found in sea water none of these ions would interfere to any extent. It was also noted that in every case the interference was much less than that found in the Stannous Chloride Method. For the non-extraction method Strickland and

Parsons (S-20) reported that silica caused no interference, and interference from arsenic normally was negligible. With extraction this will apply even more so. Henricksen (H-16) reported on silica interference with the Stannous chloride method (H-9), and suggested changes to the method which eliminate this interference. There was no work done on interferences of this type in this investigation, but at the levels of concentration for possible interfering ions in Great Lakes waters no significant interference is expected.

IV-2.2 AUTOMATIC ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE)

Ascorbic Acid Method

The manual ascorbic acid method without extraction was adapted for the Technicon Autoanalyzer after Chan and Riley (C-2). The equipment consists of the following: Automatic Sampler, Proportioning Pump, Manifold, Heating Bath, Colorimeter, Recorder and Mixing Coils. The flow diagram was similar to Chan and Riley (C-2). The mixed reagent was prepared as for the manual analysis. The wavelength of 650 m μ had to be used since no filters close to the optimum wavelength of 880 m μ were available. This may in part account for the poor results obtained. The experiment was tried at temperatures of 25°C and 70°C, and then cooled to room temperature. Range expansion of 1X, 2X, 4X and 10X was used. The following was observed:

1. Sample cups must be acid washed, otherwise erratic results are obtained.

2. $70^{\circ}C$ temperature in heating bath gave unsteady base line and peaks.
3. 10X range expansion gave unsteady baseline and peaks.
4. Unless acid wash cups were interposed between each sample cup the recorder trace did not return to the baseline. With a 2:1 cam (sampling:wash) and wash cup interposed this provides a sampling to wash ratio of 1:2.
5. Even with 4) there is a slight drift of increasing optical density in the baseline. Fast acid wash with 2-speed proportioning pump returns baseline to original position. Fig. 17 shows an actual recorder trace of standards in the range of 5-100 $\mu g/l$ PO_4. Further work on Ascorbic Acid Method was discontinued, in favour of the Stannous Chloride Method. As the latter method gave good results, as described below, no further work on the Ascorbic Acid Automatic Method was done. However, with the proper filters, 880 m μ, and further development work, there is no reason why the method should not give satisfactory results in this range.

Stannous Chloride Method

The method used is a modification of Gales and Julian (G-2). The procedure and flow diagram are given in Appendix A. The method gave good results over the range of 0.01 - 1.0 mg/l PO_4, using 1X, 2X and 4X range expansion. A typical recorder trace of standards is shown in Fig. 18.

To determine the precision of the method ten determinations

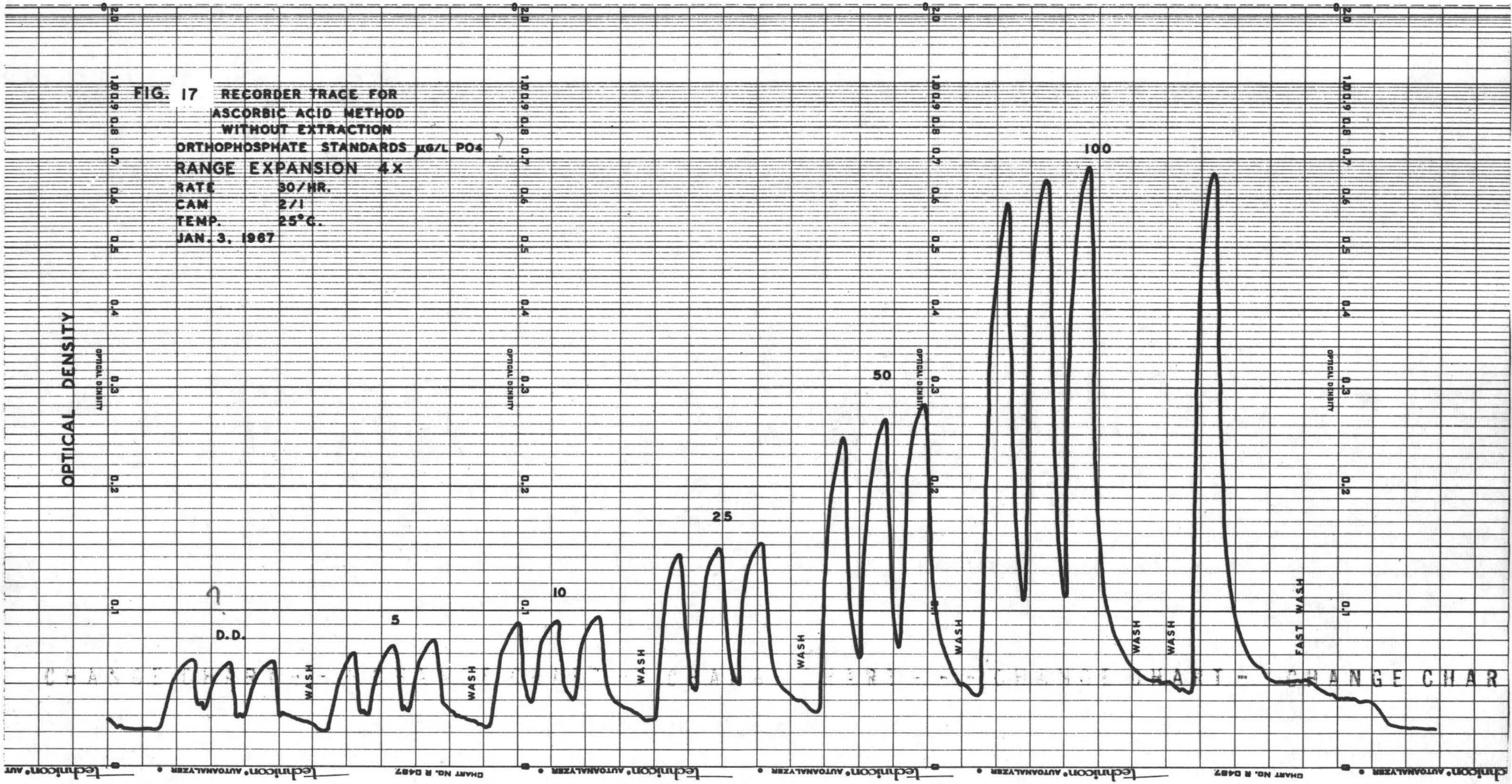


FIG. 17 RECORDER TRACE FOR ASCORBIC ACID METHOD WITHOUT EXTRACTION

ORTHOPHOSPHATE STANDARDS µG/L PO4

RANGE EXPANSION 4X

RATE 30/HR.

CAM 2/1

TEMP. 25°C.

JAN. 3, 1967

Fig 17

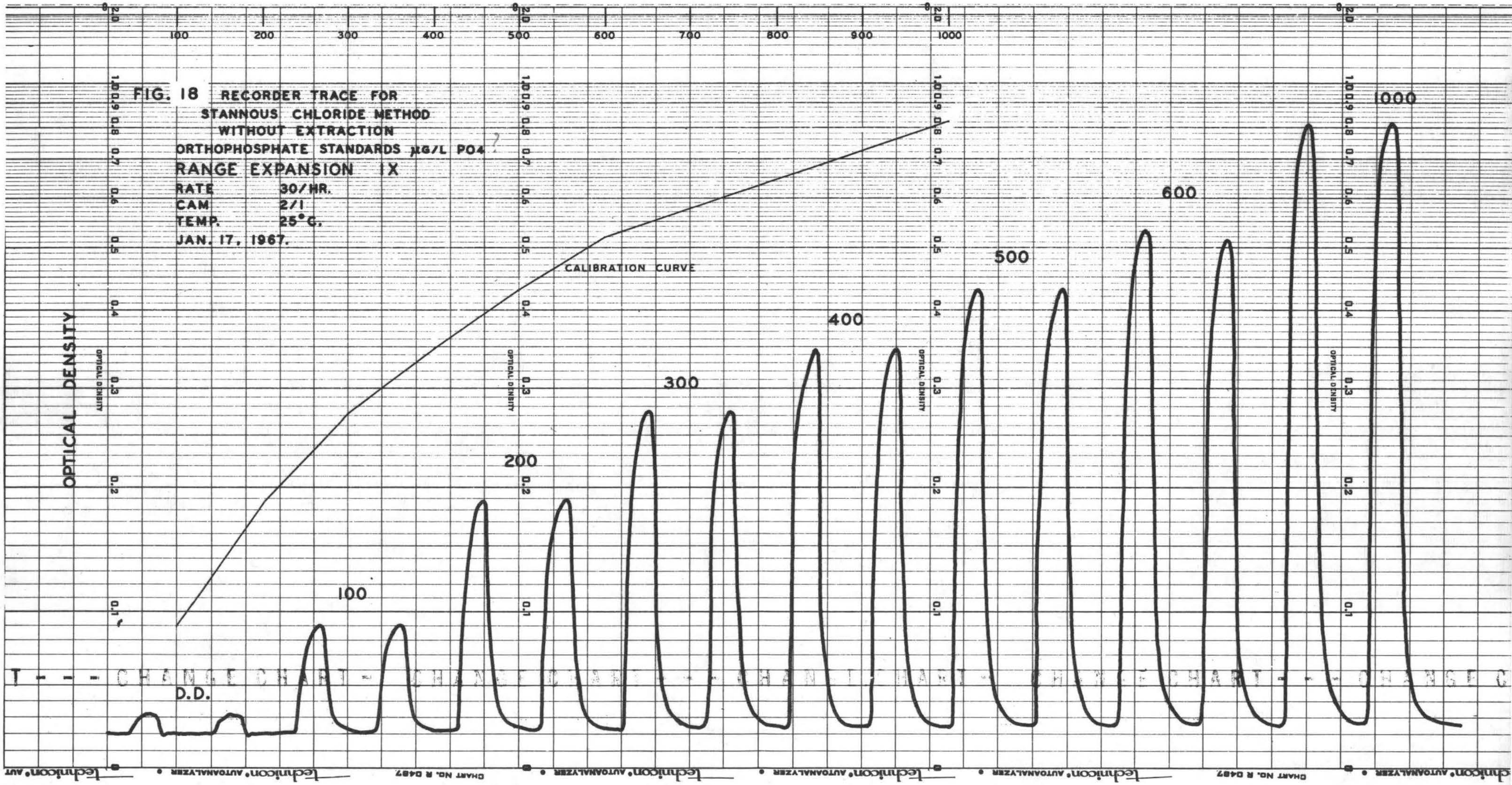


FIG. 18 RECORDER TRACE FOR
STANNOUS CHLORIDE METHOD
WITHOUT EXTRACTION
ORTHOPHOSPHATE STANDARDS μG/L PO4 ?
RANGE EXPANSION 1X
RATE 30/HR.
CAM 2/1
TEMP. 25°C.
JAN. 17, 1967.

Fig 18

each were done at two levels with the following results.

	0.5 mg/l PO_4 1X Range Expansion Optical Density	0.05 mg/l PO_4 4X Range Expansion Optical Density
Mean	0.319	0.206
Std. Deviation	0.0038	0.0049
95 percent Confidence Limit:	0.319 ± 0.0076	0.206 ± 0.0098
	0.5 ± 0.020 mg/l PO_4	0.05 ± 0.0025 mg/l PO_4

IV-2.3 MANUAL AND SEMIAUTOMATIC ANALYSIS FOR TOTAL PHOSPHORUS

The literature survey revealed a number of different methods that could be used for total phosphorus analysis on lake water and lake water plus added condensed phosphates. Particularly on the latter type of sample, where total phosphorus essentially amounts to total inorganic phosphorus, probably all methods will give satisfactory results. Due to the simplicity of the method and its previous use with an autoanalyzer the Persulfate Digestion Method of Gales and Julian (G-1) was selected for trial. The details of the digestion procedure is given in Appendix A, Method 3a. Standards must be subjected to the digestion procedure, before automatic analysis since the acid concentration is slightly different from the orthophosphate procedure. Test samples of lake water with varying amounts of added sodium tripolyphosphate were prepared and analyzed for total phosphorus by the Persulfate Digestion Method, as per Appendix A, Method 3a. The results are shown below.

Lake water Sample:		
	Total Phosphorus	0.074 mg/l PO_4
	Orthophosphate	0.039 mg/l PO_4

Added TPP mg/l PO_4	Additional total phosphorus measured mg/l PO_4
0.50	0.52
	0.48
	0.51
1.50	1.47
	1.52
	1.54

IV-2.4 CONDENSED PHOSPHATES

Gales and Julian (G-2), which was the major reference from which the automatic analysis for orthophosphate was prepared, recommends the addition of 1 ml of a sulfuric acid solution (310 ml conc. H_2SO_4 per liter of solution) to a 50 ml sample. Overnight standing will hydrolyze any condensed phosphates present. This was tried on distilled water samples to which sodium tripolyphosphate was added. Total phosphorus and orthophosphate determinations according to the methods in Appendix A were also carried out. The results are shown below.

Time after Addition of TPP	Added: 2.60 mg/l PO_4 of TPP. Incubation Temp. 20°C			Added: 2.30 mg/l PO_4 of TPP. Incubation Temp. 4°C		
	FTP	OP	OP+CP	FTP	OP	OP+CP
hrs	mg/l PO_4					
1	2.55	0.32	1.25	2.35	0.08	0.60
2	2.60	0.41	1.30	2.25	0.10	0.56
4	2.50	0.45	1.30	2.30	0.11	0.55
6	2.60	0.48	1.26	2.25	0.13	0.56
10	2.60	0.65	1.26	2.25	0.18	0.55
24	2.60	0.67	1.90[3]	2.25	0.20	0.63[3]
48	2.60	0.77	1.70[2]	2.25	0.23	0.54[2]
72	2.50	0.88	1.60[1]	2.30	0.23	0.47[1]
120	2.50	1.30	2.05[3]	2.30	0.30	0.60[3]

The time of overnight hydrolysis in acid solution was twelve hours, unless otherwise shown. If this were sufficient the results of FTP and OP+CP for this artificial sample should be the same. The results clearly indicate that overnight acid hydrolysis was not sufficient to hydrolyze all of the condensed phosphates in the sample. On four samples as shown the time of acid hydrolysis was increased to 1, 2 and 3 days. This caused, as expected, an increase in hydrolysis, but even after three days the highest value only measured about 80 percent of the phosphate present in the sample. This procedure was therefore considered unsatisfactory. However, for distilled water samples and for filtered lake water samples, to which condensed phosphates in concentration of 0.5 mg/l PO_4 or higher was added, Total Phosphorus is synomymous with ortho-plus condensed phosphate. Therefore the Total Phosphorus-Persulfate Digestion Method was used in these cases, and condensed phosphates obtained by difference.

IV-2.5 DIFFERENTIAL ANALYSIS OF A CONDENSED PHOSPHATE MIXTURE BY ION EXCHANGE CHROMATOGRAPHY

After study of the literature on the several available methods for the differential analysis of condensed phosphate mixtures the decision was made to try ion exchange chromatography. This decision was based on the following considerations.

1. Only the addition of an inexpensive ion exchange column to the available autoanalyzer equipment was necessary to be able to perform the analysis.
2. This method appeared to be the most likely one to succeed in obtaining quantitative results at the low concentrations, wastewater levels (50 mg/l PO_4 downwards) and lake water levels (0.5 mg/l PO_4 downward) necessary for this work.

The details of the method used in this work are given in Appendix A. The development work necessary to achieve success is described below for lake water and in IV-3 for wastewater.

Stannous Chloride Method

In order to extend the method to lake water levels the experimental apparatus was first set up as in the aminonaphtholsulfonic acid method (see IV-3.4) substituting the Stannous Chloride Detection Method after the digestion procedure. The sulfuric acid content was brought to the required level by utilization of the acid in the digestion procedure and adding the remaining amount in the ammonium molybdate solution. Highly unreliable colour development was the result of this. A blue precipitate formed when the sample stream was contacted with the stannous chloride solution, probably due to the fact that the ammonium molybdate solution was not "acidified" when it entered the sample stream. The reagents combining with the sample stream were made as concentrated as possible to keep the actual phosphate concentration in the stream at a maximum.

It was found that two factors affected colour development.

1. The concentration of sulfuric acid in the system. This appeared to vary due to small difference in the digestion.
2. The location of sources of acid entering the system.

The acid concentration in the stream was purposely varied with the result that too little acid caused fast total colour development even in the absence of phosphates while too much acid caused lack of colour in the presence of phosphates. To overcome the above difficulties the acid in the sample stream for digestion purposes, was neutralized by the addition of a NaOH stream after digestion. This proved effective.

The sample size for near-full scale deflection on the recorder is 30 μg PO_4. Thus for a sample with an initial concentration of TPP of 15 mg/l PO_4, 2 ml are put through the column. For samples of 0.5 mg/l initial concentration the sample size becomes quite large, 60 ml. In this case samples were drawn through the column by application of vacuum from an air ejector. Tests showed that this did not effect the amount of phosphate absorbed by the column.

The final flow diagram is shown in Appendix A. It represents the sum of about two weeks of trial runs before success was achieved. A typical response curve is shown in Fig. 19.

Correction Factor

Wash-out of the column after analysis with 1 percent HCl solution produced a small peak. This suggested that some phosphate may be retained in the column during the gradient elution. To insure that the differential phosphate analysis represents the actual composition of the mixture of ortho-, pyro- and tripolyphosphate the following experiment was designed.

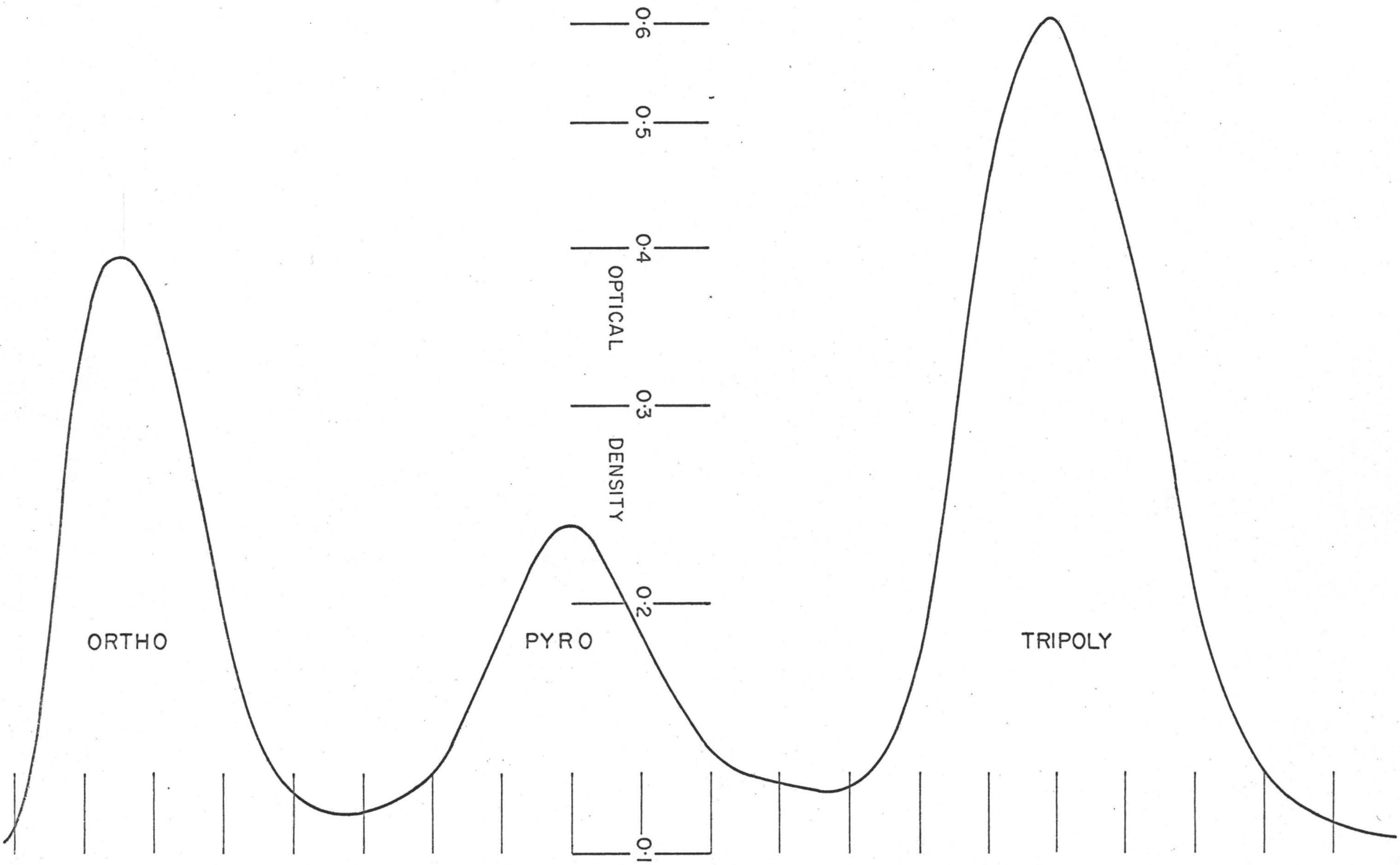


Figure 19. Elution curve of condensed phosphate mixture. Medium: Lake Ontario water, added tripolyphosphate 0.5mg/l PO_4.

Total Phosphorus Concentration: 15 mg/l PO_4

	Concentration range of prepared samples		
Sample	Percent OP	Percent PP	Percent TPP
1	5.0	11.7	83.3
2	30.0	11.2	58.8
3	45.0	10.9	44.1
4	60.0	10.6	29.4
5	85.0	10.1	4.9

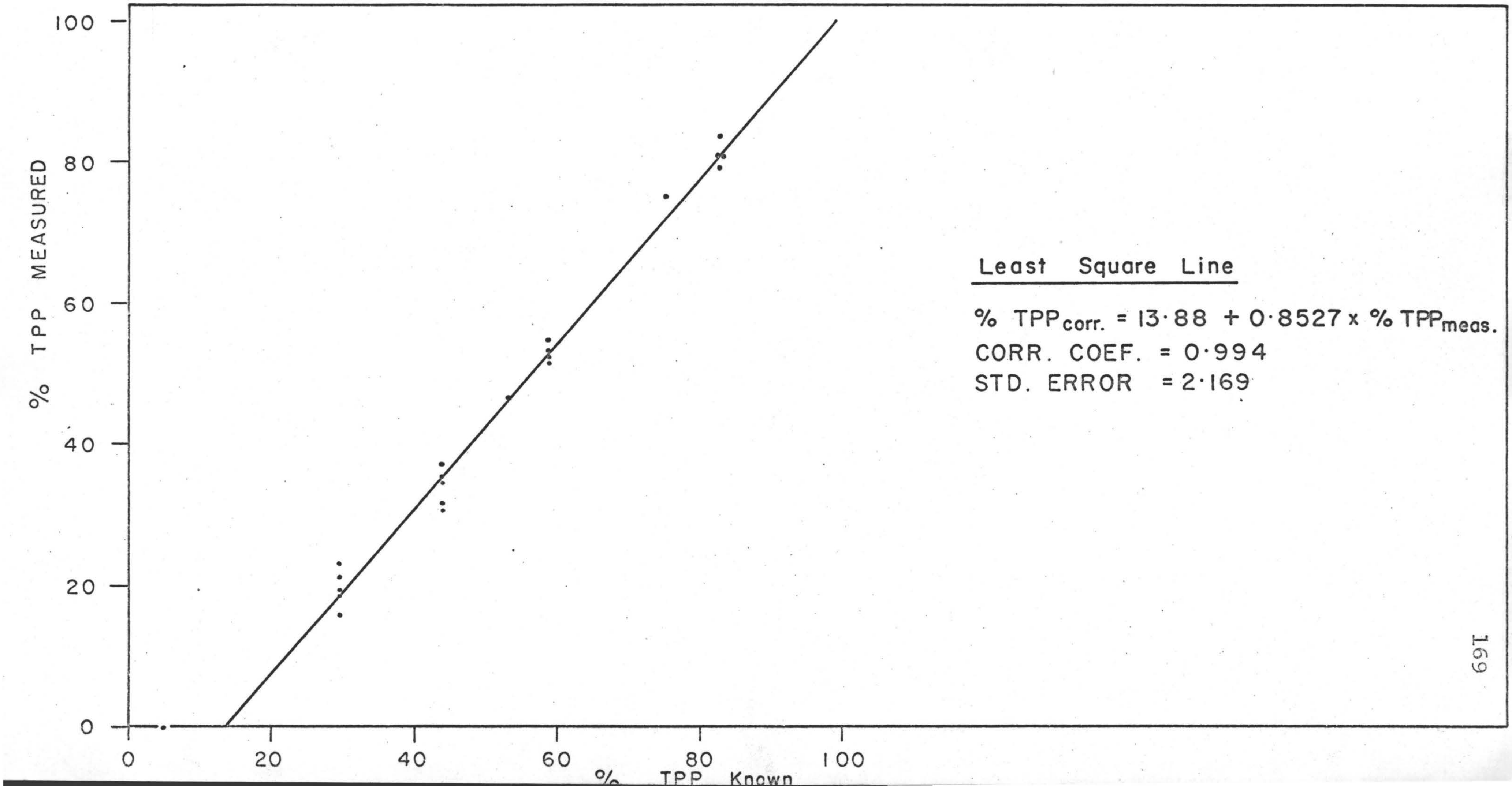
The majority of actual experiments on the various media were to be done by adding tripolyphosphate. In the hydrolysis of tripolyphosphate to pyro- and orthophosphate, the percentage of pyrophosphate in the mixture varies from zero to about twenty percent. For this reason the percentage of pyrophosphate was kept constant at about ten percent.

The above experiment was repeated five times. From these data it was apparent that correction factors were necessary, which need to be applied to the measured areas of ortho-, pyro- and tripolyphosphate. The experimental results are shown in Figs. 20 and 21. A typical result is given in Table XXVII.

The following comments are made:

1. The data in Table XXVII indicate that the tripolyphosphate measured values are lower and the ortho- and pyrophosphate measured values higher. This is in agreement with a statement of Lundgren and Loeb (L-10) :

Figure 20. Correction factor graph for tripoly phosphate in a mixture of ortho-, pyro- and tripoly phosphate by ion exchange chromatography.



Least Square Line

$\% \ TPP_{corr.} = 13{\cdot}88 + 0{\cdot}8527 \times \% \ TPP_{meas.}$

CORR. COEF. = 0·994

STD. ERROR = 2·169

Figure 21. Correction factor graph for ortho phosphate in a mixture of ortho-, pyro-, and tripoly phosphate by ion exchange chromatography.

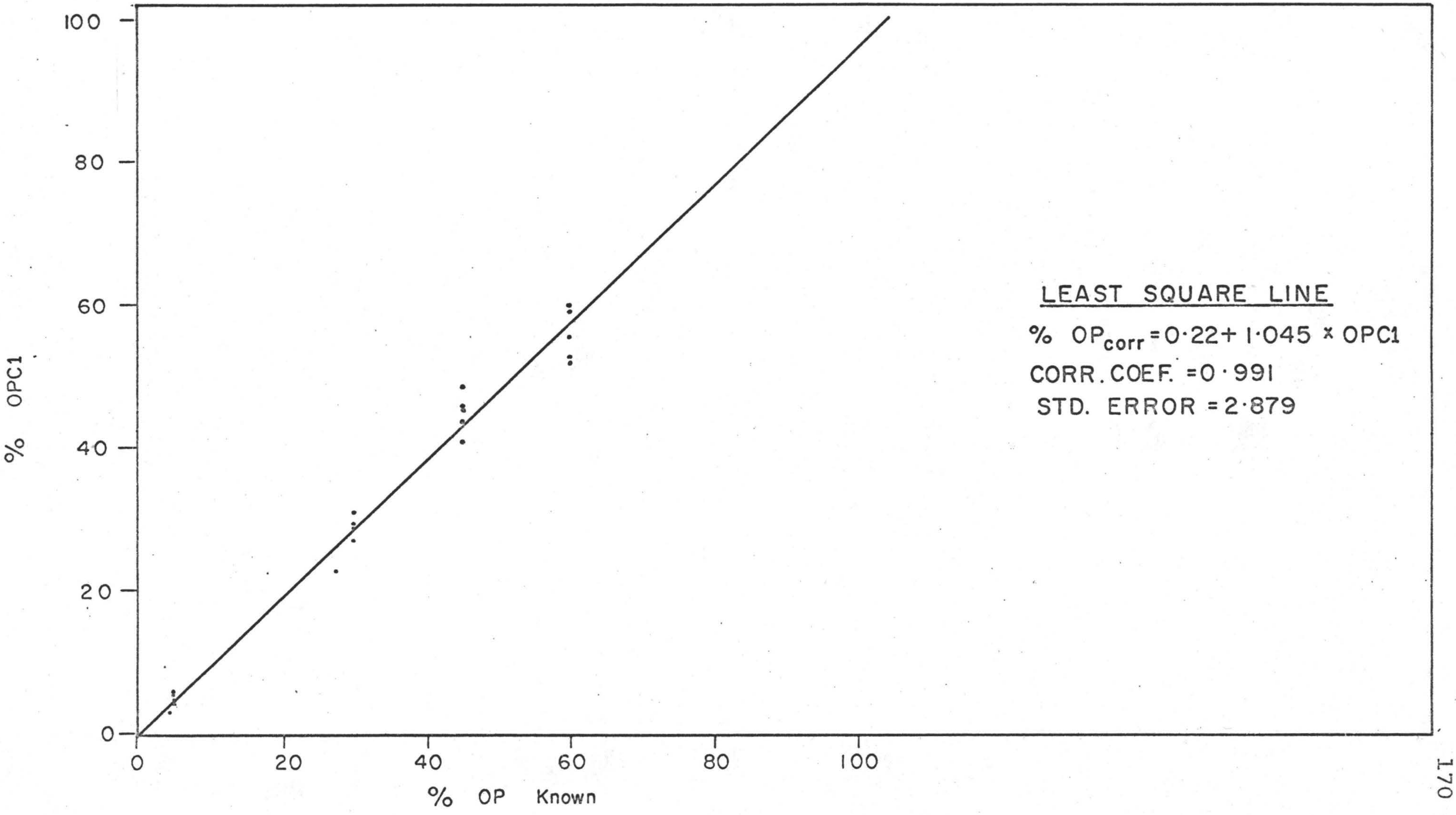


TABLE XXVII: MEASURED PHOSPHORUS DISTRIBUTION (%) OF KNOWN ORTHO-, PYRO- AND TRIPOLYPHOSPHATE MIXTURE

SAMPLE	% OP			% PP			% TPP		
	KNOWN	MEASURED	CORRECTED	KNOWN	MEASURED	CORRECTED	KNOWN	MEASURED	CORRECTED
1	5.0	4.7	4.6	11.7	14.9	12.9	83.3	80.4	82.4
2	30.0	33.6	30.1	11.2	13.4	12.1	58.8	53.0	57.8
3	45.0	50.7	46.1	10.9	13.9	9.8	44.1	35.4	44.1
4	60.0	69.3	62.6	10.6	14.8	9.9	29.4	15.9	27.5
5	85.0	80.4	See Comment 1	10.1	19.6	See Comment 1	4.9	-	See Comment 1

> "Repetitive analysis of the same mixture at successively lower concentrations, down to the limit of this most sensitive range (10 µg P_2O_5) results in successively higher ortho- and pyro-values and lower tripolyphosphate values."

No response is obtained for a sample containing about 5 percent TPP. The least square linear regression of the data in Fig. 20 indicates that below 13.9 percent (or approximately 4 µg) tripolyphosphate is not detectable. It is postulated that this amount is retained in the column, and is washed out only with the 1 percent HCl wash solution. Sample 5 was therefore not included as a point in the statistical analysis.

2. After correction of the measured tripolyphosphate values according to the equation shown in Fig. 20, the orthophosphate and pyrophosphate measured values are adjusted proportionally. This adjusted ortho-value (referred to as OPC1) is plotted against known percent ortho in Fig. 21, and a linear regression line is calculated. As can be seen the OPC1 values are somewhat lower than the known values. A correction is therefore applied to the OPC1 value according to the equation shown. This second correction may be necessary due to a slightly lower area response for ortho-, than for pyro- and tripolyphosphate. This is in agreement with the findings of Czech and Hrycyshyn (C-17). No physical explanation is given.

3. The corrected pyrophosphate value is obtained by subtracting the corrected ortho- and tripolyphosphate value

from 100 percent.

4. A computer program was written for the correction of data.

5. The recovery of total phosphorus in the mixture, as indicated by the total area response, remains relatively constant (± 5 percent). When the orthophosphate ion constitutes the major fraction in a mixture the total area is lower due to the lower area response for orthophosphate.

6. To ascertain that a larger or smaller than 10 percent pyrophosphate fraction does not alter the correction factors calculated, the following experiment was carried out.

	Percent OP			Percent PP			Percent TPP		
Sample	Known	Meas.	Corr.	Known	Meas.	Corr.	Known	Meas.	Corr.
1	50.0	57.9	50-51	1.0	Trace	Trace to 1.0	49.0	42.1	48.9
2	33.3	38.6	35.0	33.3	36.0	29.5	33.3	25.4	35.5

The results are within the error found for the previous experiments.

7. Standard Deviation: From the data of the five runs the standard deviation for ortho-, pyro- and tripolyphosphate measurement at each level were calculated. The results are shown below.

Relative Concentration of

Ortho-			Pyro-			Tripoly-		
	Measured			Measured			Measured	
Known	Mean	Std. Dev.	Known	Mean	Std. Dev.	Known	Mean	Std. Dev.
5.0	5.3	1.01	$\sim$11.0	10.9	1.70	5.0	see comment 1	
30.0	30.6	1.54				29.4	30.7	2.46
45.0	46.6	3.08				44.4	42.6	2.64
60.0	58.4	3.74				58.8	58.9	1.04
85.0	see comment 1					83.3	83.1	1.46

8. Interferences: With lake water samples to which condensed phosphates were added, the elution curves at times had some sharp peaks superimposed on the Gaussian phosphate curves. The data analysis for phosphate distribution was still possible but more difficult and less accurate. It was suspected that some ions present in lake water cause the interference. These ions may be partly retained on the column, are then eluted, and must also react with Stannous Chloride Method to give a blue colour complex. Several trial experiments were made with distilled water to which ions common in lake water were added in naturally occurring concentrations (Co_3 =, HCO_3^- SO_4=, SiO_2, Fe). While some interferences were observed in these artificial samples, it was not possible to identify and eliminate the interferences from the lake water samples. Further work will be required on this.

IV-3 APPLICATION TO WASTEWATERS

IV-3.1 MANUAL ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE), CONDENSED PHOSPHATES AND TOTAL PHOSPHORUS

The literature survey initially did not reveal a recommended method for the analysis of phosphorus in wastewater. The decision was made to try the ascorbic acid method without extraction. A wastewater sample, primarily domestic sewage but with some industrial waste, was obtained. The sample was analyzed for orthophosphate and total phosphorus, both by the Stannous Chloride Method of Standard Methods (A-3) and the Ascorbic Acid Method, described in Appendix A, Method 1b and 3b. Orthophosphate was added to the wastewater sample in varying amounts and analyzed by the Stannous Chloride Method and the Ascorbic Acid Method for orthophosphate and total phosphorus, using the Persulfate Digestion Method. The phosphorus values measured with the Stannous Chloride Method were from 10-30 percent lower than the theoretical values, due to some interference. The results of the ascorbic acid method are shown in Fig. 23 for domestic waste and a meat packing waste. The difference between the measured amounts and the known amounts are within the accuracy of the ascorbic acid method. From this work it was concluded that the ascorbic acid method does not suffer from interference from other materials contained in wastewater. For industrial wastes this may need to be checked for each waste. A calibration curve for orthophosphate (20:1 Dilution) and total phosphorus (50:1)

Figure 22. Calibration curve for phosphorons in wastewater by ascorbic acid method.

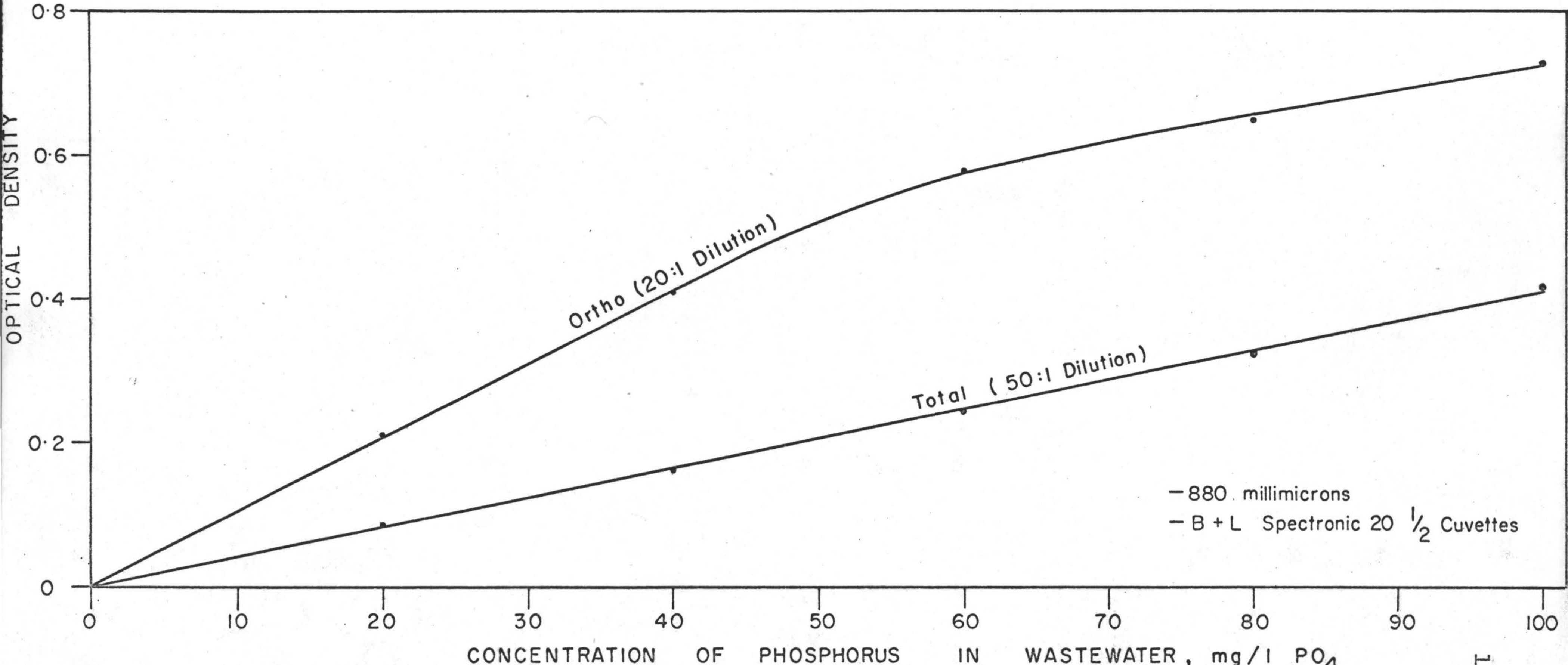
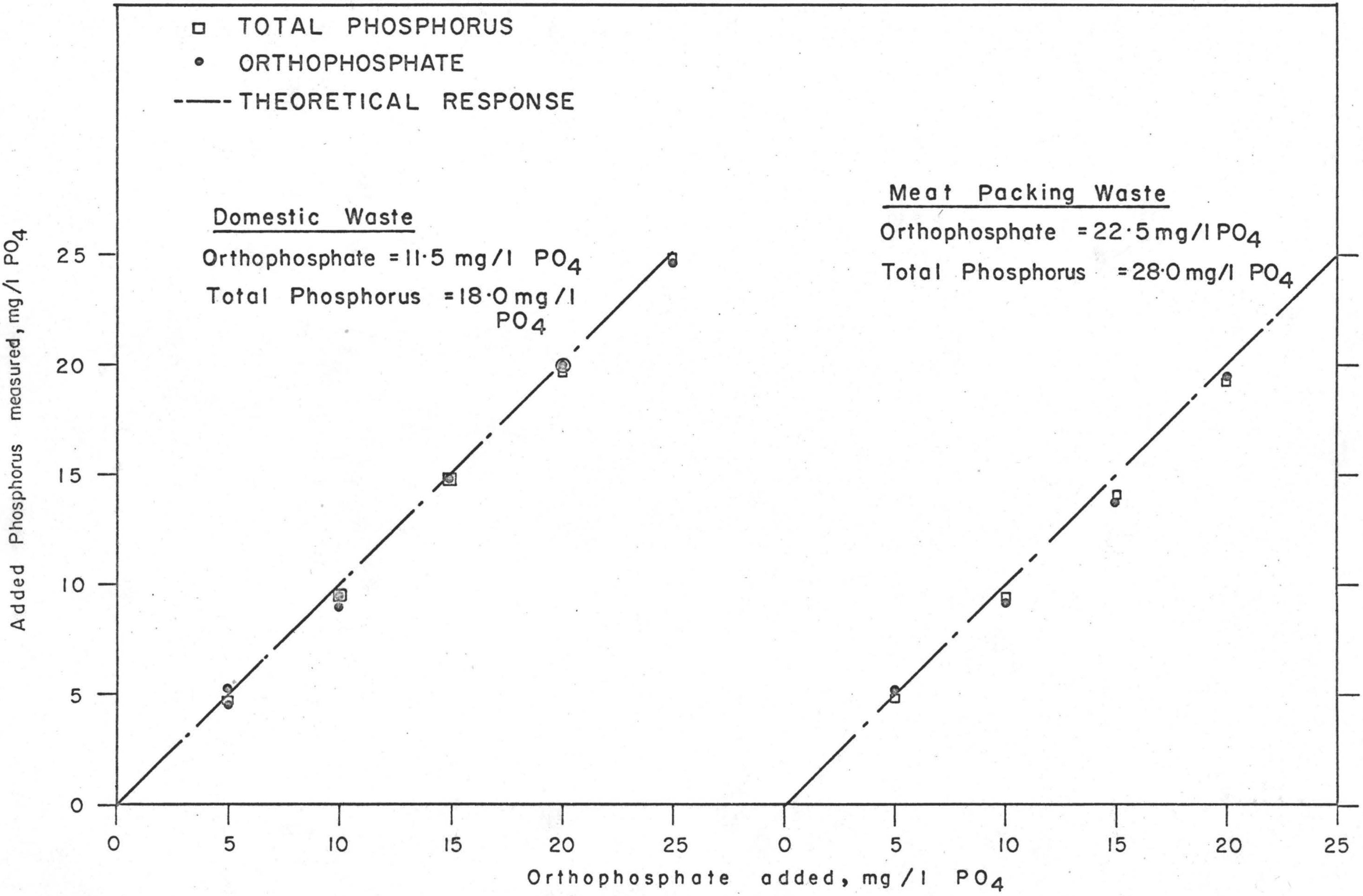


Figure 23. Phosphorus measurement in wastewater by manual ascorbic acid method.



dilution is shown in Fig. 22. With the dilution of 20:1 used, Beer's Law is obeyed to about 50 mg/l PO_4 orthophosphate.

As mentioned in the literature survey a very recent publication by Jankovic, Mitchell and Buzzell Jr. (J-1) also examined the problem of phosphorus measurement in wastewaters. Their findings on the use of the ascorbic acid method and the digestion with potassium persulfate provided support for the methods adopted in this work. There are small differences in the method suggested, which do not appear to be significant. The complete write-up of the method used in this work is given in Appendix A.

IV-3.2 AUTOMATIC ANALYSIS FOR REACTIVE PHOSPHATE, (ORTHO-PHOSPHATE), CONDENSED PHOSPHATES AND TOTAL PHOSPHORUS

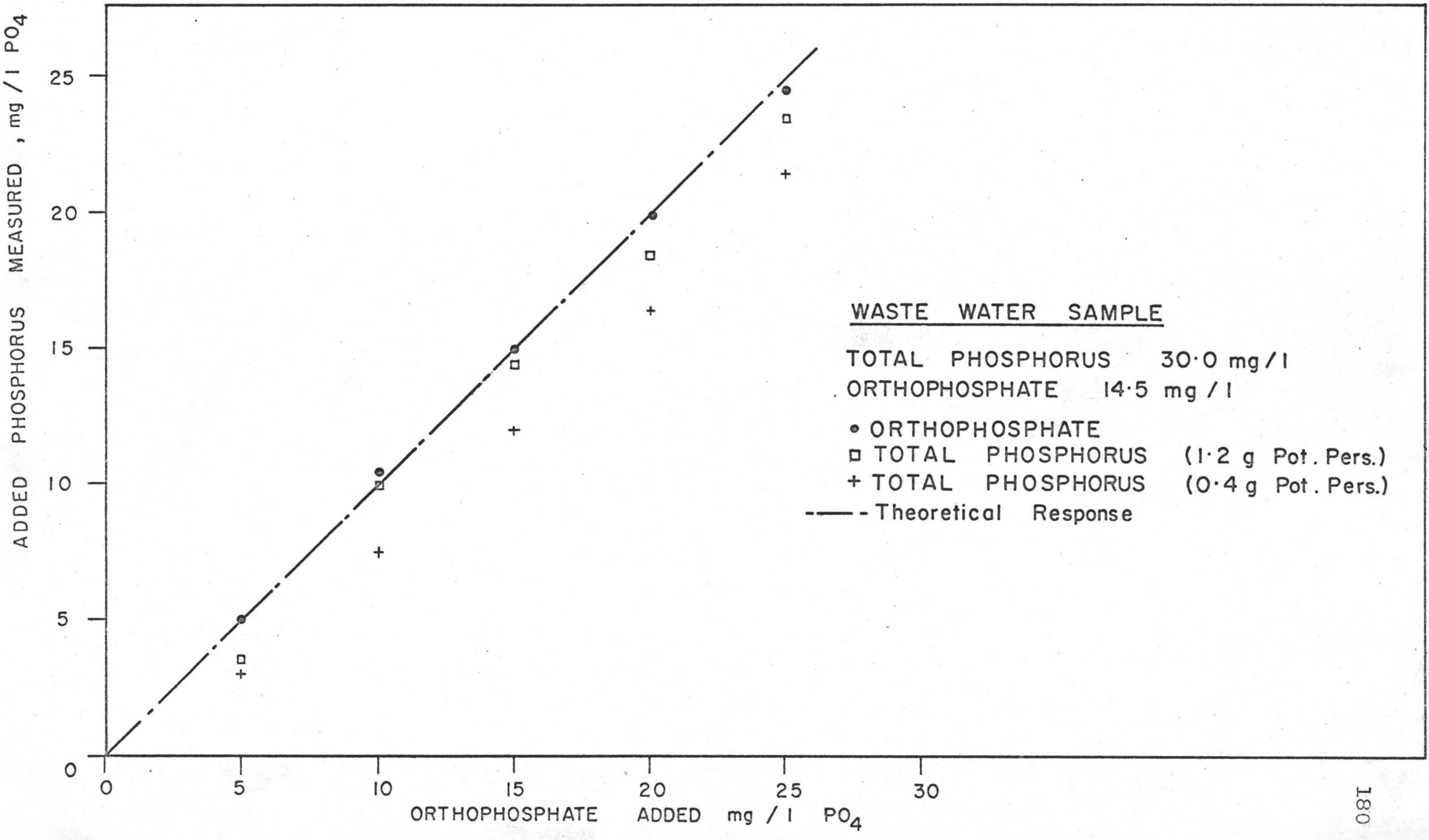
The Amino-naphtolsulfonic Acid Method of Standard Methods (A-3) was adapted to the autoanalyzer. The flow diagram and details of the method are given in Appendix A. The method was first tried on distilled water samples in the range of 1 to 100 mg/l. Subsequently the method was checked for possible interferences in sewage samples.

To determine the precision of the method ten determinations were done at each of two levels with the following result.

	100 mg/l PO_4 1 x range expansion Optical Density	5 mg/l PO_4 1 x range expansion Optical Density
Mean:	0.863	0.046
Std. Deviation:	0.0100	0.0022
95 percent Conf. Lt.:	0.863 ± 0.020	0.046 ± 0.0044
From calibration curve:	100 ± 2.5 mg/l PO_4 for single determination	5 ± 0.50 mg/l PO_4

The response of the Amino-naphtolsulfonic Acid Automatic method to added orthophosphate in a wastewater sample was checked. A raw sewage sample, obtained from the Dundas Sewage Treatment Plant was filtered and orthophosphate ($K\ H_2PO_4$) was added in amounts from 5 to 25 mg/l PO_4. Orthophosphate and total phosphorus were determined. The total phosphorus method used initially was Method 3a), using 0.4 g of potassium persulfate per 30 ml sample. The results are shown in Fig. 24. It shows that there is no interference for the orthophosphate test. The total phosphorus values (+), using 0.4 g potassium persulfate gave results, which were too low. This was attributed to an insufficient amount of persulfate to carry out the digestion. This amount was therefore increased from 0.4 g to 1.2 g. The results obtained are shown on Fig. 24 and give satisfactory agreement. Method 3b for wastewater analysis uses therefore a larger amount of persulfate for wastewater analysis. The influence of varying the amount of

Figure 24. Phosphorus measurement in wastewater by aminonaptholsulfonic acid automatic method.



sulfuric acid solution (310 ml conc. H_2SO_4/liter of solution) from 0.5 to 2.0 ml per 30 ml sample was investigated. Potassium persulfate was kept constant at 1.2 g. The results showed no influence over this range.

IV-3.3 COMPARISON OF TOTAL PHOSPHORUS DIGESTION METHODS

To measure total phosphorus in wastewater three digestion methods (Persulfate, Perchloric Acid, and Sulfuric-Nitric Acid Method) were compared. The samples analyzed were activated sludge supernatant (in triplicate), 50 mg/l TPP standard, 50 mg/l OP standard, and a distilled water blank. The amino-naphtolsulfonic acid automatic method for orthophosphate analysis was used after the digestion step. The numbers shown below are averages of triplicates.

TABLE XXVIII: COMPARISON OF TOTAL PHOSPHORUS DIGESTION METHODS

	Persulfate Method	Perchloric Acid Method	Sulfuric-Nitric Acid Method
Distilled Water Blank	0.0	0.0	0.0
Orthophosphate (50 mg/l) in Distilled water	51.0	45.5	38.5
Sodium tripolyphosphate in distilled water (50 mg/l)	49.5	43.5	40.5
Activated Sludge Supernatant			
Sample 1	76.5	52.5	60.0
Sample 2	77.0	50.5	65.0
Sample 3	Sample lost	47.0	61.5

For details of each digestion method see:

Persulfate Method: Appendix A, Method 3b

Perchloric Acid Method: Lee, Clesceri and Fitzgerald (L-1)

Sulfuric Nitric Acid Method: Lee, Clesceri and Fitzgerald (L-1)

The standards run with the persulfate method were subjected to the persulfate digestion procedure. The samples of the perchloric acid and sulfuric nitric acid method were neutralized before analysis by the aminonaphtolsulfonic acid method. Comparison was made against orthophosphate standards. The results show the following:

1. All methods give no response for a distilled water blank.
2. The persulfate method gave good recovery of the ortho- and tripolyphosphate sample, and the highest results on the wastewater sample.
3. The results of the orthophosphate and the tripolyphosphate sample analyzed by the perchloric acid method and the sulfuric nitric acid method show that about 10 to 20 percent of the phosphorus content of the sample was lost in the analysis. The low results on the wastewater sample indicate the same. During the boiling of the 100 ml sample down to 1 ml it was noticed that a scale formed on the flask, which probably accounts for the loss of phosphorus. As other workers have used both these methods successfully the conclusion is drawn that further refinements in the technique of the digestion step would have to be acquired

to use these two methods. However, since the persulfate digestion method gave satisfactory results and is much simpler and faster it was selected as the method for total phosphorus analysis in this work.

IV-3.4 DIFFERENTIAL ANALYSIS OF A CONDENSED PHOSPHATE MIXTURE BY ION EXCHANGE CHROMATOGRAPHY

Aminonaphtholsulfonic Acid Method

The Ion Exchange Column, Gradient Elution Assembly and Digestion System were prepared according to Czech and Hrycyshyn (C-17). The Ion Exchange resin used was a quartenary Ammonium Anion Exchange resin. The Aminonaphtholsulfonic Acid Method was substituted for their Hydrazine Sulfate Method in order to develop sufficient colour in the range of sewage level (50 mg/1 PO_4). The complete flow diagram is given in Appendix A. Samples of total phosphorus concentration of 50 mg/1 and varying percentages of ortho-, pyro-, and tripolyphosphate were analyzed. The sample size applied was varied, about 500 μg PO_4 of any species present gave close to full scale deflection on the recorder. The effectiveness of the digestion system was checked by comparing the response to samples that were digested manually by the persulfate method with a sample put through the automatic digestion setup. The samples contained varying percentages of ortho-, pyro- and tripolyphosphate. The response on all samples was an ortho peak only, of equal areas, proving the effectiveness of the automatic digestion procedure.

To check on the precision of the method five samples of varying concentrations of ortho-, pyro-, and tripolyphosphate were analyzed. This experiment was repeated five times. A typical result is shown in Table XXIX.

TABLE XXIX: MEASURED PHOSPHORUS DISTRIBUTION (PERCENT) OF KNOWN ORTHO-, PYRO-, AND TRIPOLYPHOSPHATE MIXTURE (WASTEWATER LEVEL)

	Percent Ortho		Percent Pyro		Percent Tripoly	
Sample	Known	Measured	Known	Measured	Known	Measured
1	5.0	6.9	11.7	11.4	83.3	81.7
2	30.0	31.4	11.2	11.6	58.8	57.0
3	45.0	46.5	10.9	11.7	44.1	41.8
4	60.0	60.6	10.6	12.2	29.4	27.2
5	85.0	84.2	10.1	10.4	4.9	5.4

The data indicated that no correction factor was necessary at the sewage level of concentration. From the data of the five runs of five samples each, the standard deviation for ortho-, pyro- and tripolyphosphate of each level were calculated. The results are shown below.

Relative Concentration of

Ortho-, Percent			Pyro-, Percent			Tripoly-, Percent		
	Measured			Measured			Measured	
Known	Mean	Std. Dev.	Known	Mean	Std. Dev.	Known	Mean	Std. Dev.
5.0	5.5	±1.05	11.0	10.9	±1.09	4.9	4.6	±1.28
30.0	30.5	±1.20				29.4	28.4	±1.59
45.0	44.8	±1.44				44.1	44.0	±1.35
60.0	60.4	±1.68				58.8	58.5	±1.26
85.0	84.4	±2.00				83.3	83.5	±1.44

For wastewater samples the difference between the Filtered Total Phosphorus (FTP) determination and Filtered Orthophosphate (OP) will give the sum of condensed phosphates, either naturally present or added, and any soluble organic phosphorus compounds naturally present. As discussed in Chapter V under Wastewater Studies, in some samples organic phosphorus compounds may have been present. By means of simultaneous analysis of a wastewater sample for Filtered Total Phosphorus (FTP), Filtered Orthophosphate (OP) and differential condensed phosphate analysis an estimate of the soluble organic phosphorus and any higher complex condensed phosphates present can be obtained at the same time. This is done in the following way

$$\underset{\text{(from direct analysis)}}{\text{OP, mg/l } PO_4} = X. \times \underset{\text{(from differential analysis)}}{\text{orthophosphate, \%}}$$

where $X = OP + PP + TPP$, and calculated from above equation

$$\text{Organic phosphorus plus any complex condensed phosphates} = \underset{\text{(From direct analysis)}}{FTP} - X$$

To check the response of the differential condensed phosphate analysis in wastewater, pyrophosphate and tripolyphosphate was added to Dundas S.T.P. final effluent. The results are shown below:

<u>Final Effluent</u> FTP = 12.0 mg/l PO_4
OP = 9.5 "
and OP = 80.2%, PP = 7.5% and TPP = 12.3%
Therefore X = 9.5/.802 ≐ 11.8
Est. Sol. Organic Phosphorus = 0.2
PP = 0.9
TP = 1.4

It is realized that the soluble organic phosphorus value may be explained simply by errors in the measurement of orthophosphate, rather than attribute it to organic phosphorus.

To this 20 mg/l PO_4 each of PP and TPP were added.

		Measured Comp.	
	Known Comp.	Direct Analysis	Diff. Analysis
FTP	52.0 mg/l PO_4	48.5 mg/l PO_4	
OP	9.5 mg/l PO_4 or 18.3%	9.0 mg/l PO_4	19.1%
PP	20.9 mg/l PO_4 or 40.5%		40.9%
TPP	21.4 mg/l PO_4 or 41.4%		40.0%
X	51.8 mg/l PO_4 or 100.0%		
Sol. Org.	0.2 mg/l PO_4		

In both cases the comparison between known composition and measured composition of OP, PP and TPP in the wastewater samples is well within the variation calculated in distilled water samples.

The effect of the presence of large amounts of organic phosphorus on the elution curves of ortho-, pyro-, and tripolyphosphate was investigated. Samples were prepared that contained 1 g/l adenosine triphosphate and 1 g/l of ortho-, pyro-, or tripolyphosphate. There was no apparent separation of adenosine triphosphate, but diffusion over approximately the same length of time as it takes to separate ortho-, pyro-, and tripolyphosphate. The organic phosphorus interfered with the development of Gaussian curves for the other phosphorus compounds. If Gaussion curves are obtained on a wastewater sample it is therefore likely that organic phosphorus compounds are not present, or only in small amounts. A variety of organic phosphorus compounds would need to be tested by differential analysis.

V EXPERIMENTAL STUDIES AND DISCUSSION

V-1 MATERIALS AND METHODS

Chemicals used in this work were of reagent grade with the exception of sodium tripolyphosphate ($Na_5 P_3 O_{10}$), which was of High Purity, anhydrous. It was obtained through the courtesy of Mr. R. N. Bell, Stauffer Chemical Co. Their analysis gave 98 percent tripolyphosphate, 2 percent pyrophosphate. This was also checked in this work and found to be correct.

Stock phosphate solutions were prepared in appropriate strength by using double distilled (glass) water. Potassium dihydrogen phosphate ($K H_2 PO_4$), sodium pyrophosphate ($Na_4 P_2 O_7 . 10 H_2O$) and sodium tripolyphosphate ($Na_5 P_3 O_{10}$) were used. The stock solutions were stored at 4°C.

Experimental vessels for batch experiments varied in size from 2 liter Erlenmeyer flasks to 5 gallon carboys. The size of vessel was chosen so that at least one-third of the batch sample was still remaining after all test sampling had been completed. The vessels were stored in Freas incubators for temperature control. The sensitivity of temperature control was ± 1°C. Magnetic stirrers were used in all experiments. Aeration was carried out in certain experiments as noted. The air was double-filtered and water-saturated. Lighting conditions were chosen to simulate natural conditions in this region of Lake Ontario. One 15-watt fluorescent daylight lamp was installed in each incubator to provide approximately 200 foot-candles. It was controlled by a day-night timer, which was set to give 12 hours light and 12 hours darkness. Comments and analysis of the various media used are given under each particular experiment.

The experimental methods used for phosphorus analysis are stated in Appendix A. All other measurements were carried out according to Standard Methods (A-3).

V-2 DISTILLED WATER STUDIES

Experiments on the rate of hydrolysis of condensed phosphates in distilled water were primarily carried out to be able to compare results of this study to other workers. Due to the differences in lake water and wastewater between this study and others, only an order of magnitude comparison is possible for these media. In order to allow a proper evaluation of the literature data at high concentrations (Fig. 11 and 12), experiments were carried out in the range of concentration where no literature data were available. The effect of concentration on the rate and order of hydrolysis at low concentrations was investigated in a series of experiments. Finally, the effect of pH on the rate of hydrolysis at low concentrations was checked.

Experimental Results and Analysis of Data

Table XXX summarizes all experimental studies in distilled water. Data of individual series are presented in graphical form.

TABLE XXX: SUMMARY OF EXPERIMENTAL WORK IN DISTILLED WATER

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	CONDENSED PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL CONDITIONS				TYPE OF ANALYSIS	REMARKS
			TYPE ADDED	INITIAL CONC. mg/l PO_4		TEMP. ^oC	pH	LIGHTING	AERATION		
IX	Oct.67	Rate of hydrolysis study at high concentration (non-sterile)	TPP	50	698	20	7.3	D-N	Cont.	UTP, OP, Diff. Anal.	
X	Oct.-Nov.67	Rate of hydrolysis study on sterile distilled water for concentration effect	TPP	50	1310	20	7.2-7.4	D-N	Mag. Mix	UTP, OP Diff. Anal.	
			TPP	15	1311	20	7.2	"	"	"	
			TPP	2.5	106	20	7.1-7.2	"	"	"	
XI	Jan.68	Rate of hydrolysis study on sterile distilled water for concentration effect	TPP	15	698	20	6.8-7.2	D-N	Mag. Mix	Diff-Anal.	
			TPP	2.5	191	20	6.7-6.3	"	"	"	
			TPP	0.5	118	20	5.7-6.1	"	"	"	
			TPP	0.5 (buffered)	194	20	7.5	"	"	"	Dist.water buffered with NaH CO_3 to pH = 7.5

TABLE XXX -(Cont'd.)

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	CONDENSED PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL CONDITIONS				TYPE OF ANALYSIS	REMARKS
			TYPE ADDED	INITIAL CONC. mg/l PO_4		TEMP. °C	pH	LIGHTING	AERATION		
XIV	Feb.-April 68	Rate of hydrolysis study on pyrophosphate in sterile distilled water. Effect of concentration	PP	50	1128	20	7.2-7.4	D-N	Mag.-Mix	Diff. Anal.	
			PP	15	1536	20	6.9-7.3	"	"	"	
			PP	2.5	336	20	6.4	"	"	"	
			PP	0.5	168	20	6.3	"	"	"	
XVII	April-May 68	Rate of hydrolysis study on tripolyphosphate in sterile distilled water. Effect of pH.	TPP	0.5	74	20	4.3	D-N	Mag.-Mix	Diff. Anal.	.01M sodium phtalate buffer
			TPP	0.5	373	20	6.8-7.0	"	"	"	No buffer added
			TPP	0.5	354	20	9.8-10.0	"	"	"	.01M borax buffer
XX	April-May 68	Rate of hydrolysis study on tripolyphosphate and pyrophosphate in sterile distilled water at high concentration	TPP	500	145	55	4.0	D-N	Mag.-Mix	Diff. Anal.	for additional point on literature data of Fig. 11 and 12.
			TPP	100	309	75	7.4	"	"	"	
			PP	500	144	55	4.0	"	"	"	
			PP	100	310	75	7.4	"	"	"	

SERIES XX - RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE AND PYROPHOSPHATE AT HIGH CONCENTRATION IN DISTILLED WATER

The purpose of these experiments is to provide data on the rate of hydrolysis of tripolyphosphate and pyrophosphate in distilled water at concentrations in the region of 100 to 500 mg/l PO_4. The results will be used for additional points on Fig. 11 and 12, in the area where no experimental data are available. High temperatures and low pH values had to be used in order to effect reasonably high conversion. In addition, the results can be used to check the independence of the rate of hydrolysis of pyrophosphate on the presence or absence of tripolyphosphate, and vice versa.

Experimental Conditions

Date: April-May 1968

Medium: Distilled water

Sample Preparation:

XX-1 500 mg/l PO_4 of TPP added, pH = 4.0
-2 500 mg/l PO_4 of PP added, pH = 4.0
-3 100 mg/l PO_4 of TPP added, pH = 7.4
-4 100 mg/l PO_4 of PP added, pH = 7.4

Incubation Temperature: XX-1,-2 55°C
XX-3,-4 75°C

Day-Night Lighting Conditions. Samples were mixed by magnetic stirrer.

Tests: Percent OP, Percent PP, Percent TPP, pH.

Experimental Data: These are presented in Fig. 25-1 to -5. In Fig. 25-5 rate constants k_1 are evaluated for XX-1 and -3, and rate constants k_2 for XX-2 and -4. Although the data for XX-3 appear to follow a zero-order law at the beginning and second-order law at the end, a first-order, straight line, fit was made, since all literature data in this concentration range report first-order hydrolysis. The value of k_1 obtained from XX-1, together with the value of k_2 from XX-2, were used to calculate the curves shown in Figs. 25-1 and -3 for the rate of hydrolysis of tripolyphosphate according to the theory of consecutive reactions (see Appendix B). As can be seen, a reasonably good agreement with the experimental data is evident. The same procedure resulted in rather poor comparison on Fig. 25-3. For this reason a value for k_2 was calculated from the experimental data of XX-3 directly. The agreement of these calculated curves with the data is still not very good due to the aforementioned deviation from a first-order response. The pH stayed constant throughout each experiment.

Rate of Hydrolysis

XX-1: $T = 55^\circ C$ $pH = 4.0$ $k_1 = 2.1 \times 10^{-4}\ min^{-1}$, $k_2 = 7.3 \times 10^{-5}\ min^{-1}$
-2: $T = 55^\circ C$ $pH = 4.0$ $k_2 = 7.3 \times 10^{-5}\ min^{-1}$
-3: $T = 75^\circ C$ $pH = 7.5$ $k_1 = 2.4 \times 10^{-4}\ min^{-1}$, $k_2 = 1.0 \times 10^{-4}\ min^{-1}$
-4: $T = 75^\circ C$ $pH = 7.5$ $k_2 = 4.9 \times 10^{-5}\ min^{-1}$

These rate constants were adjusted to $20^\circ C$ and $pH = 7.0$ by the methods of Chapter III and are shown below.

XX-1: $k_1 = 4.3 \times 10^{-7}\ \text{min}^{-1}$

-2: $k_2 = 1.4 \times 10^{-7}\ \text{min}^{-1}$

-3: $k_1 = 2.7 \times 10^{-7}\ \text{min}^{-1}$

-4: $k_2 = 6.5 \times 10^{-8}\ \text{min}^{-1}$

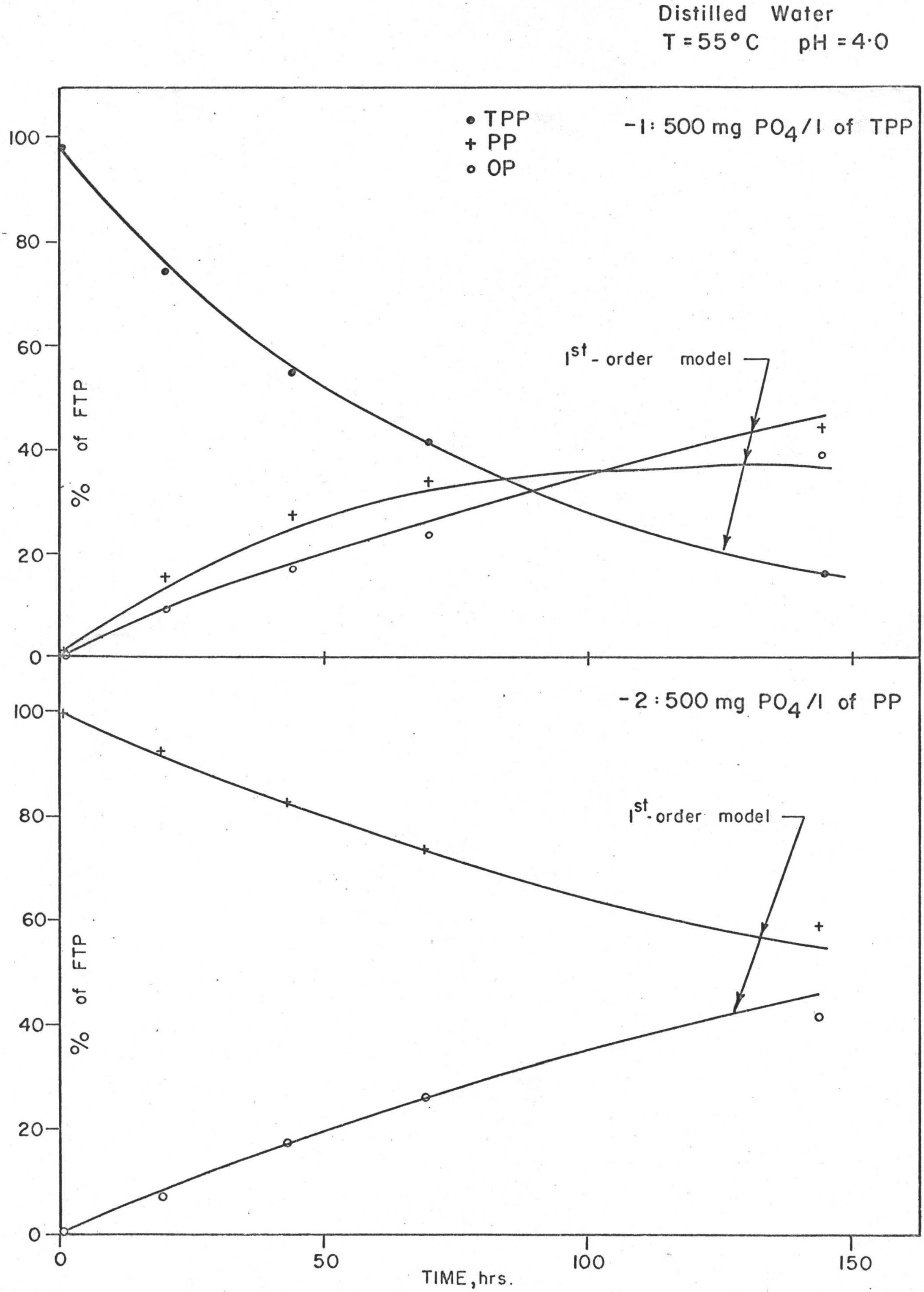


Figure 25-1 and -2. Experimental data for series XX-1 and -2.

Distilled Water
T = 75° C pH = 7·4

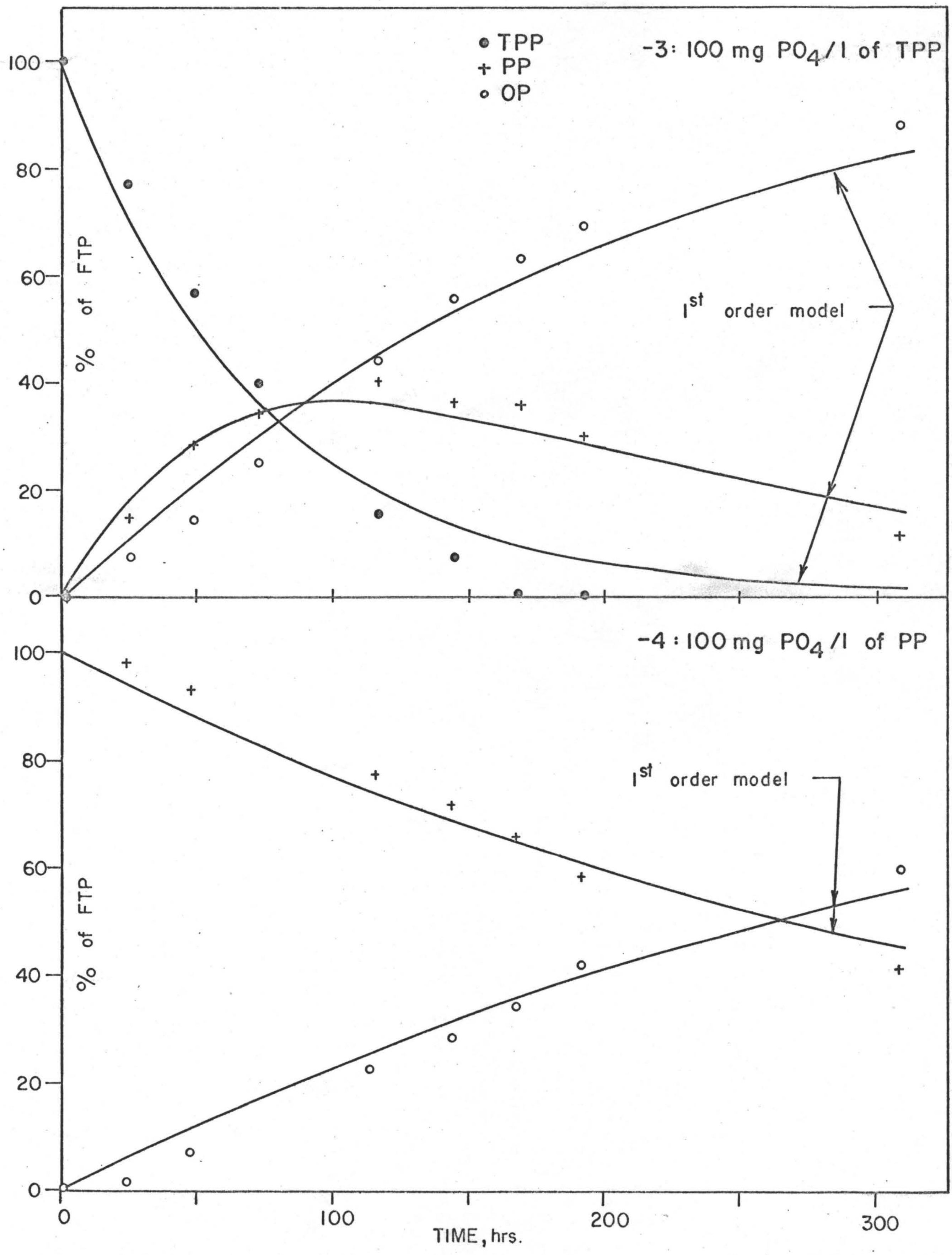


Figure 25-3 and -4. Experimental data for series XX-3 and -4.

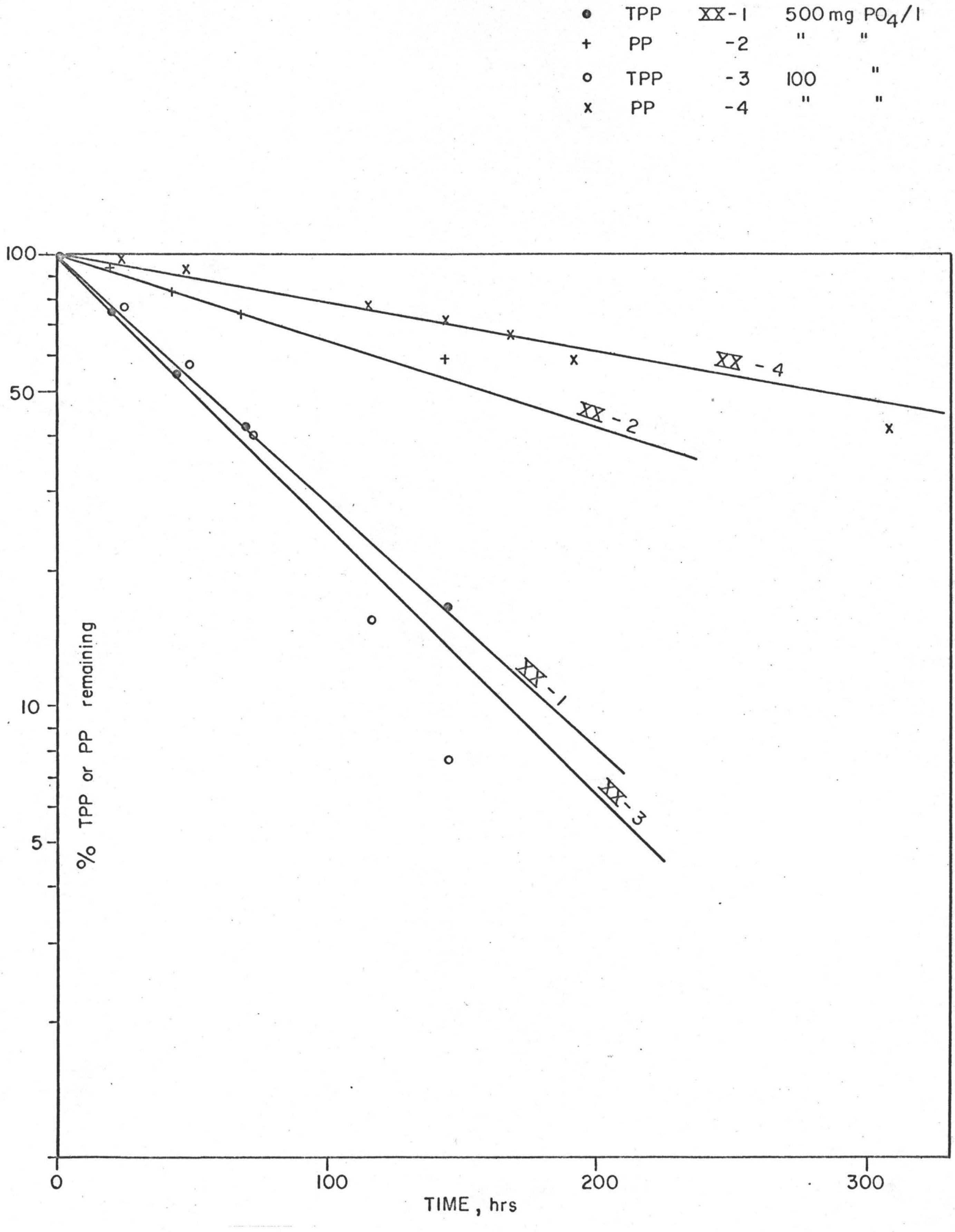


Figure 25-5. Experimental data for series XX.

SERIES IX, X AND XI - EFFECT OF CONCENTRATION ON THE RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN LAKE WATER

The purpose of these experiments is to establish rates of hydrolysis of tripolyphosphate in distilled water at low concentrations. The concentrations chosen were 0.5, 2.5, 15 and 50 mg PO_4/l. The effect of sterile versus nonsterile conditions is also investigated.

Experimental Conditions

Date: Oct.-Nov. 1967, Jan. 1968

Medium: Distilled Water, Sterile (with exception of IX)

Sample Preparation: addition of amounts of TPP as follows.

IX:	50 mg PO_4/l (nonsterile)	X-1:	2.5 mg PO_4/l	XI-1:	2.5 mg PO_4/l
		-2:	15 mg PO_4/l	-2:	15 mg PO_4/l
		-3:	50 mg PO_4/l	-3:	0.5 mg PO_4/l
				-4:	0.5 mg PO_4/l, buffered with $NaHCO_3$

Incubation Temperature: 20°C

Day-Night lighting conditions. Samples were mixed by magnetic stirrer. Series IX was also continuously aerated.

Tests: Percent TPP, Percent PP, Percent OP, pH, UTP and OP at times.

Experimental Data: The data for TPP are presented in Fig. 26 and 27. Fig. 26 shows the effect of sterilizing the distilled water for 50 mg PO_4/l concentration. Since the amount hydrolyzed is small, particularly for the sterile sample, little can be concluded about the order of response. However, for purposes of comparison to the lower concentration samples a straight line, zero-order fit has been shown. All other experiment, with the exception of XI-4, show a lag period of slow rate of hydrolysis, followed by a more rapid hydrolysis. The data can be fitted reasonably well by a zero-order straight line. The pH was measured throughout all experiments and showed the following variation.

IX: 7.3 ± 0.1
X-1: 7.1 ± 0.1
-2: 7.2 ± 0.1
-3: 7.3 ± 0.1
XI-1: 6.6 ± 0.15
-2: 7.2 ± 0.1
-3: 5.9 ± 0.2
-4: 7.5 ± 0.0

Rate of Hydrolysis

All measured rates were adjusted to pH = 7.0 according to Fig. 13. Since the rate during the lag period is very difficult to estimate, the average of the experiments is shown only.

IX: 50 mg PO_4/l: (nonsterile) $k_1 = 5.6\text{x}10^{-4}$ mg PO_4/l-min
Avg. of X and XI: (Lag rate) $k_1 = 4 \text{ x } 10^{-5}$ mg PO_4/l-min ($2.1\text{x}10^{-6}$ to $9.8\text{x}10^{-5}$)
X-3: 50 mg PO_4/l: $k_1 = 4.9\text{x}10^{-5}$ mg PO_4/l-min
X-2: 15 mg PO_4/l: $k_1 = 1.5\text{x}10^{-4}$ mg PO_4/l-min
XI-2: 15 mg PO_4/l: $k_1 = 1.2\text{x}10^{-4}$ mg PO_4/l-min
X-1: 2.5 mg PO_4/l: $k_1 = 3.7\text{x}10^{-4}$ mg PO_4/l-min
XI-1: 2.5 mg PO_4/l: $k_1 = 1.8\text{x}10^{-4}$ mg PO_4/l-min
XI-3: 0.5 mg PO_4/l: $k_1 = 1.1\text{x}10^{-4}$ mg PO_4/l-min
XI-4: 0.5 mg PO_4/l: $k_1 = 2.1\text{x}10^{-6}$ mg PO_4/l-min

Figure 26. Experimental data for series IX, X and XI.

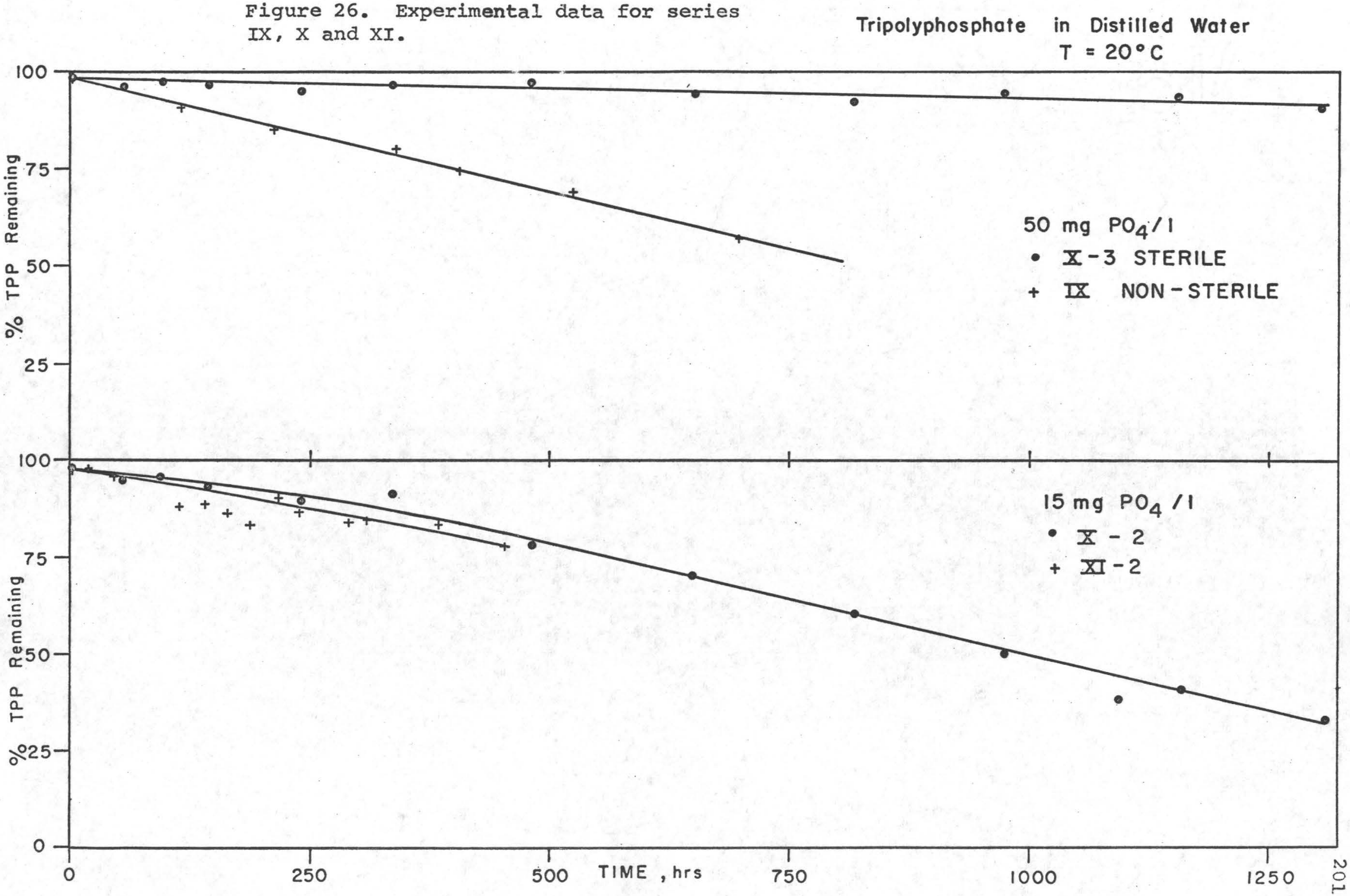
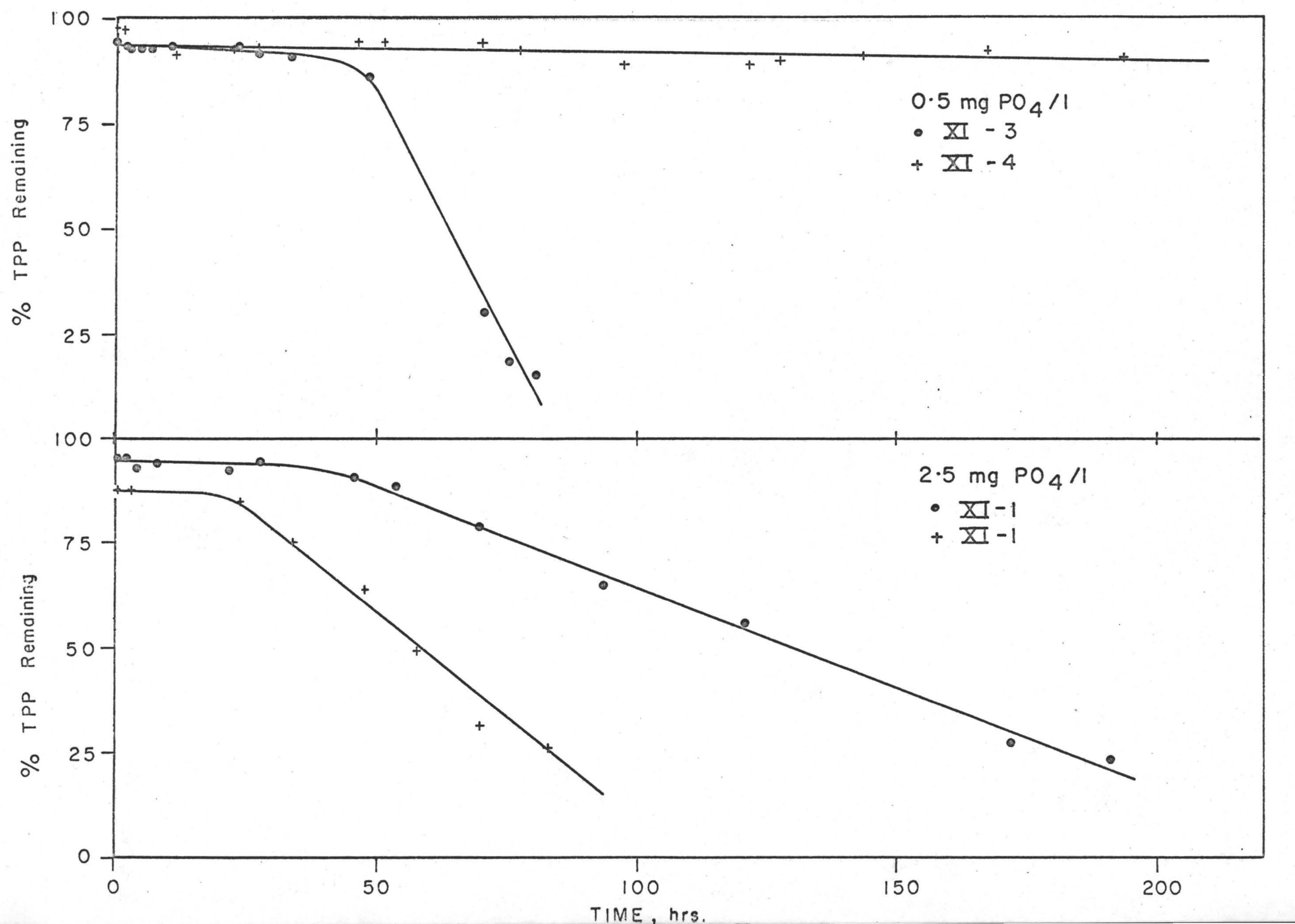


Figure 27. Experimental data for series X and XI.



SERIES XIV - EFFECT OF CONCENTRATION ON THE RATE OF HYDROLYSIS OF PYROPHOSPHATE IN DISTILLED WATER

The purpose of this experiment is to establish rates of hydrolysis of pyrophosphate in distilled water at low concentrations. These were 0.5, 2.5, 15 and 50 mg/l PO_4.

Experimental Conditions

Date: Feb. - April 1968

Medium: Distilled Water, Sterile

Sample Preparation: addition of amounts of PP as follows.

XIV-1: 0.5 mg PO_4/l
-2: 2.5 mg PO_4/l
-3: 15 mg PO_4/l
-4: 50 mg PO_4/l

Incubation Temperature: 20°C

Day-Night Lighting Conditions. Samples were mixed by magnetic stirrer.

Tests: Percent PP, Percent OP, pH.

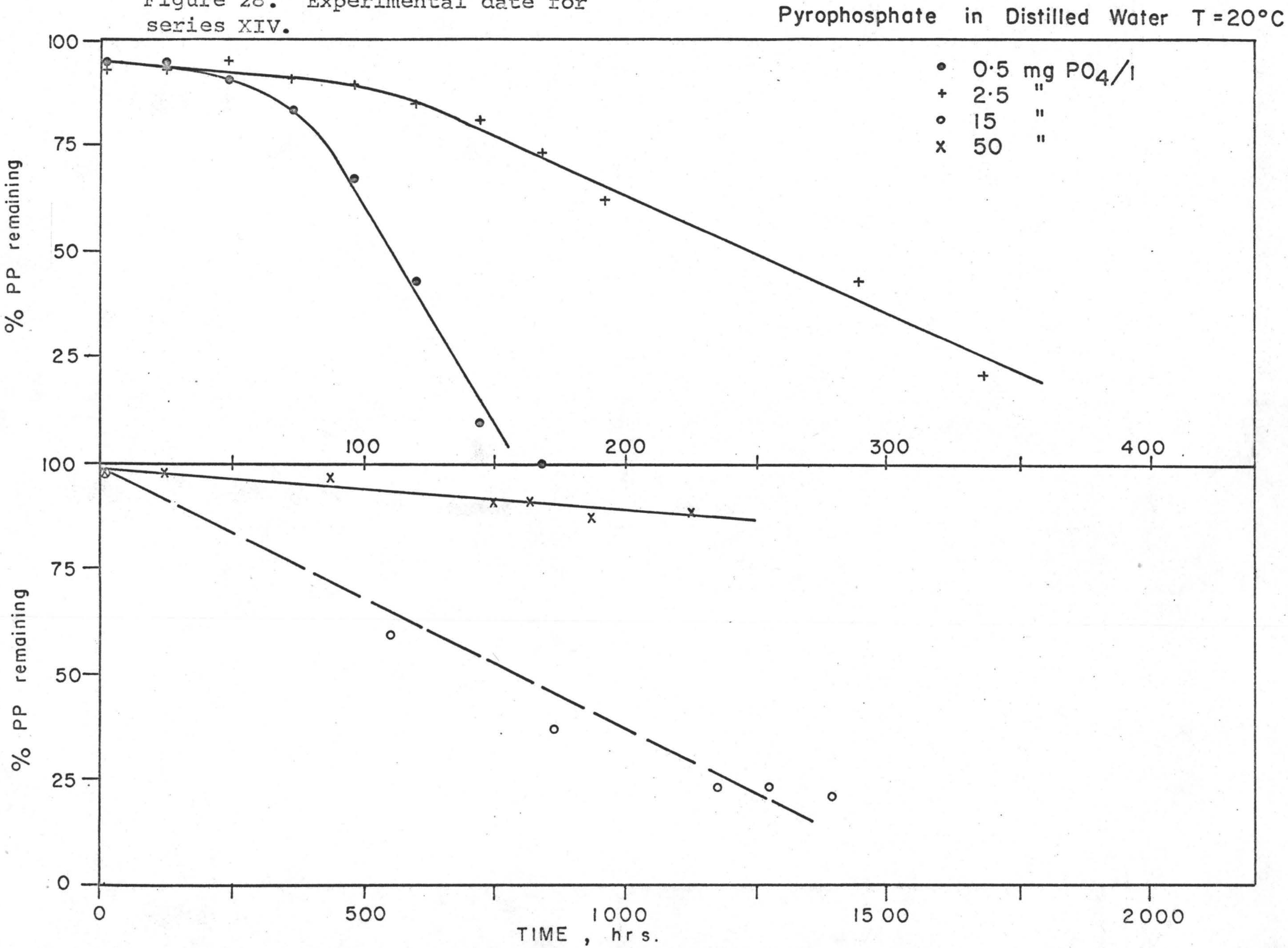
Experimental Data: The data for PP are presented in Fig. 28. The experiment at 0.5 and 2.5 mg PO_4/l show a lag period of slow rate of hydrolysis, followed by more rapid hydrolysis. The data can be fitted reasonably well by a straight line. The data for 50 mg/l PO_4 show so little hydrolysis, that nothing can be said about the order of response. However, for purposes of comparison a straight line, zero-order fit is made. The data for 15 mg PO_4/l are few and scattered. A first-order fit may be best, but for comparison a straight line zero-order fit is used. The pH was measured throughout all experiments and showed the following:

XIV-1: 6.3 ± 0.0
-2: 6.4 ± 0.0
-3: 7.0 ± 0.1
-4: 7.3 ± 0.1

Rate of Hydrolysis: All measured rates were adjusted to pH = 7.0 according to Fig. 14. Since the rate during the lag period is very difficult to estimate, the average is shown only.

XIV-1: 0.5 mg PO_4/l $k_2 = 6.0 \times 10^{-5}$ mg PO_4/l-min
-2: 2.5 mg PO_4/l $k_2 = 8.7 \times 10^{-5}$ mg PO_4/l-min
-3: 15 mg PO_4/l $k_2 = 1.5 \times 10^{-4}$ mg PO_4/l-min
-4: 50 mg PO_4/l $k_2 = 7.6 \times 10^{-5}$ mg PO_4/l-min
Avg. value of lag rate $k_2 = 7 \times 10^{-6}$ mg PO_4/l-min

Figure 28. Experimental date for series XIV.



SERIES XVII - EFFECT OF pH ON THE RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN DISTILLED WATER

The effect of pH on the rate of hydrolysis of tripolyphosphate and pyrophosphate at high concentrations is well established. Fig. 13 and 14 show the agreement among the various workers. This experiment is designed to establish if this pH dependence holds at very low concentrations of 0.5 mg PO_4/1 of tripolyphosphate.

Experimental Conditions

Date: April-May 1968

Medium: Distilled Water

Sample preparation:

XVII-1: pH = 4.3 sodium phthalate buffer added
-2: pH = 6.9 no buffer added
-3: pH = 9.9 borax buffer added

To all three flasks 0.5 mg PO_4/1 of TPP was added.

Incubation Temperature: 20°C

Day-Night Lighting Conditions. Samples were mixed by magnetic stirrer.

Tests: Percent OP, Percent PP, Percent TPP, pH.

Experimental Data: The data for TPP for all three pH levels are shown in Fig. 29. The pH stayed constant in all cases within ± 0.1 unit. The data are somewhat erratic. Nevertheless, an estimate of the rate can be obtained, as shown by the zero-order response straight line fit.

Rate of Hydrolysis:

XVII-1: pH = 4.3 $k_1 = 1.6 \times 10^{-4}$ mg PO_4/l-min

-2: pH = 6.9 $k_1 = 1.7 \times 10^{-5}$ mg PO_4/l-min

-3: pH = 9.9 $k_1 = 2.4 \times 10^{-6}$ mg PO_4/l-min

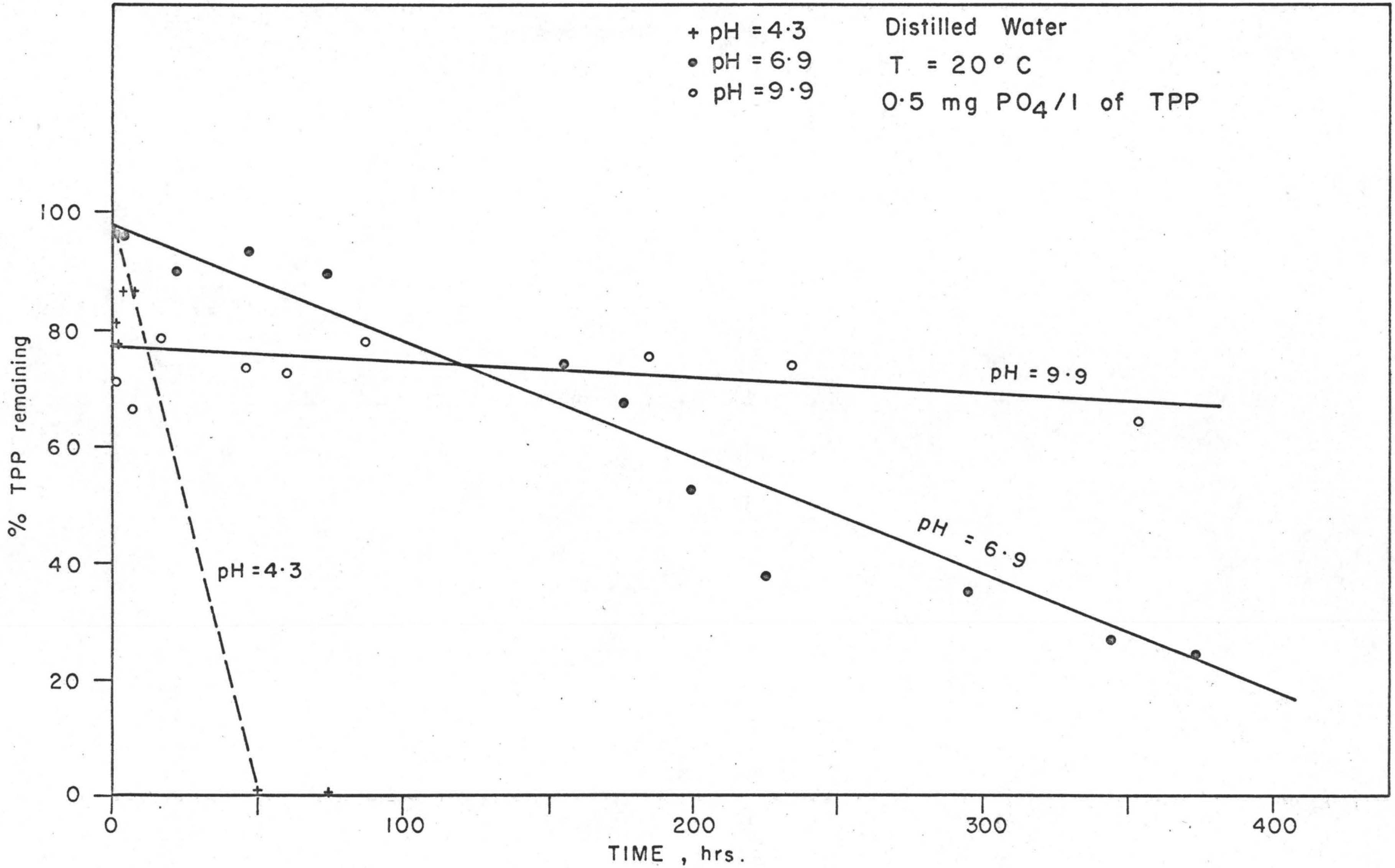


Figure 29. Experimental data for series XVII.

V-3 LAKE WATER STUDIES

All lake water used in these studies was Lake Ontario water. It was obtained either from Humber Bay or from the Hamilton Water Treatment Plant. The location of the Humber Bay sampling point was at longitude 79° 24.0'W and at latitude of 43° 34.1'N, which is approximately four miles from shore. The Humber Sewage Treatment Plant outlet sewer discharges into Humber Bay, approximately one-half mile from shore. The samples were obtained from the surface. Samples from the Hamilton Water Treatment Plant are at a depth of about thirty feet, approximately three thousand feet from shore.

A typical analysis of Lake Ontario-Humber Bay water is given in Table XXXI.

Experimental Results and Analysis of Data

Table XXXII summarizes all experimental studies in lake water. Data of individual series are generally presented in graphical form.

TABLE XXXI: LAKE ONTARIO WATER ANALYSIS*

Date: February 7, 1968

Location: Humber Bay, 43° 34.1'N, 79° 24.0'W

Hardness (as Ca CO_3)	138 mg/l
Alkalinity, Total (as Ca CO_3)	99 mg/l
Alkalinity, Phen. (as Ca CO_3)	0 mg/l
Iron (as Fe)	0.15 mg/l
Chloride (as Cl)	31 mg/l
Sulphate (as SO_4)	27 mg/l
Calcium (as Ca)	42 mg/l
Magnesium (as Mg)	8 mg/l
Manganese (as Mn)	0.0 mg/l
Diss. Silica (as Si O_2)	0.91 mg/l
COD	12 mg/l
Nitrogen, Free Ammonia (as N)	0.2 mg/l
Nitrogen, Tot. Kjeldahl (as N)	0.3 mg/l
Nitrogen, Nitrate (as N)	0.2 mg/l
Phosphorus, UTP (as PO_4)	0.110 mg/l
Phosphorus, FTP (as PO_4)	0.075 mg/l
Phosphorus, OP (as PO_4)	0.065 mg/l
pH	7.9
Temperature	4°C

---

* all analysis with the exception of pH, temperature and phosphorus were done by the laboratories of the Ontario Water Resources Commission, Toronto.

TABLE XXXII: SUMMARY OF EXPERIMENTAL WORK ON LAKE WATER

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	CONDENSED PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL COND.				TYPE OF PHOSPH. ANALYSIS	REMARKS
			TYPE ADDED	INITIAL CONC. mg/l PO_4		TEMP. °C	pH	LIGHTING	AERATION		
I	May 67	Preliminary - Humber Bay	TPP	~0.5	336	20	~8.5	D-N	Cont.	UTP,OP, FTP	
	May-Aug.67	Preliminary - Humber Bay	TPP	~0.5	2900	4	8.0-8.3	"	"	"	
III	June 67	Influence of Diss. Oxygen level (aeration) on rate of hydrolysis	TPP	~1.0	456	20	~8.4	D-N	Air	FTP,OP	D.O. = 8.7-9.1
			TPP	~1.0	456	20	8.9-9.5	"	N_2	"	D.O <1.0
XII	Feb.68	Rate of Hydrolysis study on Humber Bay water. Effect of storage and filtration.									
		unfilt. sample	TPP	0.5	28	20	8.1	D-N	Cont.	FTP, Diff. Anal.	
		unfilt.sample (2 weeks old)	TPP	0.5	168	20	8.1	"	"	"	
		sterile sample (2 weeks old)	TPP	0.5	192	20	8.1	"	"	"	

TABLE XXXII - (Cont'd.)

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	CONDENSED PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL COND.				TYPE OF PHOSPH. ANALYSIS	REMARKS
			TYPE ADDED	INITIAL CONC. mg/l PO_4		TEMP. °C	pH	LIGHTING	AERATION		
XIII	March-April 68	Rate of hydrolysis study on Hamilton intake water. Effect of temperature.	TPP TPP	0.5 0.5	94 1464	20 4	8.1 8.1	D-N "	Cont. "	FTP, Diff. Anal. "	
XVIII	May 68	Rate of hydrolysis study on Humber Bay water. Effect of pH.	TPP TPP TPP	0.5 0.5 0.5	85 279 237	24 24 24	5.0 7.0 9.0	D-N " "	Cont. " "	Diff. Anal. " "	
XIX	May 68	Rate of hydrolysis study on Humber Bay water. Effect of addition of glucose.	TPP TPP	0.5 0.5	279 48	24 24	7.0 7.0	D-N "	Cont. "	Diff. Anal. "	 50 mg/l Glucose added
XXII-1	Feb.67	Humber Bay field study			1 day					FTP OP	Preliminary investigation to establish phosph.conc levels
XXII-2	June 68	Humber Bay field study	TPP	2000 lbs added	3 days					UTP, FTP, OP, Diff. Anal.	Survey of level of conc. of types of phosph.compounds near a major sewage outlet. 2000 lbs.of TPP added an traced.

SERIES I - RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN LAKE WATER

The purpose of this series is to establish rates of hydrolysis of tripolyphosphate in lake water in summer (20°C) and winter (4°C) water temperatures. Experimental procedures were checked out during this first series.

Experimental Conditions

Date: Series I-1 (20°C) May 2-16, 1967

Series I-2 (4°C) May 2 - August 31, 1967

Medium: Humber Bay

UTP = .065 mg/l PO_4

FTP = .045 mg/l PO_4

OP = .040 mg/l PO_4

Sample Preparation: added .45 mg/l PO_4 of TPP

Incubation Temperature: I-1 20°C

I-2 4°C

Day-Night Lighting conditions. Continuous aeration

Tests: UTP, OP, FTP, and pH at times.

Experimental Data: These are presented in Fig. 30-1, and -2. FTP were determined on four samples each. They indicated that the particulate fraction, PAP, stayed essentially constant at the initial value of .020 mg/l PO_4. Condensed phosphate values, CP, were obtained by subtracting the results of OP and PAP from UTP at each measurement.

Rate of Hydrolysis: Although there is considerable straying of individual data, a straight line fit is reasonable.

I-1: $20^{\circ}C$ $k_{avg} = 2.0 \times 10^{-5}$ mg PO_4/l-min

I-2: $4^{\circ}C$ $k_{avg} = 2.0 \times 10^{-6}$ mg PO_4/l-min

Estimate of Activation Energy: E = 22.2 k cal/mole

Figure 30-1. Experimental data for series I-1.

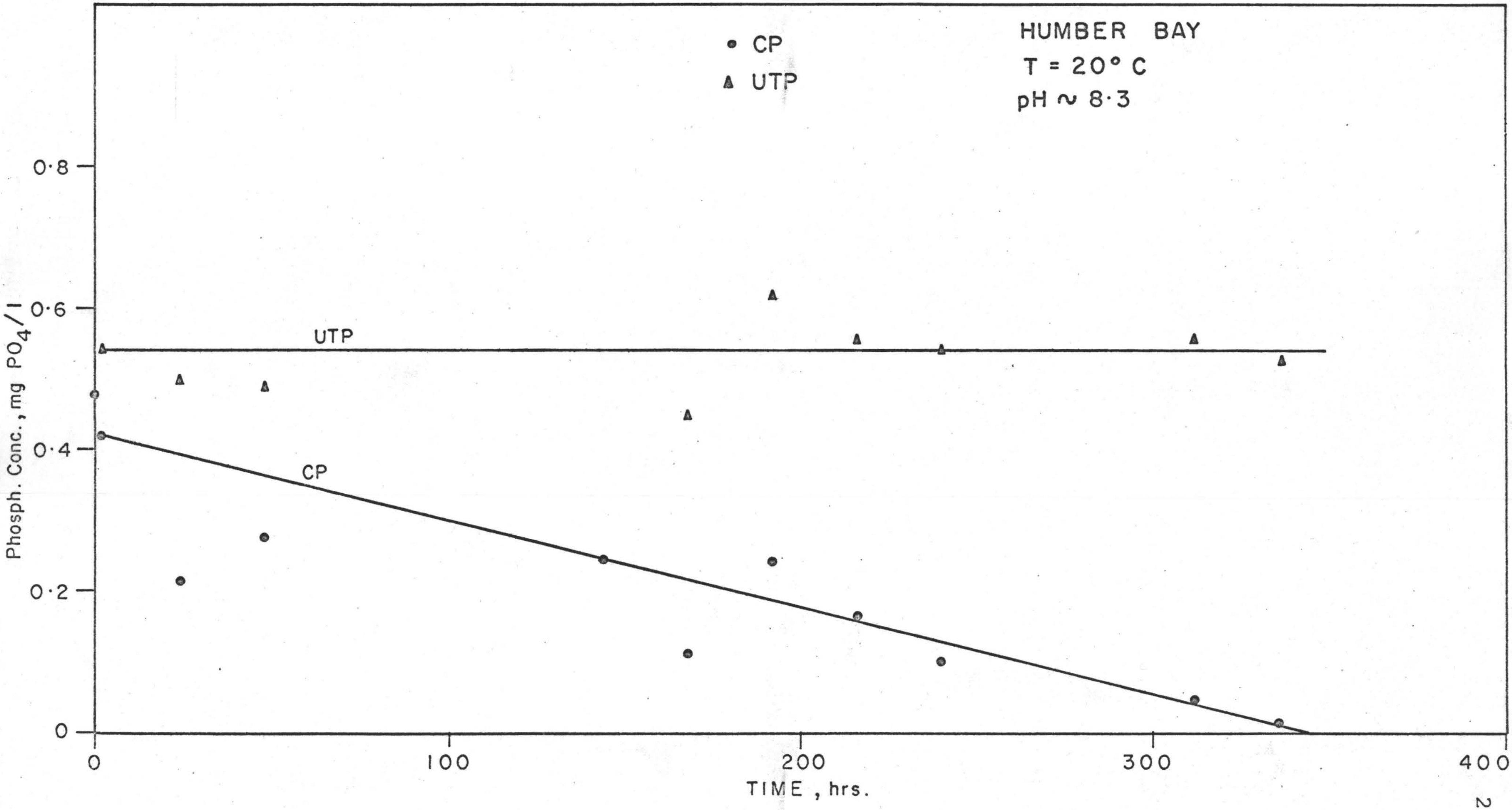
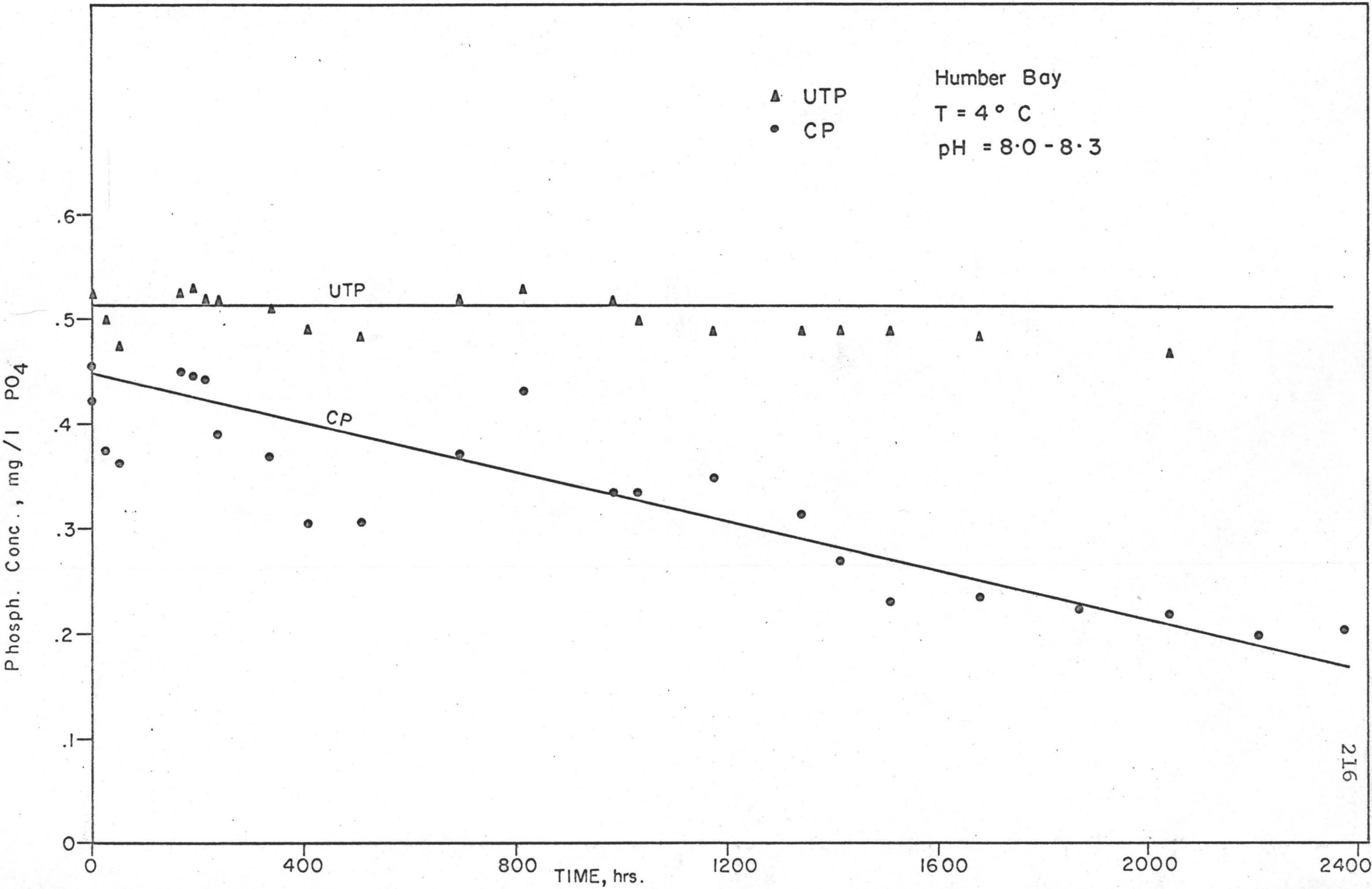


Figure 30-2. Experimental data for series I-2.



SERIES III - EFFECT OF DISSOLVED OXYGEN CONCENTRATION ON RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN LAKE WATER

The purpose of this experiment is to establish what effect, if any, the concentration of dissolved oxygen has on the rate of hydrolysis of condensed phosphates in lake water. One experiment was carried out under continuous aeration, representing saturated dissolved oxygen conditions. A second experiment was made under otherwise identical conditions, but using nitrogen gas instead of air, representing low oxygen conditions.

Experimental Conditions

Date: June 7-17, 1967

Medium: Humber Bay

FTP = .022 mg/l PO_4

OP = .017 mg/l PO_4

Sample Preparation: added .950 mg/l PO_4 as TPP

Incubation Temperature: 20°C

Day-Night Lighting Conditions. III-1: Continuous supply of air

III-2: Continuous supply of nitrogen gas

Tests: FTP, OP, D.O., pH

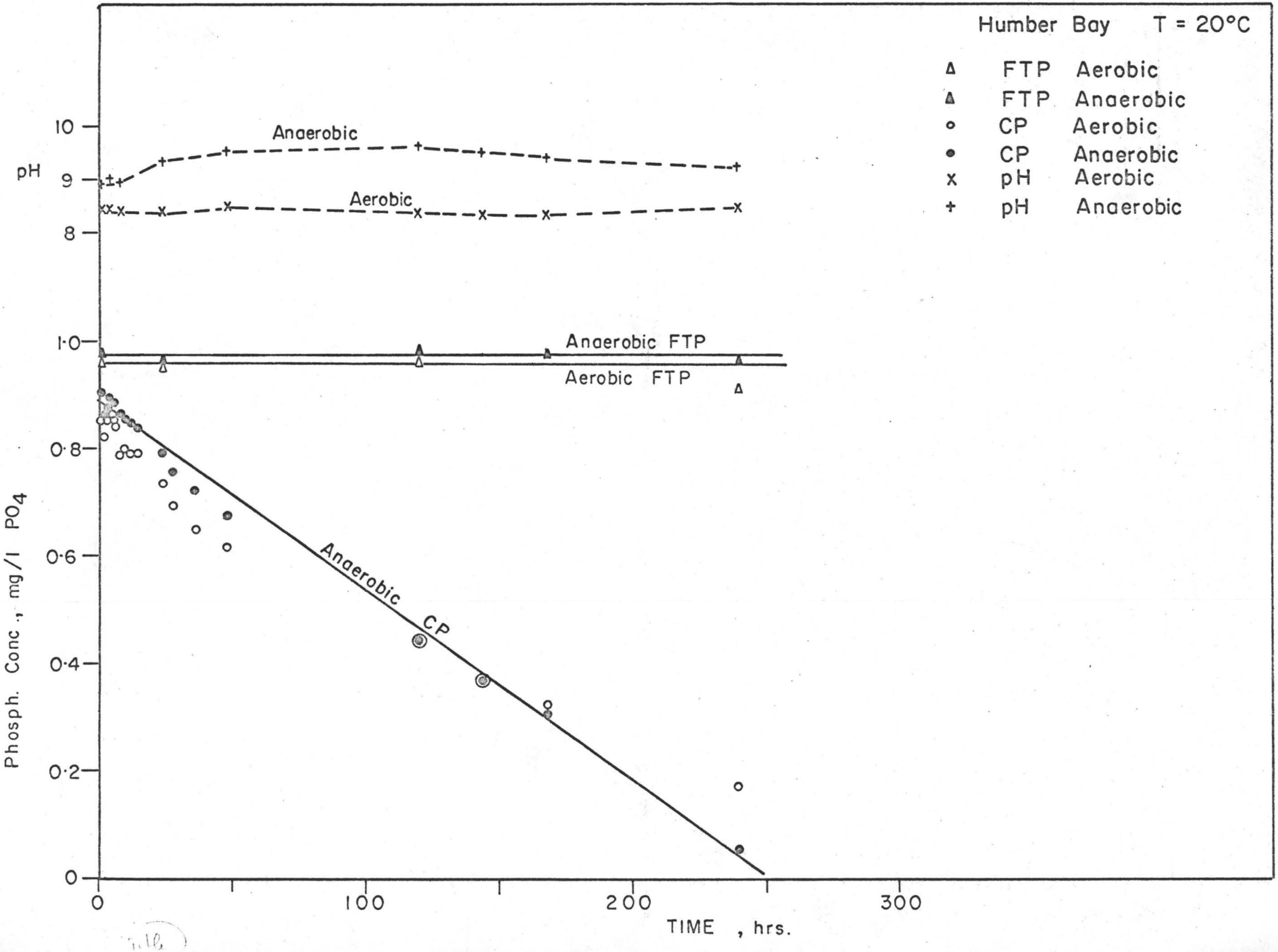
Experimental Data: Fig. 31 presents the data on phosphorus and pH. The dissolved oxygen concentration was measured frequently. It showed a concentration of 9.1 mg/l in III-1, which represents saturation levels. III-2 had levels of concentration of less than 1.0 mg/l, with the exception of the period from about 100 to 168 hrs. when the concentration rose to a maximum of 5.1 mg/l at 168 hrs. This occurred because of exhaustion of the nitrogen gas supply during this time.

Rate of Hydrolysis: The anaerobic sample data are fitted by a straight line.

$$k_{avg}/\text{anaerobic} = 5.9 \times 10^{-5} \text{ mg } PO_4/\text{l-min.}$$

The aerobic sample data cannot be fitted reasonably by a straight line, although the overall rate of hydrolysis is close to the rate of anaerobic sample. The difference in pH level of about one unit is noted (see also Series XVIII).

Figure 31. Experimental data for series III.



SERIES XII - EFFECT OF LENGTH OF STORAGE, STERILE CONDITIONS AND ADDITION OF GLUCOSE ON THE RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN LAKE WATER

The purpose of this experiment is to investigate to what extent the rate of hydrolysis differs between a fresh lake water sample and one that had been stored for some time before the addition of tripolyphosphate. In addition, food in the form of glucose was added to the stored sample some time after the start of the experiment to see if this has any effect in increasing organism activity and thus increasing the rate of hydrolysis. Finally, the rate of hydrolysis in sterile lake water was investigated.

Experimental Conditions

Date: February 1968

Medium: Humber Bay
UTP = 0.110 mg/l PO_4
FTP = 0.075 mg/l PO_4
OP = 0.065 mg/l PO_4
pH = 7.9
T = 4^oC

Sample Preparation:

XII-1 unfiltered, started experiment within 48 hrs. after collection of sample.

XII-2 unfiltered, lake water stored for about two weeks at 4^oC, before start of experiment. 76 hrs. after start of hydrolysis experiment 50 mg/l glucose was added.

XII-3 sterile, (filtered (0.45 micron) and autoclaved)

To all three samples 0.5 mg/l PO_4 of tripolyphosphate was added.

Incubation Temperature: 20^oC

Day-Night Lighting Conditions. Samples were mixed by magnetic stirrer and aeration (except -3).

Tests: Percent OP, Percent PP, Percent TPP, pH, FTP at times.

Experimental Data: These are presented in Fig. 32-1 to -3. The data on filtered total phosphorus are not shown, but indicate that there was little uptake of the added phosphate by the organisms while extensive hydrolysis occurred.

Rate of Hydrolysis: Zero-order straight line fit is made in accordance with the theory of consecutive reactions (see Appendix B). Both k_1 and k_2 values were calculated from the data.

XII-1: $k_1 = 3.2 \times 10^{-4}$ mg PO_4/l-min, $k_2 = 2.7 \times 10^{-5}$ mg PO_4/l-min

-2: $k_1 = 2.8 \times 10^{-5}$ mg PO_4/l-min, $k_2 = 8.3 \times 10^{-6}$ mg PO_4/l-min

-2 (+ Glucose): $k_1 = 2 \times 10^{-4}$ mg PO_4/l-min, k_2 not calculated

-3: $k_1 = 1.2 \times 10^{-5}$ mg PO_4/l-min, $k_2 = 2.4 \times 10^{-6}$ mg PO_4/l-min

Figure 32-1. Experimental data for series XII-1.

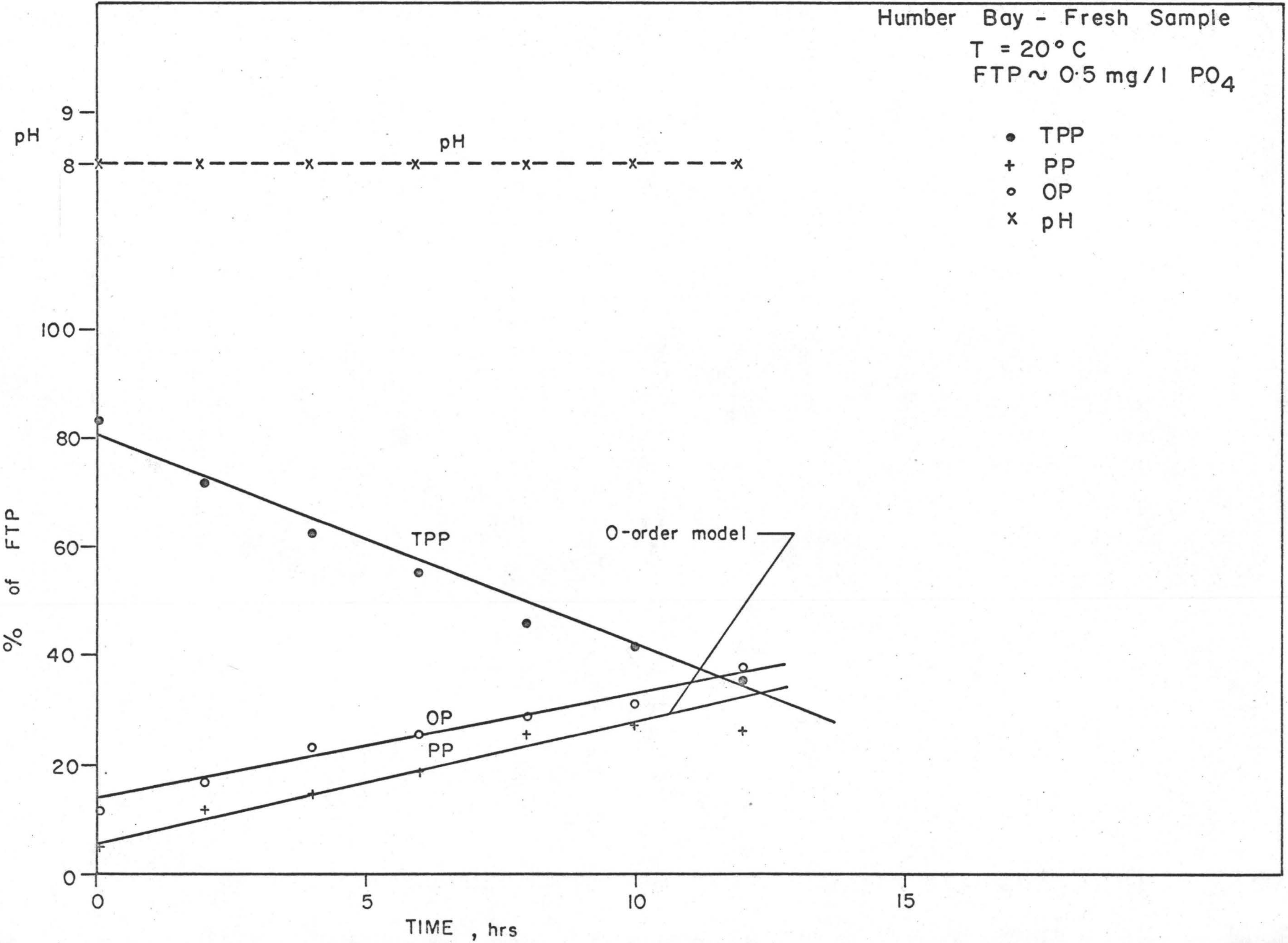


Figure 32-2. Experimental data for series XII-2.

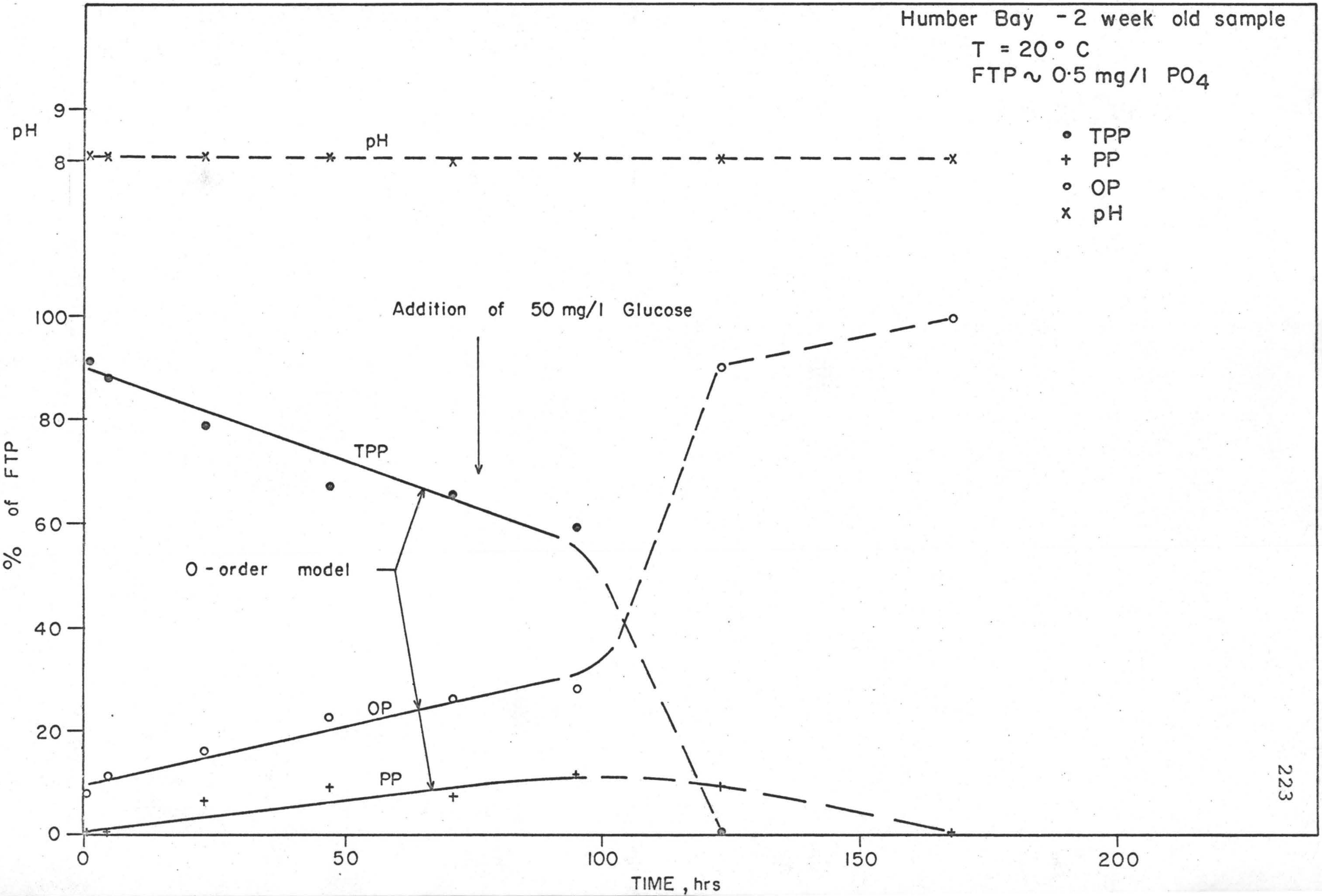
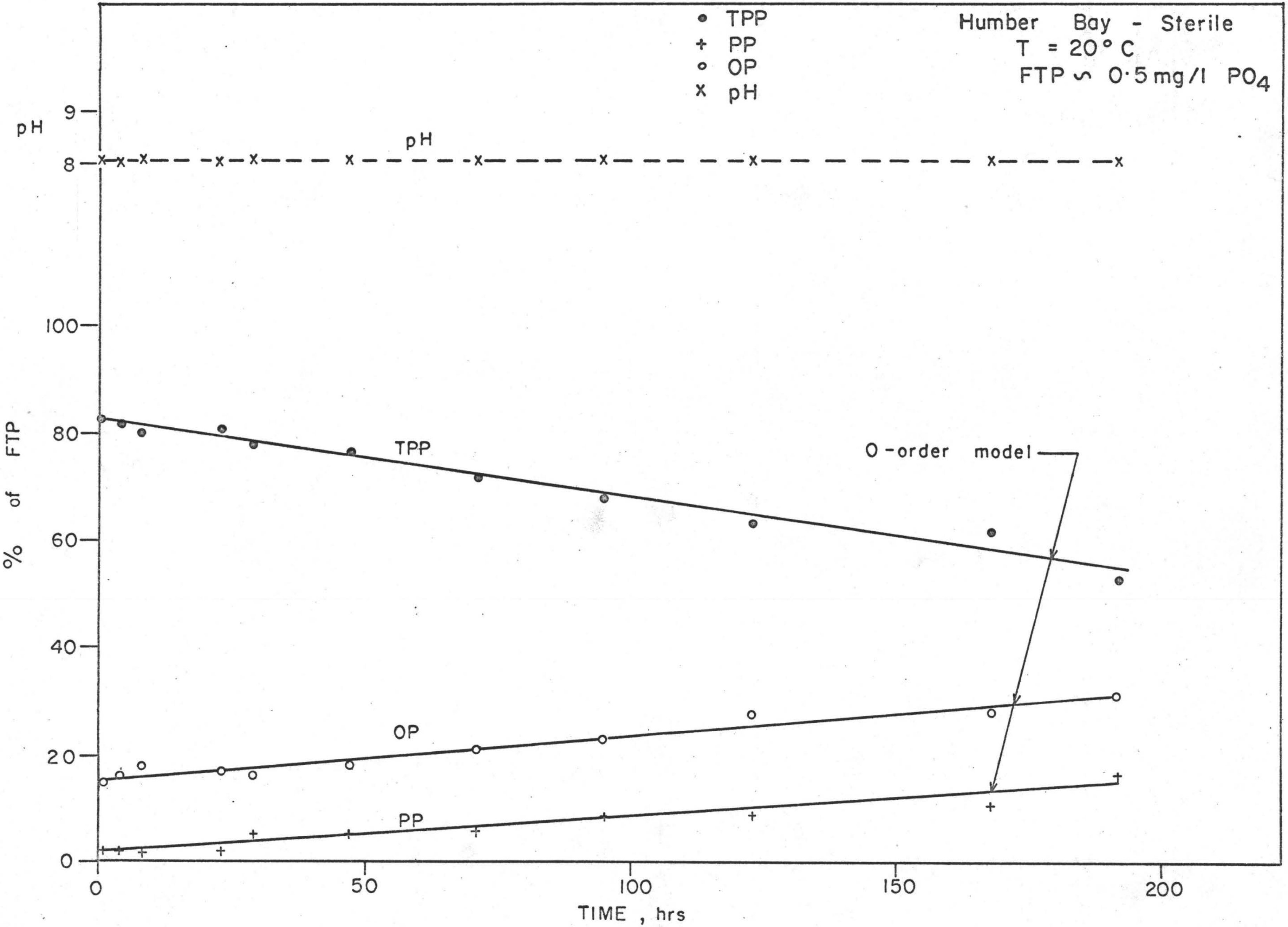


Figure 32-3. Experimental data for series XII-3.



SERIES XIII - EFFECT OF TEMPERATURE AND SAMPLING DEPTH ON THE RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN LAKE WATER

The purpose of this experiment is to investigate the effect of temperature on the rate of hydrolysis of tripolyphosphate in a lake water sample obtained in the winter. It was not possible to obtain a sample from the Humber Bay. As an alternative the sample was taken from the intake of the Hamilton Water Treatment Plant. The depth at the intake is about 30 feet.

Experimental Conditions

Date: March-April 1968

Medium: Lake Ontario water, Hamilton water intake

Sample preparation: addition of 0.5 mg/l PO_4 of TPP

Incubation Temperature: XIII-1 20°C
XIII-2 4°C

Day-Night Lighting Conditions. Samples were mixed by magnetic stirrer and aeration.

Tests: Percent OP, Percent PP, Percent TPP, pH, FTP at times.

Experimental Data: These are presented in Fig. 33-1, -2. The data on filtered total phosphorus are not shown, but indicate that there was little uptake of the added phosphate by the organisms while extensive hydrolysis occurred.

Rate of Hydrolysis: A zero-order straight line fit is made in accordance with the theory of consecutive reactions (see Appendix B). Both k_1 and k_2 were calculated from the data. The data of XIII-2 are scarce, and the last two points were disregarded since they are obviously in error.

XIII-1: $k_1 = 2.0 \times 10^{-5}$ mg PO_4/l-min, $k_2 = 1.9 \times 10^{-6}$ mg PO_4/l-min

XIII-2: $k_1 = 2.9 \times 10^{-6}$ mg PO_4/l-min, $k_2 = 4.4 \times 10^{-7}$ mg PO_4/l-min

Estimate of Activation Energy:

TPP: $E = 19.1$ k cal/mole

PP: $E = 14.7$ k cal/mole

Figure 33-1. Experimental data for series XIII-1.

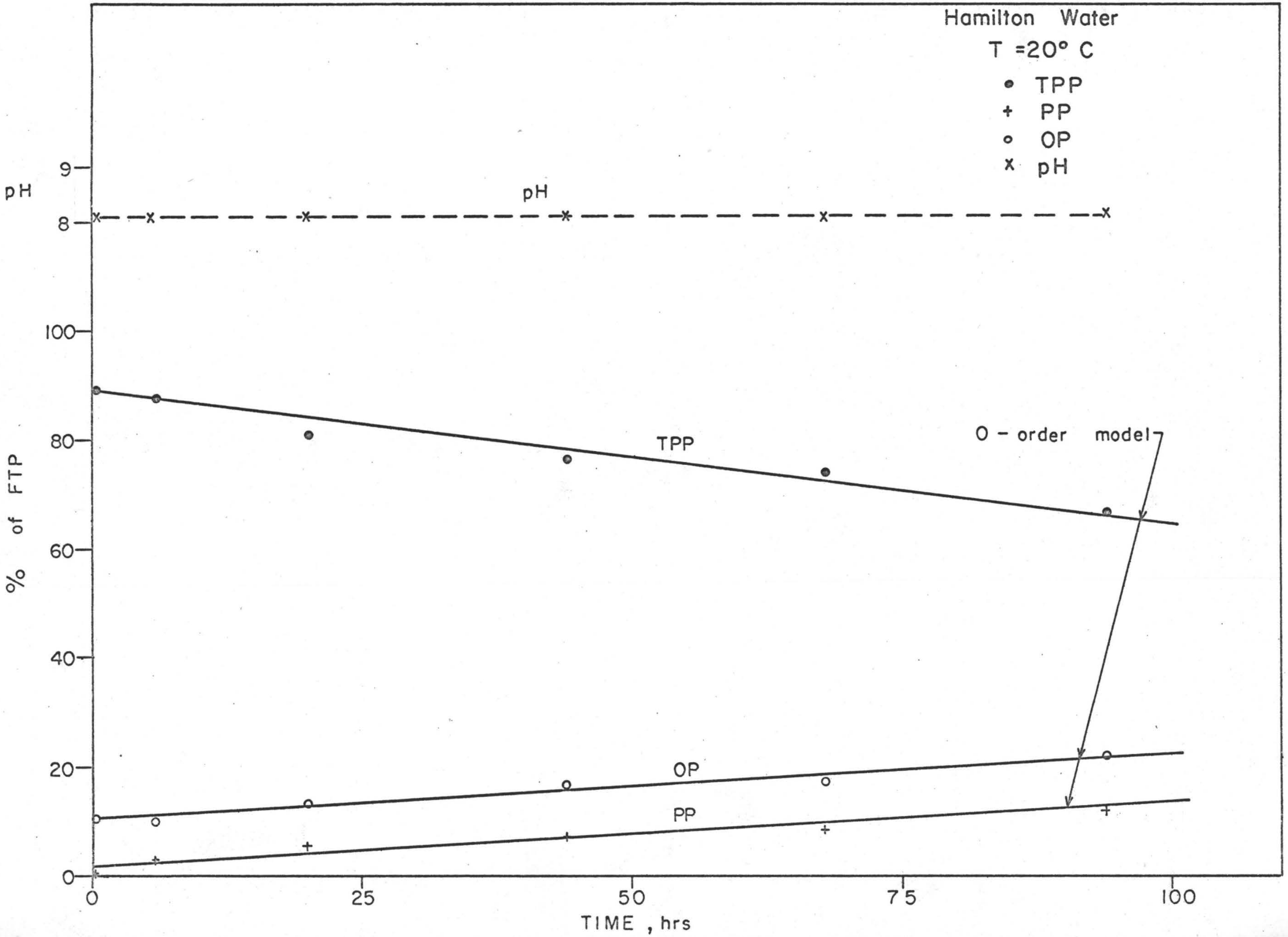
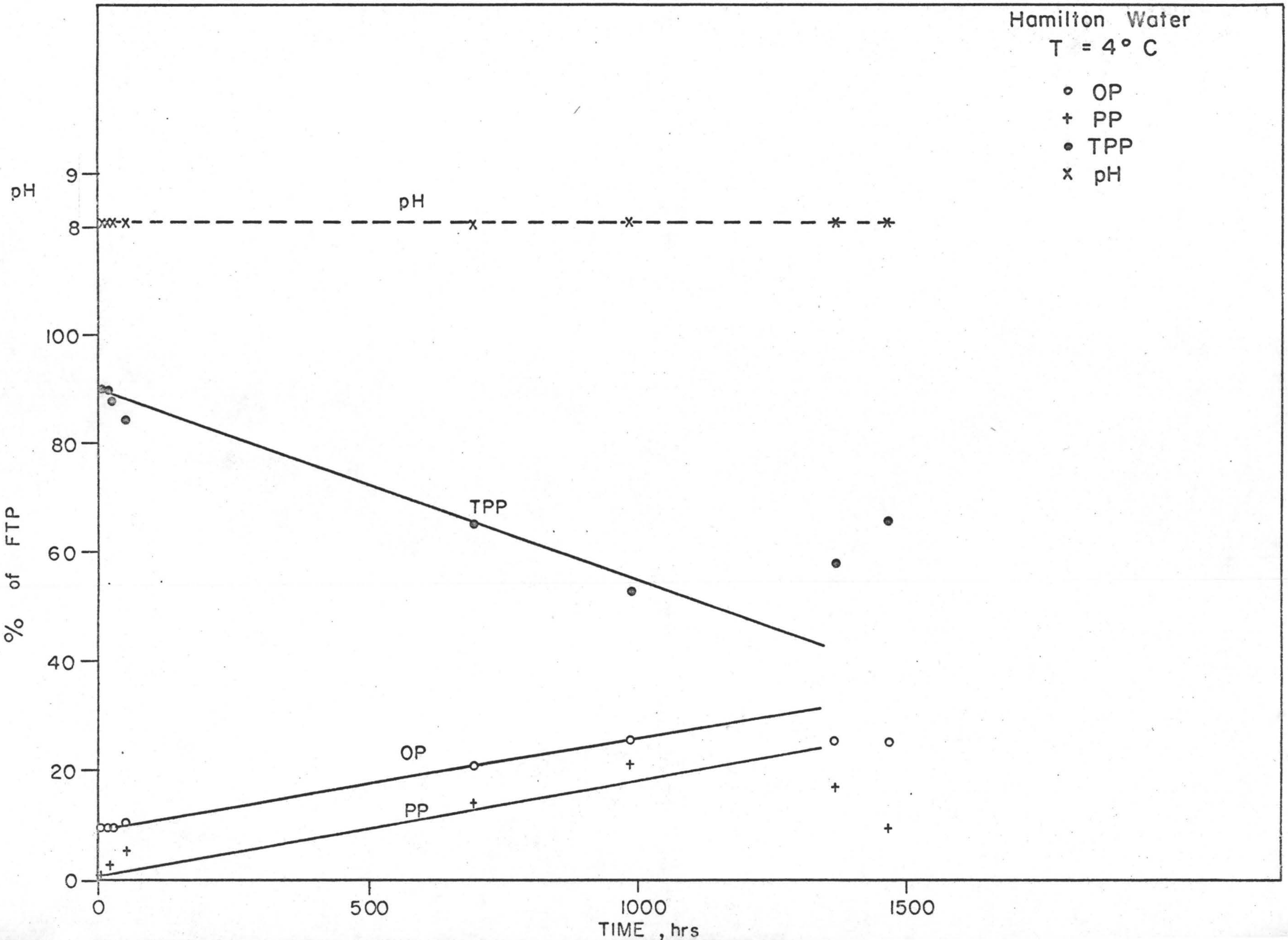


Figure 33-2. Experimental data for series XIII-2.



SERIES XVIII - EFFECT OF pH ON THE RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN LAKE WATER

The purpose of this series is to establish what effect the variation of pH has on the rate of hydrolysis of tripolyphosphate in lake water.

Experimental Conditions

Date: May 1968

Medium: Humber Bay

Sample preparation:

XVIII-1: pH ~ 5 sodium phthalate buffer added
-2: pH ~ 7 dilute hydrochloric acid added
-3: pH ~ 9 sodium carbonate buffer added
0.5 mg/l PO_4 of TPP was added to the three samples.

Incubation Temperature: 24°C

Day-Night Lighting Conditions. Samples were mixed by magnetic stirrer and aeration.

Tests: Percent OP, Percent PP, Percent TPP, pH.

Experimental Data: These are presented in Fig. 34. The pH was checked each time phosphorus measurements were made. It stayed constant in all three samples.

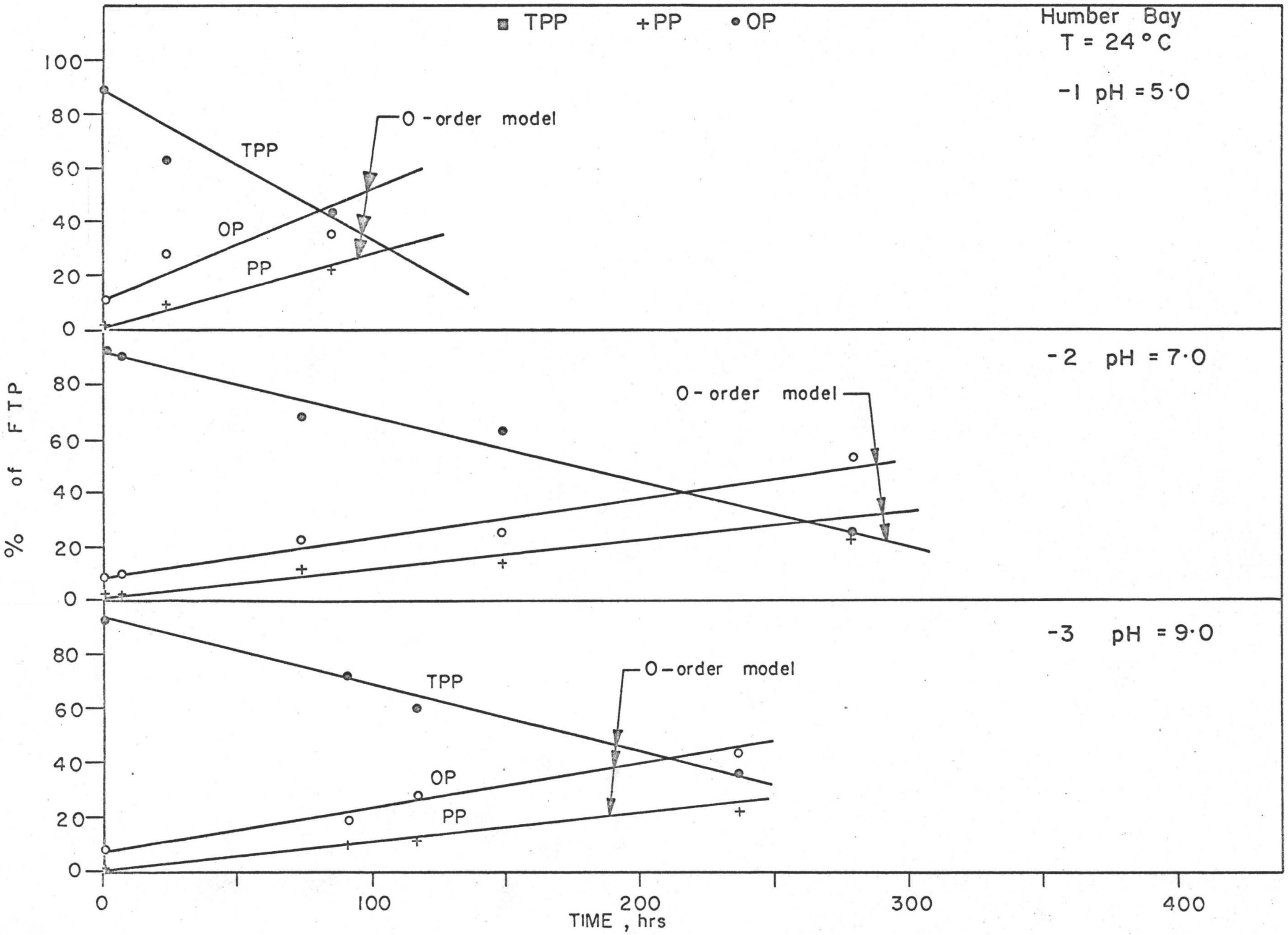
Rate of Hydrolysis: A zero-order straight line fit is made in accordance with the theory of consecutive reactions (see Appendix B). Both k_1 and k_2 were calculated from the data. Unfortunately only few data points were obtained in this series. The rate constants were converted to a temperature of 20°C.

XVIII-1: pH = 5: $k_1 = 3.5 \times 10^{-5}$, $k_2 = 7.1 \times 10^{-6}$ mg PO_4/l-min

-2: = 7: $k_1 = 1.6 \times 10^{-5}$, $k_2 = 3.7 \times 10^{-6}$ mg PO_4/l-min

-3: = 9: $k_1 = 1.8 \times 10^{-5}$, $k_2 = 4.9 \times 10^{-6}$ mg PO_4/l-min

Figure 34. Experimental data for series XVIII.



SERIES XIX - EFFECT OF ADDITION OF GLUCOSE ON THE RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE ON LAKE WATER

The purpose of this series is to check the effect of addition of 50 mg/l glucose on the rate of hydrolysis of tripolyphosphate in lake water.

Experimental Conditions

Date: May 1968

Medium: Humber Bay

Sample preparation: XIX-1 pH = 7.0 0.5 mg/l PO_4 of TPP
(Data of XVIII-2) no food added
-2 pH = 7.0 0.5 mg/l PO_4 of TPP
50 mg/l glucose

Incubation Temperature: 24°C

Day-Night Lighting Conditions. Samples were mixed with magnetic stirrer and aeration.

Tests: Percent OP, Percent PP, Percent TPP, pH.

Experimental Data: These are presented in Fig. 35. Glucose was added at the beginning of Series XIX-2. The sample stayed clear for the first day, and then turned cloudy, presumably due to increase in organisms. The rapid decrease in TPP coincided with the increase in cloudiness.

Rate of Hydrolysis: The data for Series XIX-2 are too few to estimate k_1 and k_2; therefore k_1 was estimated only, and adjusted for temperature to 20°C.

XIX-1: $k_1 = 1.6 \times 10^{-5}$ mg PO_4/l-min

XIX-2: $k_1 = 1.5 \times 10^{-4}$ mg PO_4/l-min
(glucose)

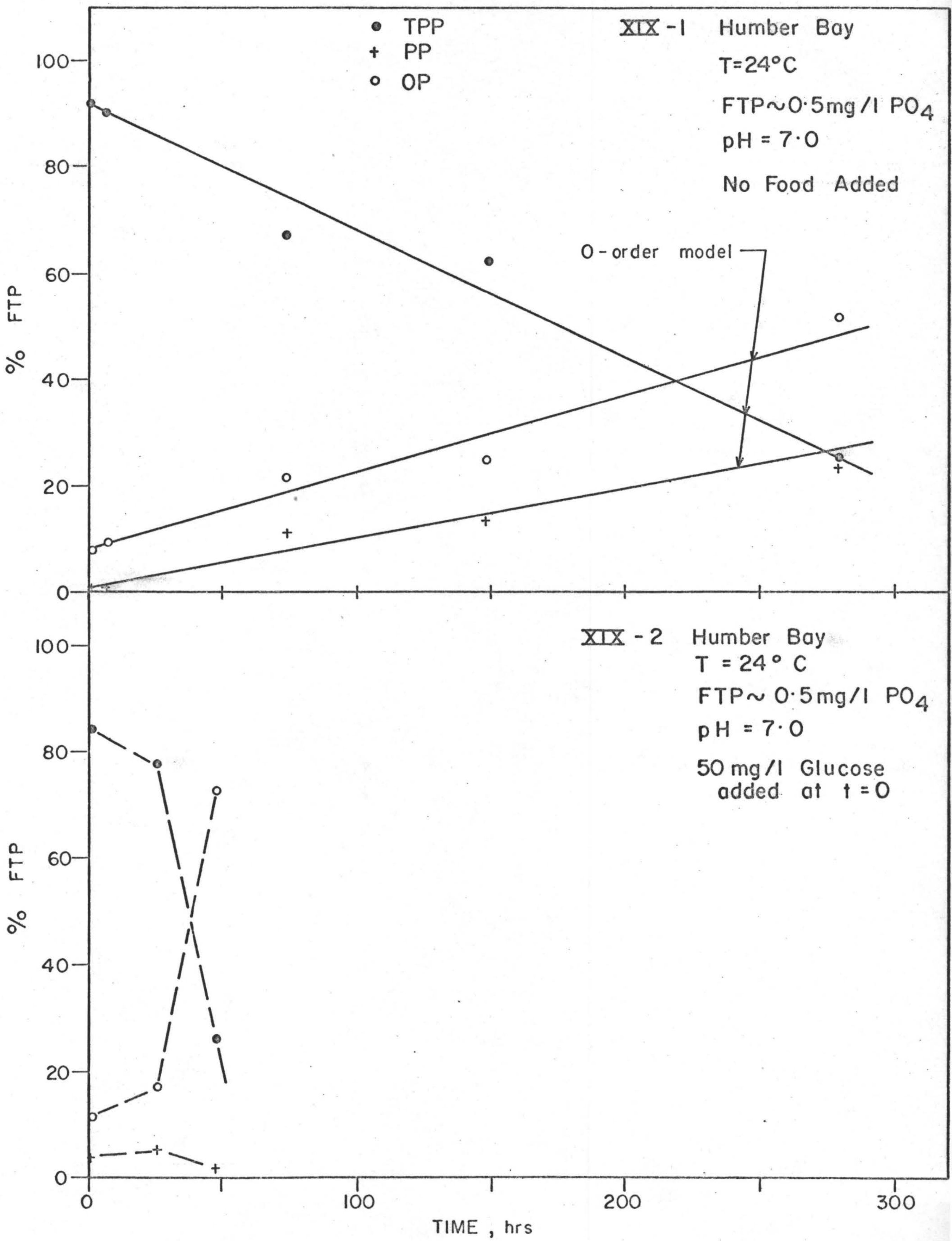


Figure 35. Experimental data for series XIX.

SERIES XXII - HUMBER BAY FIELD INVESTIGATION

The purpose of this investigation is to establish

a) concentration levels of phosphorus in lake water in the vicinity of a major sewage treatment plant outlet. The findings will decide realistic levels of concentration of phosphorus for laboratory experiments.

b) rates of hydrolysis of condensed phosphates in lake water in situ. Results can be compared to rates found in laboratory experiments.

Method of Investigation: The effluent from the Humber Sewage Treatment Plant is discharged through a ten-foot diameter concrete pipe into Humber Bay, approximately 3000 feet from shore and at a water depth of about 25 feet. The effluent rises through fourteen 48 inch diameter diffusers.

The observational programme was carried out with the help of the research vessel, C.C.G.S. Porte Dauphine, Great Lakes Institute, University of Toronto. The efforts of the captain, crew and technical staff are hereby gratefully acknowledged. A network of stations in a semicircle around the sewage outlet was laid out; radii of 1000 feet, one-half, one, two and three miles were used (see Fig. 36). Samples were obtained at several depths. Series XX-1 was carried out at the beginning of the research, February 1967. For series XX-2, June 1968, condensed phosphates were added to the effluent, in order to increase concentrations in the bay for rate of hydrolysis measurements.

SERIES XXII-1 - CONCENTRATION LEVELS OF PHOSPHORUS IN HUMBER BAY

Date: Feb. 9, 1967

Stations: 22, samples taken at surface, mid-depth, and near bottom.

Tests: FTP, OP, (by Manual Ascorbic Acid Method)

Temperature, pH, chloride, optical density at 200 millimicrons.

Experimental Data: A brief summary is presented only.

Orthophosphate (OP):	.018-.725 mg/l PO_4
Filtered Total Phosphorus (FTP):	.032-1.0 mg/l PO_4
Temperature :	1.1-2.0°C
pH :	7.8-8.0
Optical Density (200 mμ):	.33-.43
Chlorides :	29-60 mg/l

The following observations are made from the data:

1) Realistic levels of concentrations for phosphorus in laboratory studies to be 0.5 mg/l PO_4.

2) Phosphorus data indicated a definite current in the bay in a north-easterly direction towards Sunnyside beach. Chloride and optical density data generally supported this, but not as pronounced.*

3) Within three miles of the sewage outlet phosphorus concentrations were reduced to levels generally found in near-shore areas of Lake Ontario (Heinke (H-8)).

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* Phosphorus concentrations were high within this stream of heavily polluted water. The maximum condensed phosphate concentration measured was 0.25 mg/l PO_4.

SERIES XXII-2 - RATE OF HYDROLYSIS STUDY IN HUMBER BAY

Date: June 3-6, 1968

On June 3 and 4 measurements were taken at the sewage outlet and at selected stations at time intervals to establish "steady-state" conditions. On June 5 2000 lbs. of sodium tripolyphosphate were dumped in a 2-hour period into the effluent at the treatment plant. The effect of this was monitored at the sewage outlet and several stations in the bay. From the data on phosphorus concentration and form, and data on wind, water current and conductivities the relative effect of diffusion and hydrolysis was to be estimated, and ultimately rates of hydrolysis of condensed phosphates obtained.

Stations: 32, samples taken at two depths, 3 m and near bottom.

Tests: Phosphorus: UTP, FTP, OP, some differential condensed phosphate analysis.
temperature, pH, turbidity, conductivity
wind measurement
current measurement (drogue studies)
aerial photography

Addition of Tripolyphosphate to Effluent:

Material: Sodium tripolyphosphate from Electric Reduction Co., Toronto, CL-1519.
20 bags at 100 lbs.
Analysis showed it to be 95.2 percent TPP,
4.8 percent PP.

This material was contributed by the Electric Reduction Co. Their cooperation and help is gratefully acknowledged.

Flow of effluent: June 5, 9-12 a.m.: 52.5 mgd.

Rhodamine B was added to the effluent at 9:45 in sufficient quantity to give a concentration of about 200 µg/l in the effluent. The tripolyphosphate was then dry-fed at the rate of 1 bag (100 lbs) every 5 minutes. Calculations on solubility of tripolyphosphate showed that for concentrated solution feed of tripolyphosphate a holding tank of about 2000 gal. capacity and a dosing pump capable of delivering 12 gpm were required. Since these items could not be obtained from the treatment plant the decision was made to dry-feed. The material was dumped into the confluent of the effluent channels of the final settling tanks. It was thought that there was sufficient turbulence for dissolving and dilution. Samples were taken at the effluent manhole by a depth-sampler and analyzed by staff at the treatment plant. The results are shown below:

	FTP	OP
	mg/l PO_4	
30 min. before addition of TPP:	7.0	4.5
30 min. after start of addition of TPP:	14.0	7.0
90 min. after start of addition of TPP:	26.0	19.0

The theoretical increase in phosphorus concentration due to the dumping of tripolyphosphate amounts to 35 mg/l PO_4. As seen from the data the increase in FTP was much smaller. This is attributed to a likely caking of the powder as it was added to the effluent. This material would have dissolved over a longer period of time, but did not contribute to the sudden rise in concentration and slug of phosphorus hoped for. The value for orthophosphate after 90 minutes must be wrong. Experiments in the laboratory afterwards showed that the rate of hydrolysis of commercial tripolyphosphate in Humber S.T.P. effluent was about equal to previously found values and therefore hydrolysis could not have occurred as rapidly as indicated by this measurement.

Experimental Data:

Phosphorus: A sample data sheet for June 4 is shown on p.240. It indicates the lower levels of concentration with distance from the sewage outlet. After the dumping of tripolyphosphate the vessel was anchored at the outlet for three hours, during which 37 measurements each for filtered total phosphorus and for orthophosphate were made. The average and range of results are shown below:

At station 01: Sewage outlet

	FTP	CP
	mg/1 PO_4	
Prior to release of TPP:	.880 (.145-3.945)	.115 (.0-.395)
During release of TPP:	1.435 (.325-2.690)	.470 (.0-1.100)

It indicates the increase in FTP and CP, but this increase was not as large as anticipated due to the aforementioned problem. Measurements were continued at several stations for 24 hours after the release of tripolyphosphate. Within a short distance (1/4 mile) from the outlet the levels of concentration after the release of tripolyphosphate do not appear to be significantly different from the data taken prior. For this reason all data on filtered total phosphorus (FTP) at 3 meter level were combined, and concentration contours shown in Fig. 36. In total 460 phosphorus measurements were made, each measurement by duplicate automatic analysis. On 39 samples the phosphorus analysis was carried out both by manual ascorbic acid method, with or without extraction, (see Appendix A:1(a)) and by automatic method (see Appendix A:2(a)). In each case duplicate analysis were made. Comparison was generally good and within the range of precision of the methods.

Temperature: Measurements were made by reversing thermometers (111 meas.) and by baby thermographs (50). A summary of the results is shown.

Depth, m	Temp., °C
3	9.7 (7.5 - 13.2)
6 - 12	7.4 (6.4 - 9.9)
12 - 40	(5.3 - 5.9)

The higher temperatures at the 3 and 6-12 m level occurred at the sewage outlet, as expected. The baby thermographs indicated a layer of warm water for the top four to five meters. Phosphorus measurements at the 3 m level are in agreement with this, as they were, in general, higher than at lower depths, indicating that the warm sewage effluent stays in the top layers.

SERIES XXII - HUMBER BAY SURVEY ON JUNE 3-5, 1968 - SAMPLE DATA SHEET

STA. NO.	TIME OF SAMPLING EDST	STA. DEPTH m	SAMPLE DEPTH m	TEMP. °C	pH	TURB. UNITS	CONDUCT. @ 25°C MICRO-MHOS	PHOSPHORUS $\mu g/l$ PO_4			WIND	
								UTP	FTP	OP	DIREC-TION	SPEED mph
42	June 4, 9:15	12.0	3	8.4	8.1	11.5	341	125	80	85	290	06
"	"	"	7	6.7	8.0	-	343	630 (mud)	150	120		
01	9:30	8.5	3	9.2	7.8	17	370	975	650	525	310	07
"	"	"	6	-	8.0	32	366	1850	850	590		
14	9:40	12.0	3	9.6	8.1	5.5	358	435	435	140	300	08
"	"	"	9	6.4	8.0	5.5	346	225	135	60		
24	9:55	13.0	3	9.8	8.3	4.5	357	305	205	175	300	04
"	"	"	10	6.4	8.1	4.5	341	135	75	65		
34	10:15	17.5	3	10.0	8.3	8.5	352	225	135	85	350	04
"	"	"	10	6.4	8.2	9.0	338	75	30	30		
44	10:35	18.5	3	9.1	8.1	3.5	340	160	50	45	210	08
"	"	"	15	5.9	8.2	4.0	342	85	25	25		
54	10:55	33.5	3	10.4	8.5	3.8	343	160	50	45	220	11
"	"	"	30	5.9	8.1	-	341	740 (mud)	30	35		

pH: 127 measurements were made. They were generally uniform with location and depth. The average value was 8.1, with a range of 7.6 to 8.4. The low values occurred at the sewage outlet.

Turbidity: 123 measurements were made with the Hellige Turbidimeter. The average value was 6 units, with a range of 1 to 45. The high values occurred at the Humber River and the sewage outlet. The low average value of 6 indicates that the bay acts as an efficient settling basin.

Conductivity: 127 measurements were made and corrected to a standard temperature of 25°C. The average value measured was 365 micro-mhos, with a range of 330 to 625. Contours were drawn and indicated a similar pattern as the phosphorus data in Fig. 36. The high values occurred at the Humber River (500 to 600) and at the sewage outlet (about 400). In general conductivities were higher at the 3 m level than at lower depths.

Wind measurements: During the entire survey relatively calm weather occurred. The wind speed varied from 0 to 13 mph. Winds blew in a north-easterly direction, which is parallel and towards the shoreline.

Current measurements: Drogue studies were carried out using Great Lakes Institute canvas drogues. The canvas was set at an average depth of about 3 m. They were equipped with flashing lights to facilitate tracking at night. Drogues were set out in intervals of 2-3 hours at the sewage outlet and their location (bearing and distance from the sewage outlet) was measured by dead-reckoning. The paths are shown in Fig. 36. All drogues moved towards shore, near the vicinity of Sunnyside Beach. In general, drogues moved in the direction of the wind. The average speed was 7 ft./min., with a range of 2-16. The direction of drogue travel and high levels of phosphorus generally coincide, as seen in Fig. 36, indicating that during the survey the sewage travelled from the outlet pipe towards the shoreline at Sunnyside Beach. Since the prevalent winds in the area apparently are usually in a north-easterly direction, as occurred during the survey, this is indeed an undesirable situation.

Aerial Photography: Two flights were made, on June 4 and June 5, 1968. Colour photography was used. The picture on June 5 was taken after the release of the Rhodamine B, but did not show the effect of this. It only indicated the effect of the Humber River current entering the bay.

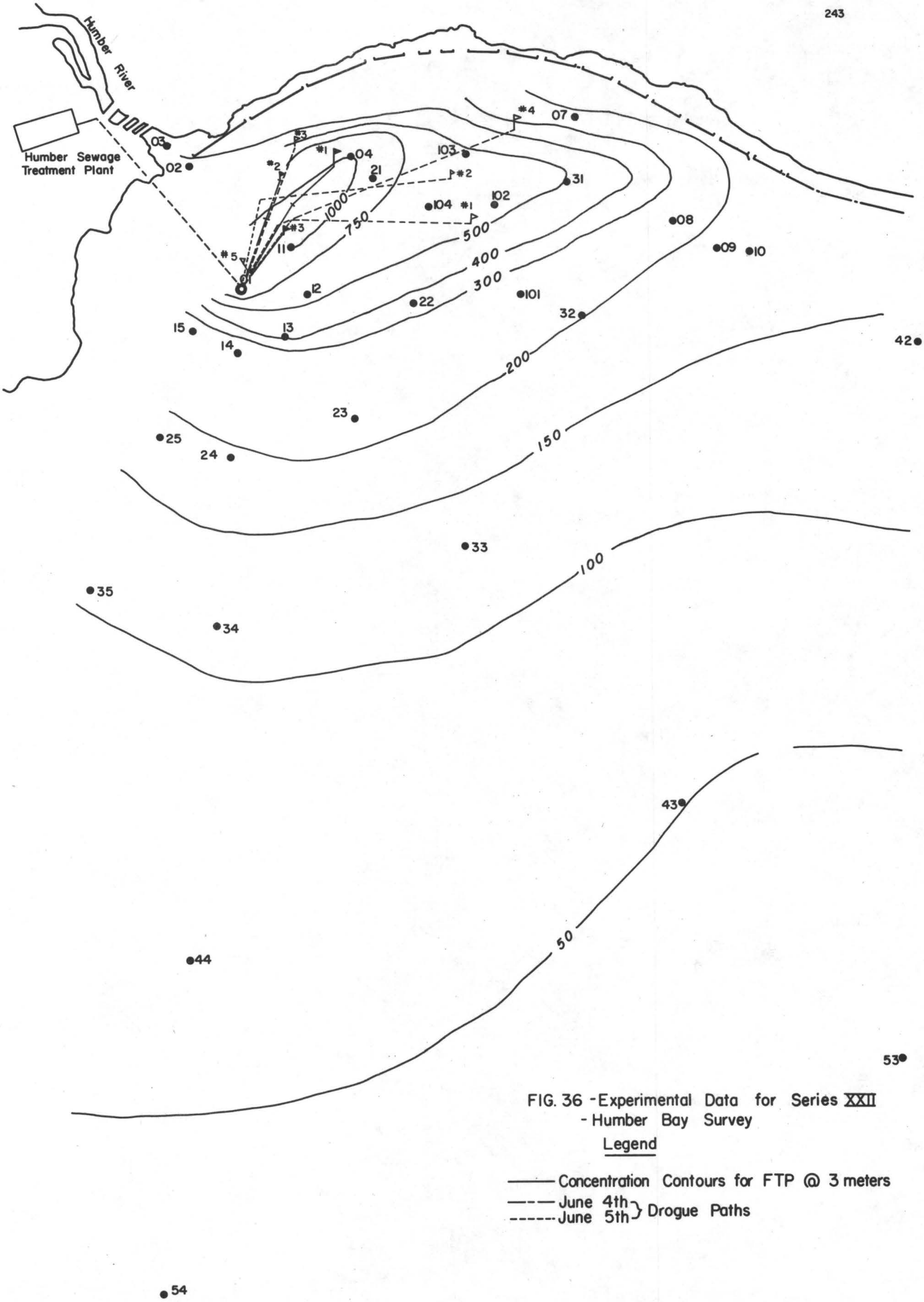


FIG. 36 - Experimental Data for Series XXII
- Humber Bay Survey

Legend

——— Concentration Contours for FTP @ 3 meters
— — — June 4th
------ June 5th } Drogue Paths

V-4 WASTEWATER STUDIES

Two field studies were made at the Dundas Sewage Treatment Plant to obtain data on concentration and type of phosphorus present in wastewater, and estimates of the rate of hydrolysis of condensed phosphates in the plant. One study was carried out during the summer, one during the winter. Batch experiments on Dundas wastewater and activated sludge were carried out in the laboratory to establish rates of hydrolysis of condensed phosphates and to estimate the effect of pH variation on the rate. Finally, an extensive field survey was made on the Humber Sewage Treatment Plant, Toronto. The majority of the work on wastewater was done prior to successful use of differential condensed phosphate analysis. Rates are therefore reported as k_{avg}.

Experimental Results and Analysis of Data

Table XXXIII summarizes all experimental studies in wastewater. Data of individual series are presented in graphical or tabular form.

TABLE XXXIII: SUMMARY OF EXPERIMENTAL WORK ON WASTEWATER

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	COND. PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL CONDITION				TYPE OF ANALYSIS	REMARKS
			TYPE ADDED	INITIAL CONC. mg/1 PO_4		TEMP. ^oC	pH	LIGHTING	AERATION		
IV	July-Aug.67	Batch study on unfiltered and filtered domestic wastewater from Dundas S.T.P.									
		Raw Waste, Unfilt.	TPP	~30	234	20	7.6 (initially)	D-N	Cont.	FTP,OP	
		" Filt.(0.8µ)	"	"	"	20	"	"	"	"	
		" Unfilt.	"	"	"	4	"	"	"	"	
		" Filt.(0.8µ)	"	"	"	4	"	"	"	"	
		" Unfilt.	-	-	"	20	"	"	"	"	Control
		" Unfilt.	-	-	"	4	"	"	"	"	"
V	July 10-13, 67	Field study on Dundas S.T.P. and in Dundas sewer system	-	-	4 days	18-19					
			At three stations within the sewer system, and on treatment plant influent, primary and final effluent the following analyses were made: UTP, FTP, OP, COD, pH, Temperature. Time of flow measurements were carried out and samples taken in timed sequence.								To obtain data on conc., type of phosph. compound and rate of hydrolysis in raw sewage and in various stages in an activated sludge treatment plant.

TABLE XXXIII - (Cont'd.)

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	COND. PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL CONDITION				TYPE OF ANALYSIS	REMARKS
			TYPE ADDED	INIT. CONC. mg/l PO_4		TEMP. °C	pH	LIGHTING	AERATION		
VII	Aug.-Sept. 67	Batch study on unfiltered, filtered, and filtered and autoclaved domestic wastewater from Dundas S.T.P.									Repeat of Series IV, attempt to eliminate effect of organisms by autoclaving filtered sewage. Some bacteriological tests and observation.
		Raw Sewage, Unfilt., 20°C	TPP	$\sim$25	408	20	8.1-8.6	D-N	Cont.	UTP, FTP, OP, OPU	
		" " Unfilt., 4°C	"	"	"	4	"	"	"	"	
		Raw Sewage, Filt. (0.8μ), 20°C	"	"	"	20	"	"	"	"	
		" " " 4°C	"	"	"	4	"	"	"	"	
		Raw Sewage, Filt & autocl., 20°C	"	"	"	20	"	"	-	"	
		" " " 4°C	"	"	"	4	"	"	-	"	
VIII	Sept.-Oct. 67	Batch study on unfiltered, and filtered domestic wastewater from Dundas S.T.P.									Repeat of Series IV & VII, but using 0.45μ filter to attempt to obtain sterile sewage. Some bacteriological tests and observations.
		Raw Sewage, Unfilt., 20°C	TPP	$\sim$22.5	228	20	8.2-8.6	D-N	Cont.	UTP, FTP, UOP, OP	
		" " " 4°C	"	"	"	4	8.4-8.6	"	"	"	
		Raw Sewage, Filt. (0.45μ), 20°C	"	$\sim$28.5	"	20	8.3-8.7	"	-	"	
		" " ", 4°C	"	"	"	4	8.4-8.7	"	-	"	

TABLE XXXIII - (Cont'd.)

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	COND.PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL CONDITION				TYPE OF ANALYSIS	REMARKS
			TYPE ADDED	INIT. CONC. mg/l PO_4		TEMP °C	pH	LIGHTING	AERATION		
XV	March 68	Field study on Dundas S.T.P. under winter conditions	-	-	1 day	8				FTP, OP Diff. Anal.	on raw sewage, primary effluent and final effluent sampled in timed sequence.
XVI	March-April 68	Batch study on domestic wastewater (settled sewage). Effect of pH.	TPP	~50	138	20	9.0-9.1	D-N	Cont.	Diff. Anal., UTP, FTP, OP	Bacteriological observations. Buffered by sodium carbonate.
			TPP	~30	58	"	7.0-7.9	"	"	"	Not buffered.
			TPP	"	124	"	5.3 +	"	"	"	Buffered by potassium acetate-acetic acid.
			TPP	~50		"	5.0-5.5	"	"	"	Buffered by potassium hydrogen phtalate.

TABLE XXXIII - (Cont'd.)

SERIES NO.	DATES	DESCRIPTION OF EXPERIMENT	COND. PHOSPH.		LENGTH OF EXPT. HRS.	ENVIRONMENTAL COND.				TYPE OF ANALYSIS	REMARKS
			TYPE ADDED	INIT. CONC. mg/1 PO_4		TEMP °C	pH	LIGHTING	AERATION		
XXI	May 68	Field study on Humber S.T.P.	-	-	1 day	15-17				Diff. Anal. TUF, TF, OP	24 hr. - hourly measurements on raw waste, primary and final effluent.
XXIII	June 68	Batch study on activated sludge mixed liquor								FTP, OP, Diff. Anal.	
		unfiltered	~TPP	50	3	20	7.7	D-N	Cont.		
		filtered (0.45 µ)	~TPP	50	68	20	7.7	"	"		

SERIES V - FIELD STUDY ON DUNDAS SEWERAGE SYSTEM AND PLANT

The purpose of this series is to obtain data on the concentration and type of phosphorus compound present in raw wastewater and after several stages of treatment. From these data an estimate of the rate of hydrolysis of condensed phosphates in wastewater may be obtained. This investigation was done under summer conditions (see Series XV for winter conditions), for a period of four days. The plant uses the activated sludge process.

Field Conditions

Date: July 10-13, 1967

Flow rates: 1.9-2.4 MGD (nominal plant capacity = 1.4 MGD)

Temp. of Influent: 19°C

Sampling Points: Three locations were chosen within the sewer system. Samples at Stations 1 and 2 were domestic wastewater, at Station 3 mainly industrial wastewater. The time of flow from the station to the treatment plant under average flow conditions was measured as 2.25, 1.45 and 1.15 hours respectively.

At the treatment plant the influent, primary and secondary effluent were sampled. The detention time in the plant was 1.15 hours for the primary, and 9.75 hours for the secondary effluent at design flow rate.

Samples were taken in a timed sequence to allow for the various detention times. One 15-minute composite sample per station per day was taken. They were stored in icepack until analyzed.

Tests: UTP, FTP, UOP, OP, and COD.

From these CP and PAP can be obtained (see Chapter IV-1)

Experimental Data: A summary of the data is given only. COD reduction varied from 81 to 90 percent, indicating satisfactory conventional treatment.

Average and Range of Concentration of Phosphorus Compounds - mg/1 PO_4

	mg/1 PO_4				
Medium	UTP	PAP	FTP	OP	CP
Wastewater at Sta.1,2 and 3	(22-67)	(3-31)	(18-56)	(9-39)	(4-31)
Influent	36(29-47)	7(4-11)	29(25-36)	10(8-13)	19(13-26)
Primary Effluent	32(27-37)	8(3-17)	24(20-28)	10(6-15)	14(13-14)
Secondary Effluent	19(13-26)	<1(0-2)	18(13-24)	17(12-24)	1(0-1)

Average and Range of Concentration of Phosphorus Compounds - Percent

	Percent of UTP		Percent of FTP	
Medium	PAP	FTP	OP	CP
Wastewater at Sta. 1, 2 and 3	(12-52)	(48-88)	(48-82)	(18-52)
Influent	19(12-23)	81(77-88)	37(28-50)	63(50-72)
Primary Effluent	25(11-46)	75(54-89)	42(30-54)	58(46-70)
Secondary Effluent	3(0- 8)	97(92-100)	96(92-100)	4(0- 8)

Average and Range of Phosphorus Reduction

Medium	Percent Reduction, based on influent conc.			
	UTP	PAP	FTP	CP
Primary Effluent	12(0-21)	6(<0-25)	18(0-44)	24(0-46)
Secondary Effluent	48(38-60)	95(82-100)	38(28-50)	96(92-100)

Rate of Hydrolysis

Avg. Detention Time in Primary Settling Tank = 50 min.

" " " Act. Sludge Tank = 260 min.

Avg. Cond. Phosph. in Influent	19 mg PO_4/1
" " Primary Effluent	14 "
" " Secondary Effluent	1 "

Primary Settling Tank: $k_{avg.} = 6 \times 10^{-3}\ min^{-1}$

Activated Sludge: $k_{avg.} = 1 \times 10^{-2}\ min^{-1}$

(It is assumed that the hydrolysis taking place in the final settling tanks can be neglected)

SERIES IV, VII AND VIII - LABORATORY BATCH STUDY ON RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN WASTEWATER

The purpose of these studies is to establish rates of hydrolysis of tripolyphosphate in wastewater under varying conditions of temperature and organism activity. Each series was carried out at 20°C and 4°C, simulating summer and winter wastewater temperature conditions. To check the effect of presence or absence of organisms experiments were carried out on unfiltered and filtered wastewater. The attempt was to obtain a 'sterile' wastewater. In Series IV a 0.8 micron filter was used. Organism grew in the filtrate after a few hours. In Series VII the same size filter was used and the filtrate was autoclaved. However, this caused precipitates to form changing the chemical properties of the wastewater. In Series VIII a 0.45 micron filter was used. Again growth occurred in the filtrate after several hours, although to a smaller extent. In all cases the vessels, stirrer bars etc. were sterilized and aseptic sampling techniques used. Microscopic examination and plate counts were carried out at times.

SERIES IV

Experimental Conditions

Date: July 31 - August 10, 1967

Medium: Influent wastewater to Dundas S.T.P.

$FTP = 19$ mg/l PO_4 pH = 7.6

$OP = 13$ mg/l PO_4 T = 19°C

Sample Preparation: IV-1, -3 unfiltered

IV-2, -4 membrane filtered (0.8 micron)

25 mg/l PO_4 of TPP was added to the four flasks.

Incubation Temperature: IV-1, -2 20°C

IV-3, -4 4°C

Samples were mixed by magnetic stirrer and aeration.

Day-Night Lighting conditions were used.

Tests: FTP, OP, (CP calculated as the difference)

Experimental Data: These are presented in Fig. 37-1 to -4.

Rate of Hydrolysis: The data for condensed phosphates for all four runs were replotted in Fig. 37-5 as logarithm (percent condensed phosphates remaining) versus time and rates of hydrolysis calculated as the slope of the straight line. With the exception of IV-1 a reasonably good fit is indicated. A lag period occurs for IV-3, -4, at 4°C.

IV-1: Unfiltered, 20°C : $k_{avg} = 2.4 \times 10^{-4}\ min^{-1}$

-2: Filtered, 20°C : $k_{avg} = 1.4 \times 10^{-4}\ min^{-1}$

-3: Unfiltered, 4°C : $k_{avg} = 9.0 \times 10^{-5}\ min^{-1}$

-4: Filtered, 4°C : $k_{avg} = 6.1 \times 10^{-5}\ min^{-1}$

Estimate of Activation Energy:

for unfiltered wastewater (IV-1, -3): E = 9.8 k cal/mole.

for filtered wastewater (IV-2, -4): E = 8.3 k cal/mole.

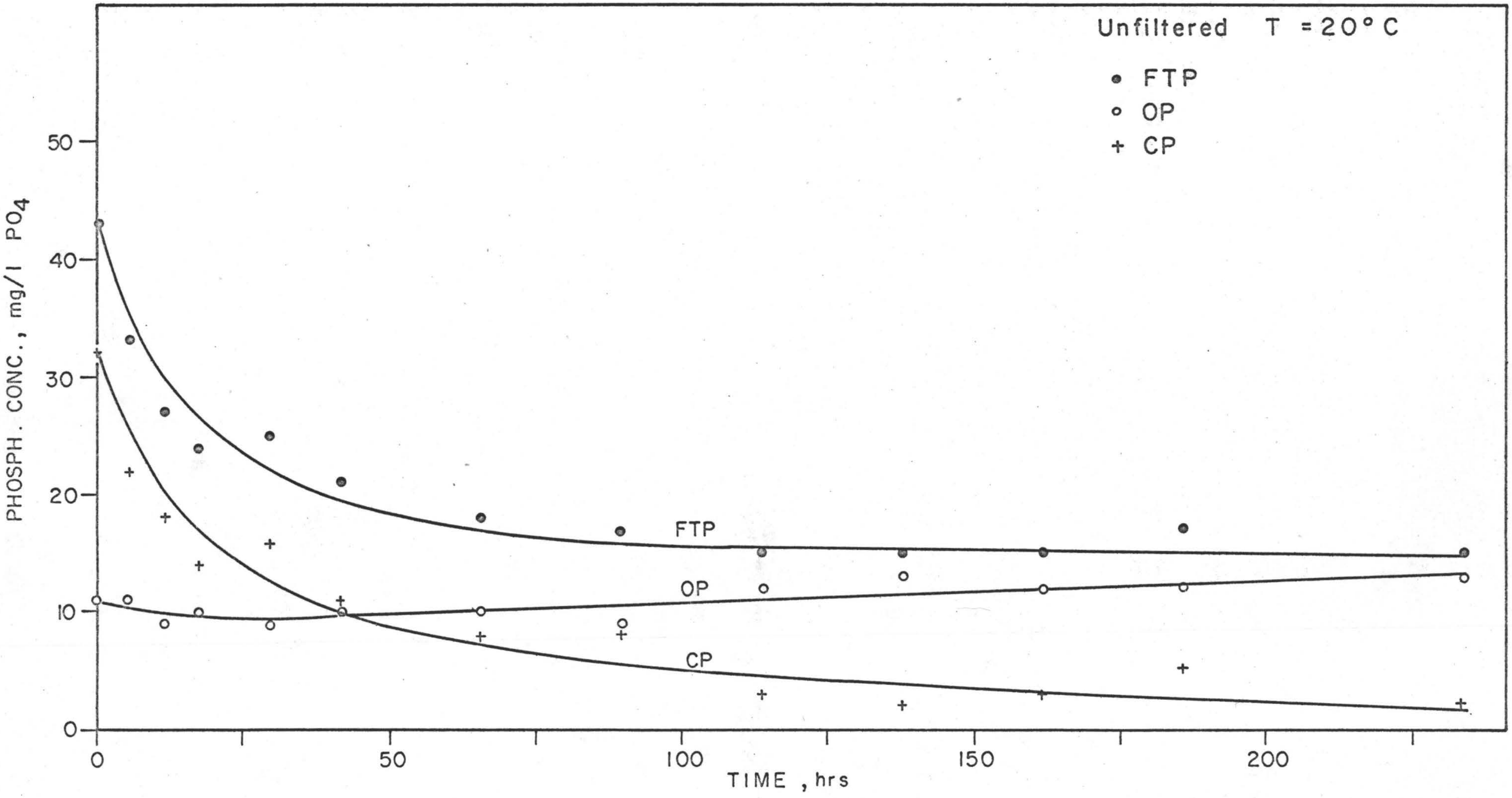


Figure 37-1. Experimental data for series IV-1.

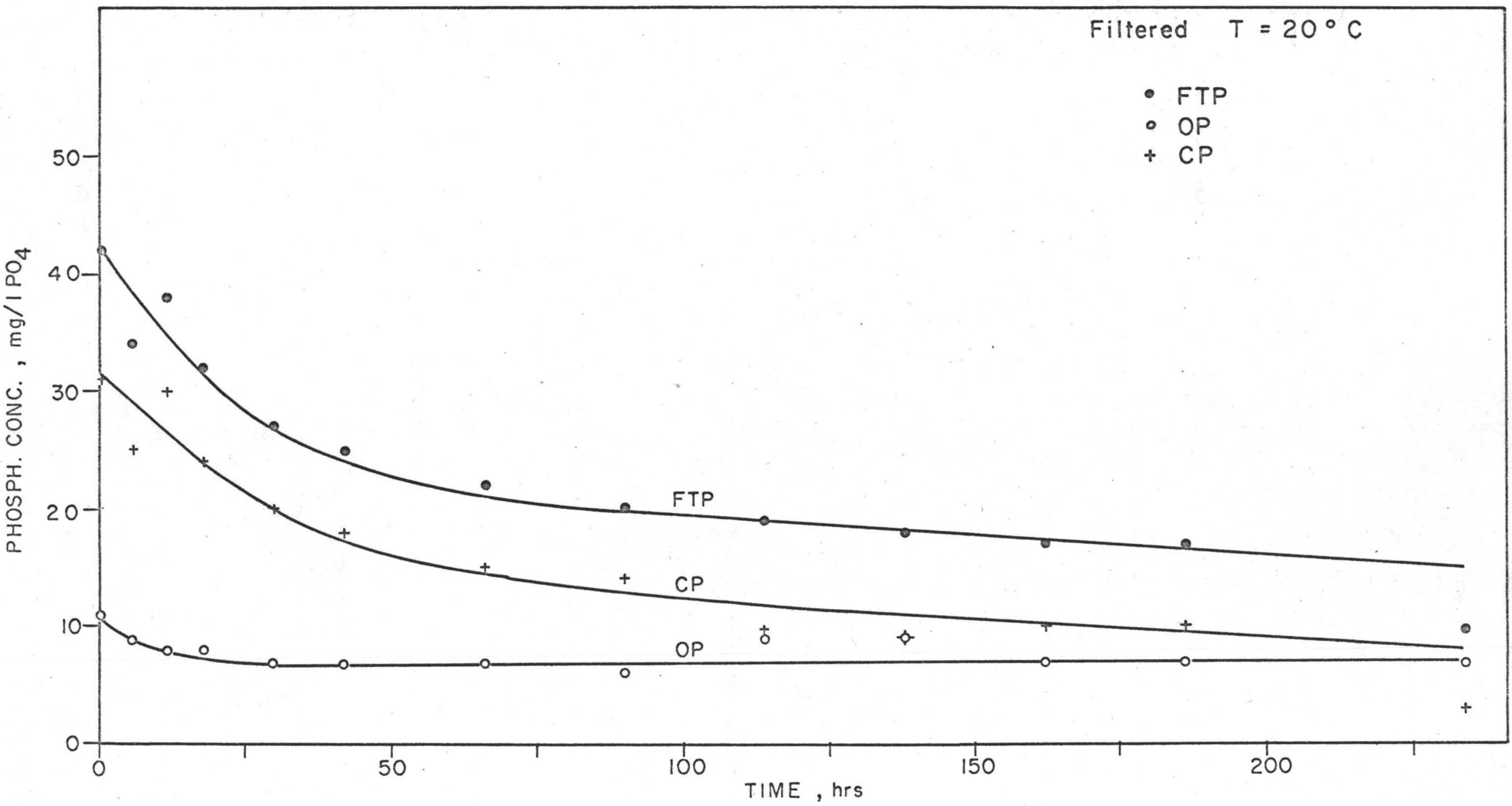


Figure 37-2. Experimental data for series IV-2.

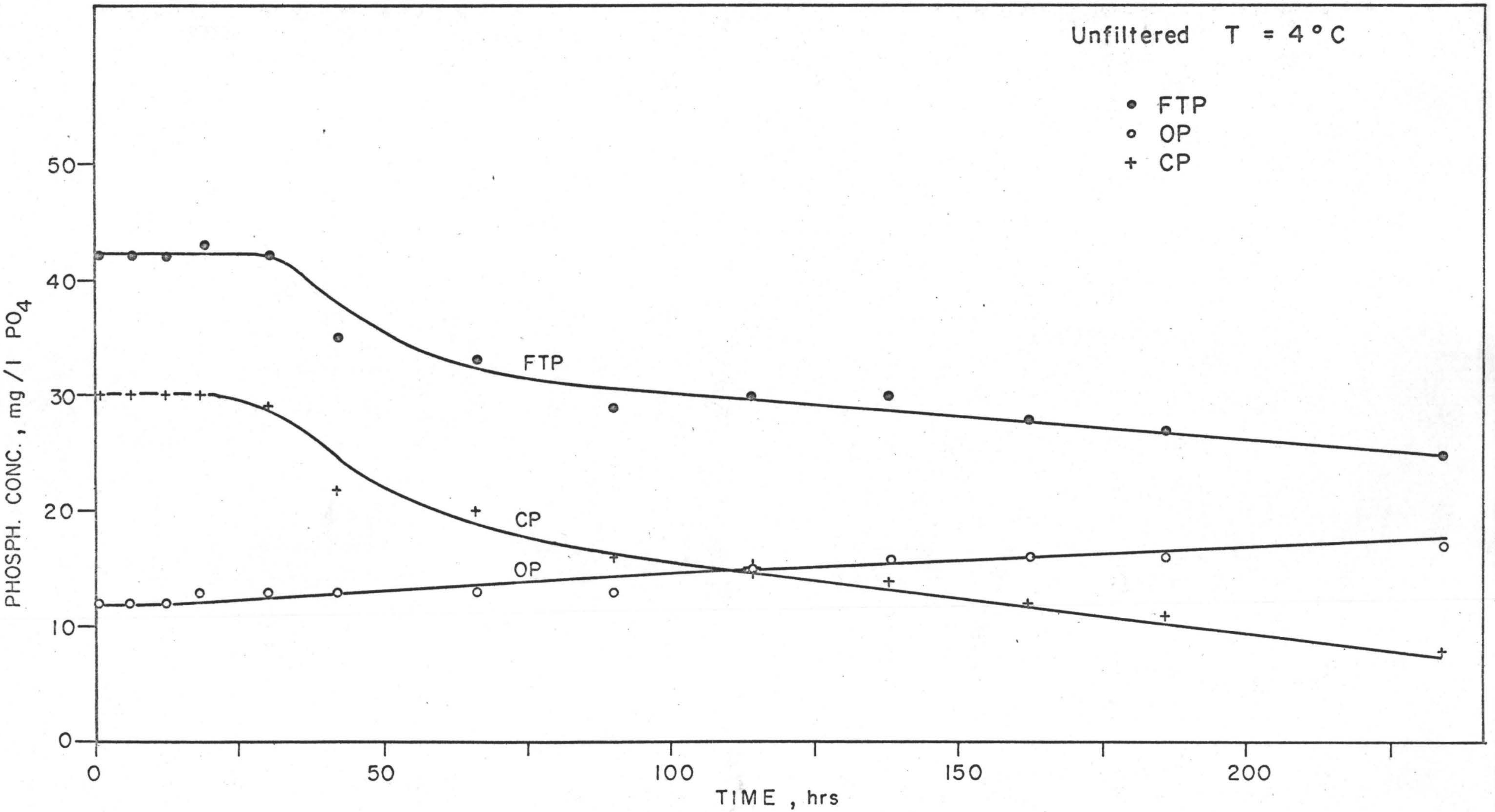


Figure 37-3. Experimental data for series IV-3.

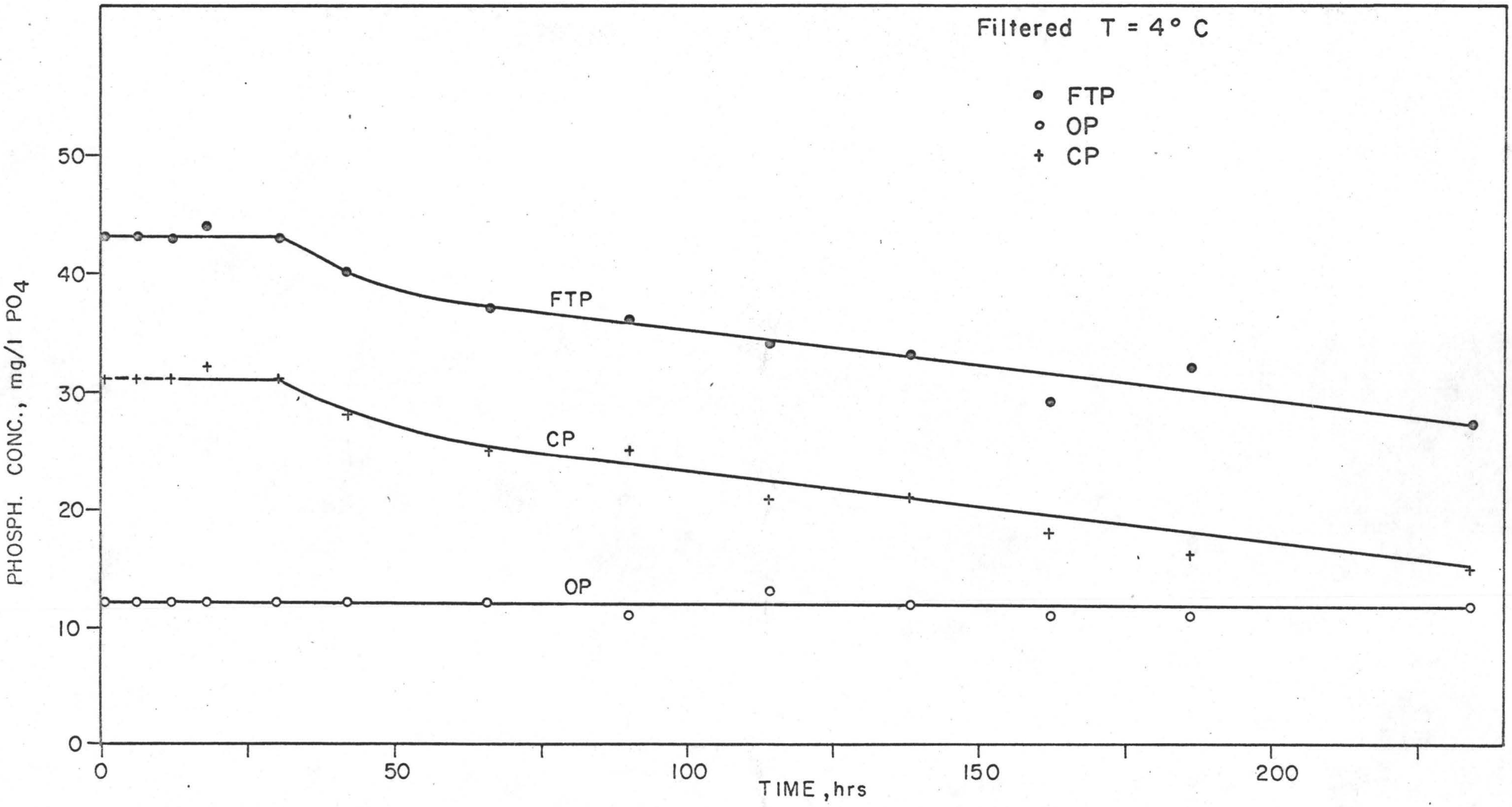


Figure 37-4. Experimental data for series IV-4.

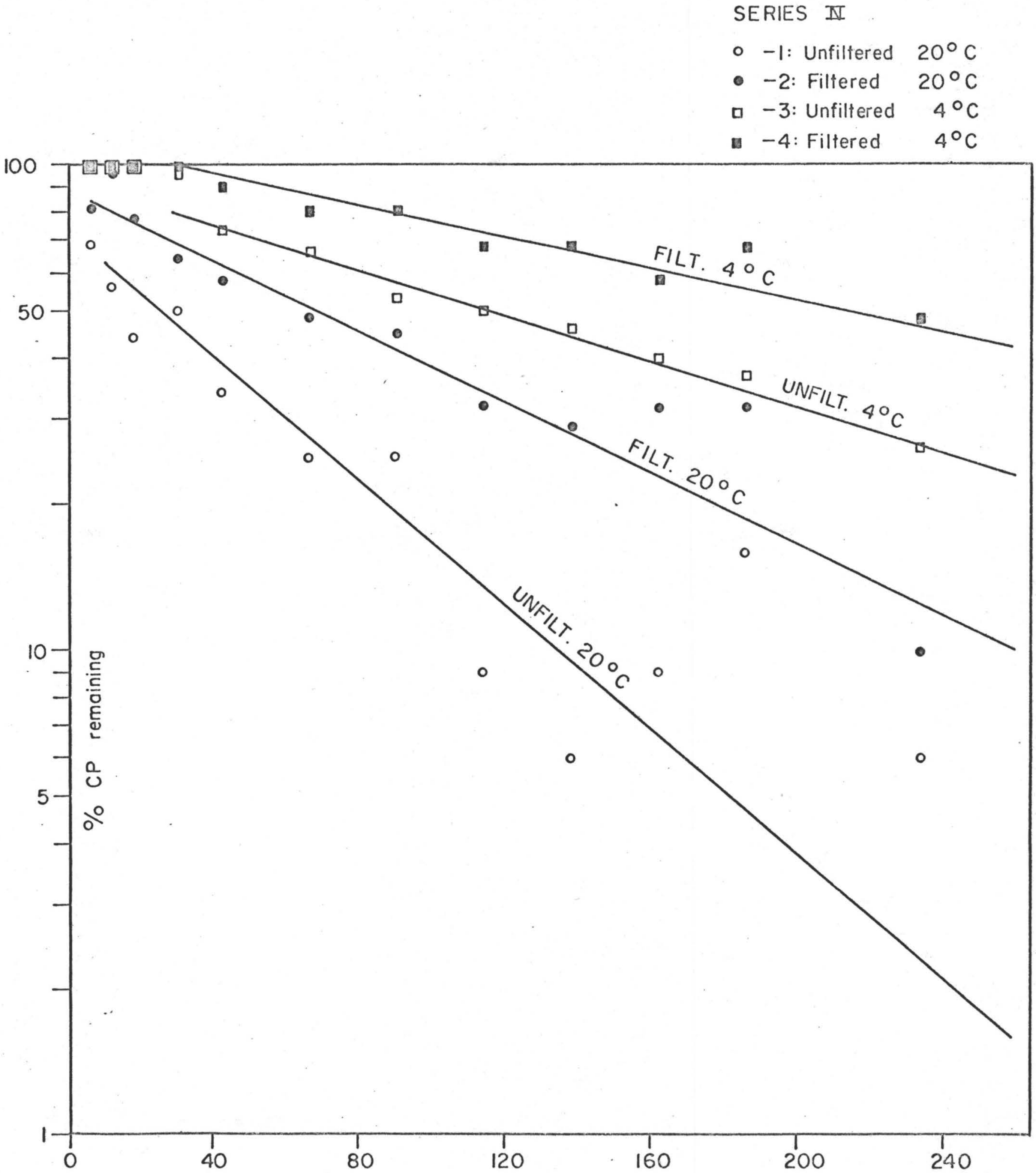


Figure 37-5. Experimental Data for Series IV.

SERIES VII

Experimental Conditions

Date: August 25 - September 11, 1967

Medium: Influent Wastewater to Dundas S.T.P.

UTP = 24 mg/l PO_4 pH = 6.4

FTP = 22 mg/l PO_4 T = 18°C

UOP = 22 mg/l PO_4

OP = 18 mg/l PO_4

Sample preparation:

VII-1, -3	Unfiltered
VII-2, -4	Filtered
VII-5, -6	Filtered and autoclaved

To all six flasks 25 mg/l PO_4 of TPP was added.

Incubation Temperature:

VII-1, -2, -5	20°C
VII-3, -4, -6	4°C

Samples were mixed by magnetic stirrer and aeration (except -5, -6) and shaken before sampling. Aseptic sampling technique was used for VII-2, -4, -5, -6. Day-Night Lighting Conditions were used.

Tests: FTP, OP, at times UTP and pH.

Experimental Data: These are presented in Fig. 38-1 to -6. No curves are drawn through the erratic data of Fig. 38-5 and 6.

Rate of Hydrolysis: The data for condensed phosphates for runs 1 to 4 were plotted in Fig. 38-7 as logarithm (percent condensed phosphate remaining) versus time and rates of hydrolysis calculated as the slope of the straight line. The fit is not as good as in Series IV and VIII, but the rates compare favourably.

VII-1: Unfiltered, 20^oC : $k_{avg} = 2.3 \times 10^{-4}\ min^{-1}$
-2: Filtered, 20^oC : $k_{avg} = 1.9 \times 10^{-4}\ min^{-1}$
-3: Unfiltered: 4^oC : $k_{avg} = 8.5 \times 10^{-5}\ min^{-1}$
-4: Filtered: 4^oC : $k_{avg} = 3.6 \times 10^{-5}\ min^{-1}$

Estimate of Activation Energy

for unfiltered wastewater (VII-1, -3): E = 10.0 k cal/mole.
for filtered wastewater (VII-2, -4): E = 16.6 k cal/mole.

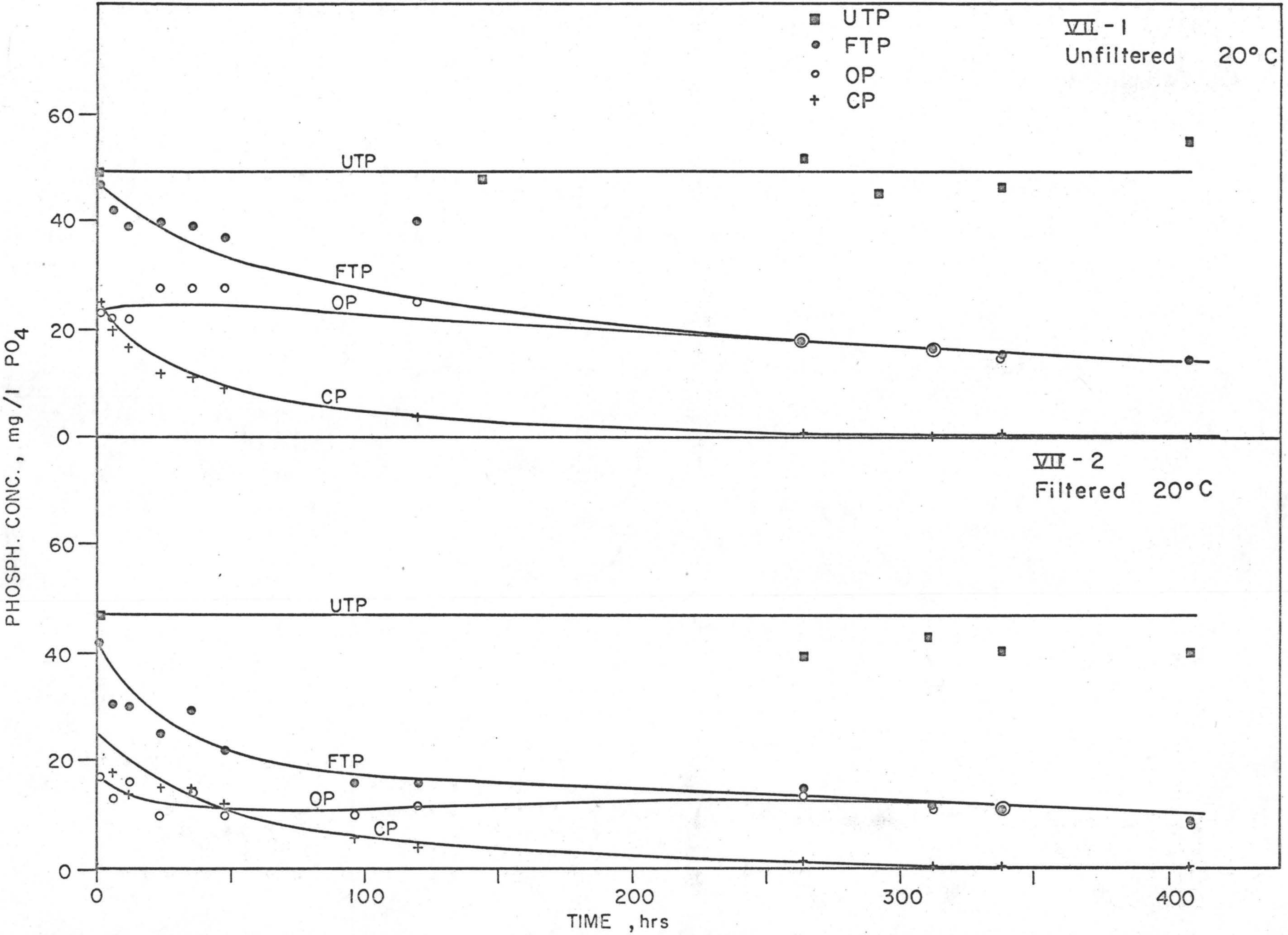
Microscopic Examination: (at t = 300 hours)

VII-1: Mostly bacterial floc, some mineral floc. Clusters of bacteria, flagelatta, few nematodes. Little dispersed growth.

VII-2: Less bacterial floc than in -1, some rods and cocci.

VII-3: Mostly mineral matter, very few rods and cocci, some small clusters of bacterial floc.

Figure 38-1. Experimental data for series VII-1.
38-2. Experimental data for series VII-2.



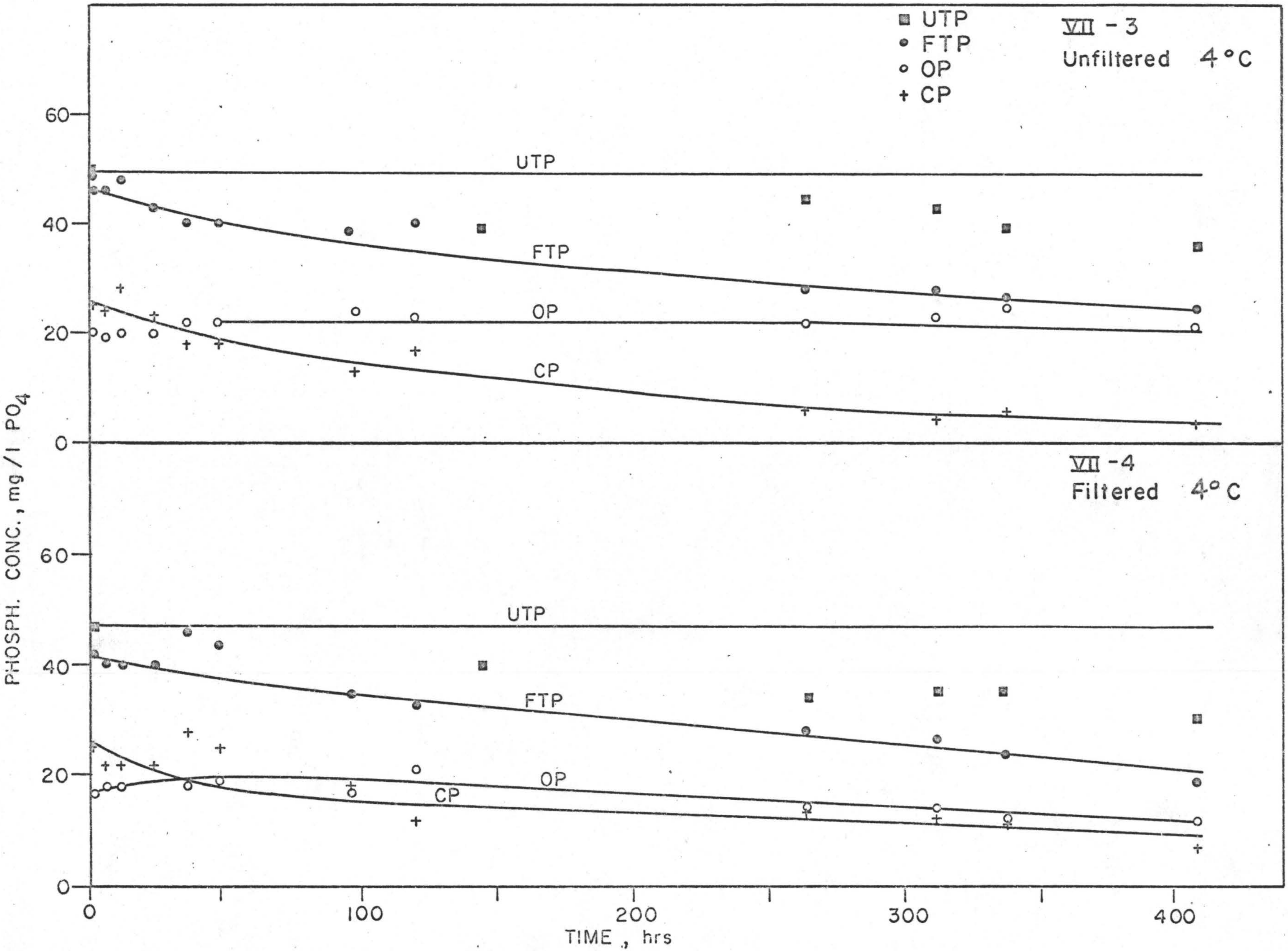


Figure 38-3. Experimental data for series VII-3.
38-4. Experimental data for series VII-4.

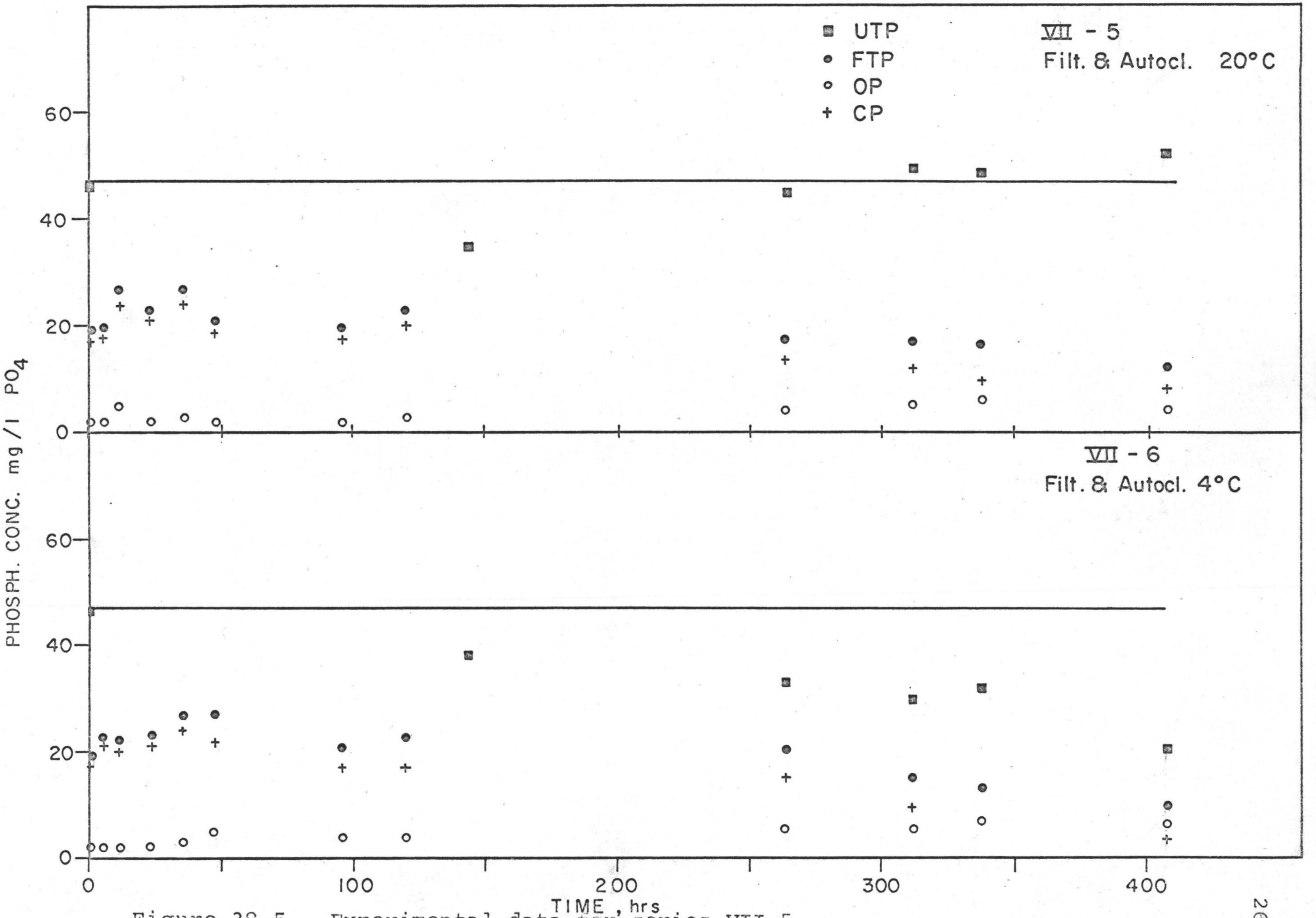


Figure 38-5. Experimental data for series VII-5.
38-6. Experimental data for series VII-6.

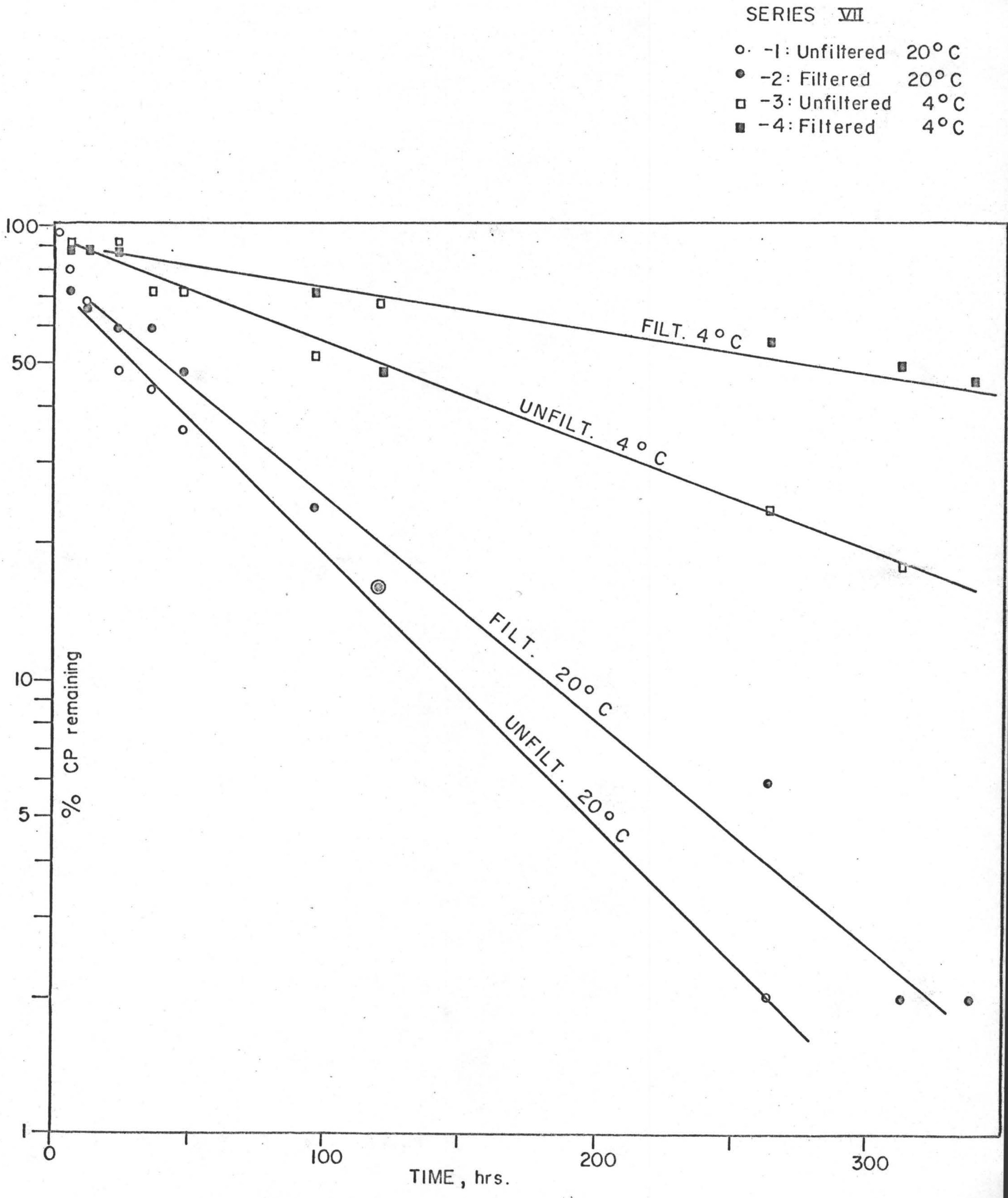


Figure 38-7. Experimental Data of Series VII.

SERIES VIII

Experimental Conditions

Date: Sept. - Oct. 1967

Medium: Influent Wastewater to Dundas S.T.P.

UTP = 27.5 mg/l PO_4 pH = 7.9
FTP = 21.5 mg/l PO_4 T = 17°C
UOP = 20.0 mg/l PO_4
OP = 15.0 mg/l PO_4

Sample Preparation: VIII-1, -3 unfiltered
VIII-2, -4 membrane filtered (0.45 micron)

Wastewater was prefiltered through Whatman paper and then through 0.45 μ filter directly into sterile flask.

To all four flasks TPP was added to bring total phosphorus concentration to about 50 mg/l PO_4. For VIII-2, -4 sterile distilled water was used for preparation of tripolyphosphate solution.

Incubation Temperature: VIII-1, -2 20°C
VIII-3, -4 4°C

Samples were mixed by magnetic stirrer, and shaken before sampling. Aseptic sampling technique was used for VIII-2, -4. Day-Night Lighting Conditions were used.

Tests: UTP, FTP, UOP, OP, and pH.

Experimental Data: These are presented in Fig. 39-1 to -4.

Rate of Hydrolysis: The data for condensed phosphates for all four runs were replotted in Fig. 39-5 as logarithm (percent condensed phosphate remaining) versus time and rates of hydrolysis calculated as the slope of the straight line. The data allow a reasonably good fit to a straight line, indicating a first-order hydrolysis of condensed phosphates. A poor fit at the beginning of the 20°C runs is apparent. A faster rate of hydrolysis than calculated seems to occur in that period.

VIII-1: Unfiltered, 20°C : $k_{avg} = 2.1 \times 10^{-4}$ min^{-1}
-2: Filtered, 20°C : $k_{avg} = 1.6 \times 10^{-4}$ min^{-1}
-3: Unfiltered, 4°C : $k_{avg} = 1.1 \times 10^{-4}$ min^{-1}
-4: Filtered, 4°C : $k_{avg} = 5.9 \times 10^{-5}$ min^{-1}

Estimate of Activation Energy:

for Unfiltered Wastewater (VIII-1, -3): E = 6.5 k cal/mole.
for Filtered Wastewater (VIII-2, -4): E = 10.0 k cal/mole.

Figure 39-1. Experimental data for series VIII-1.

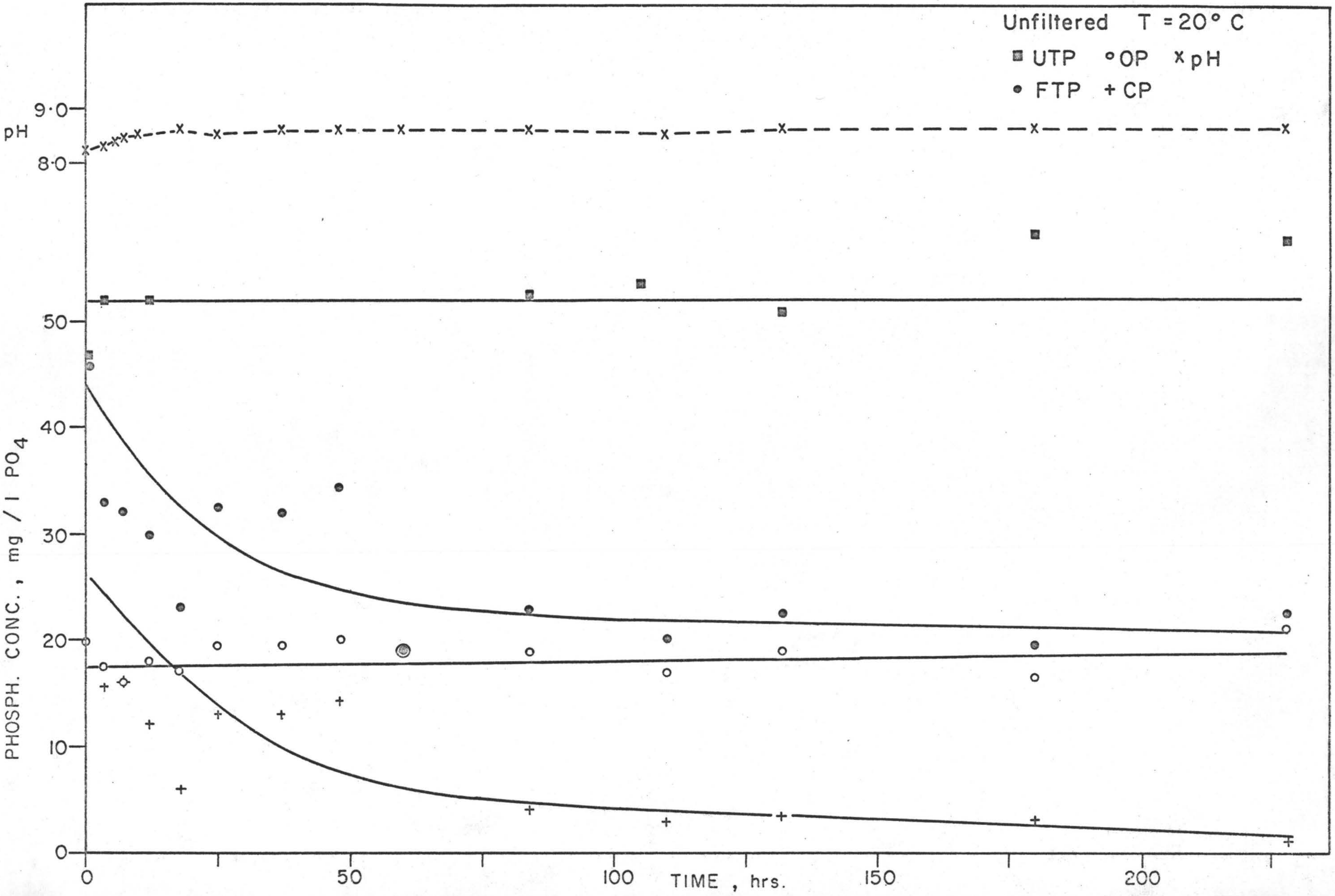


Figure 39-2. Experimental data for series VIII-2.

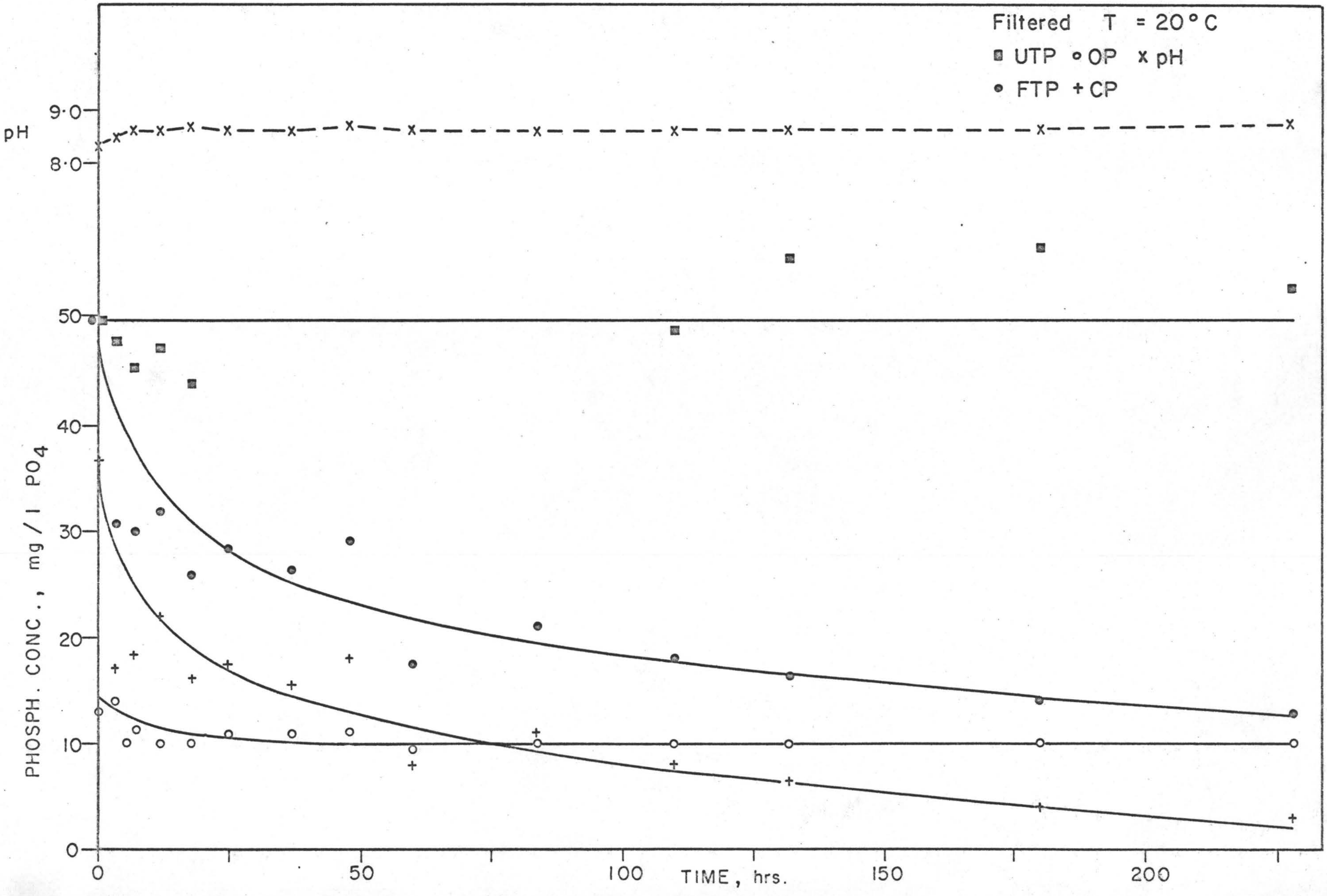


Figure 39-3. Experimental data for series VIII-3.

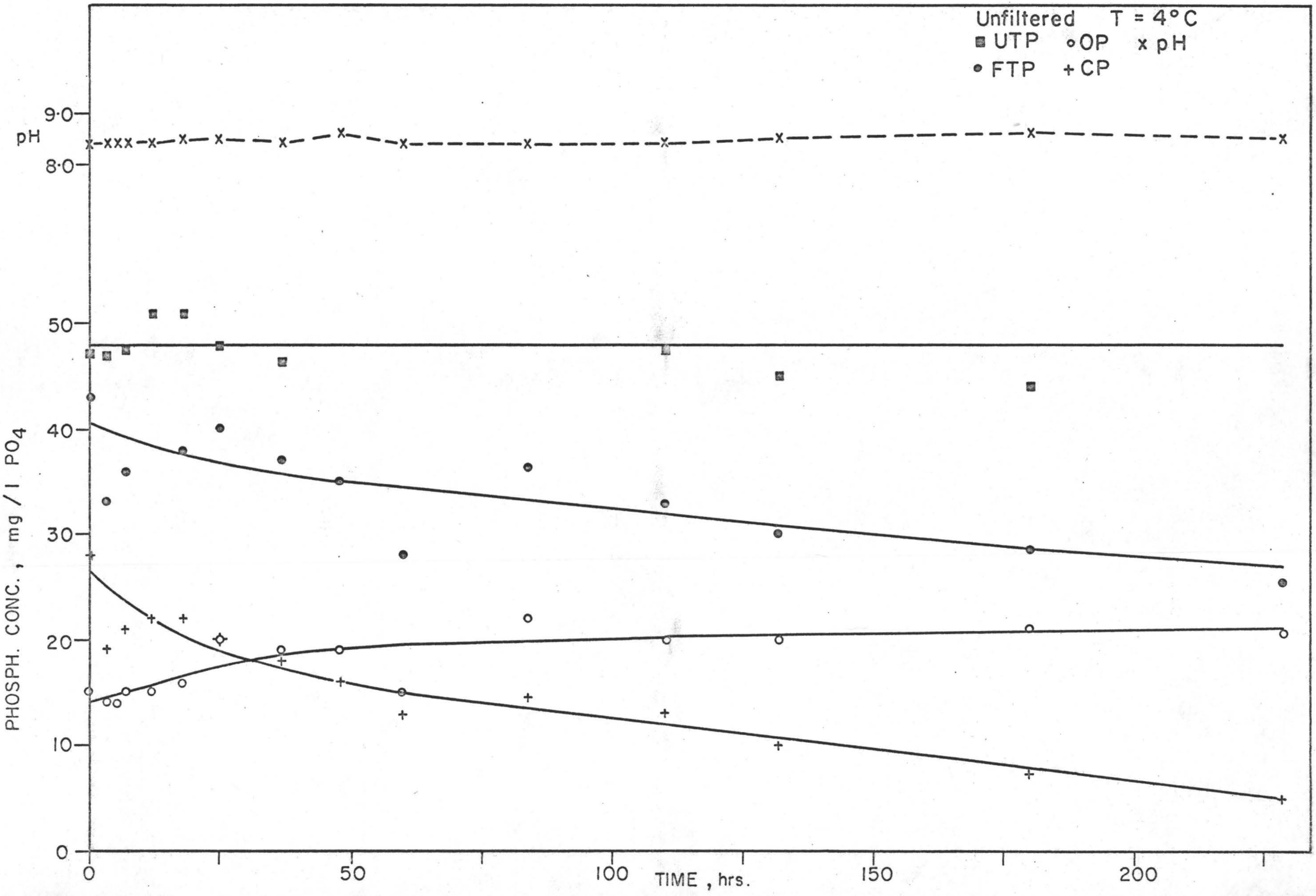
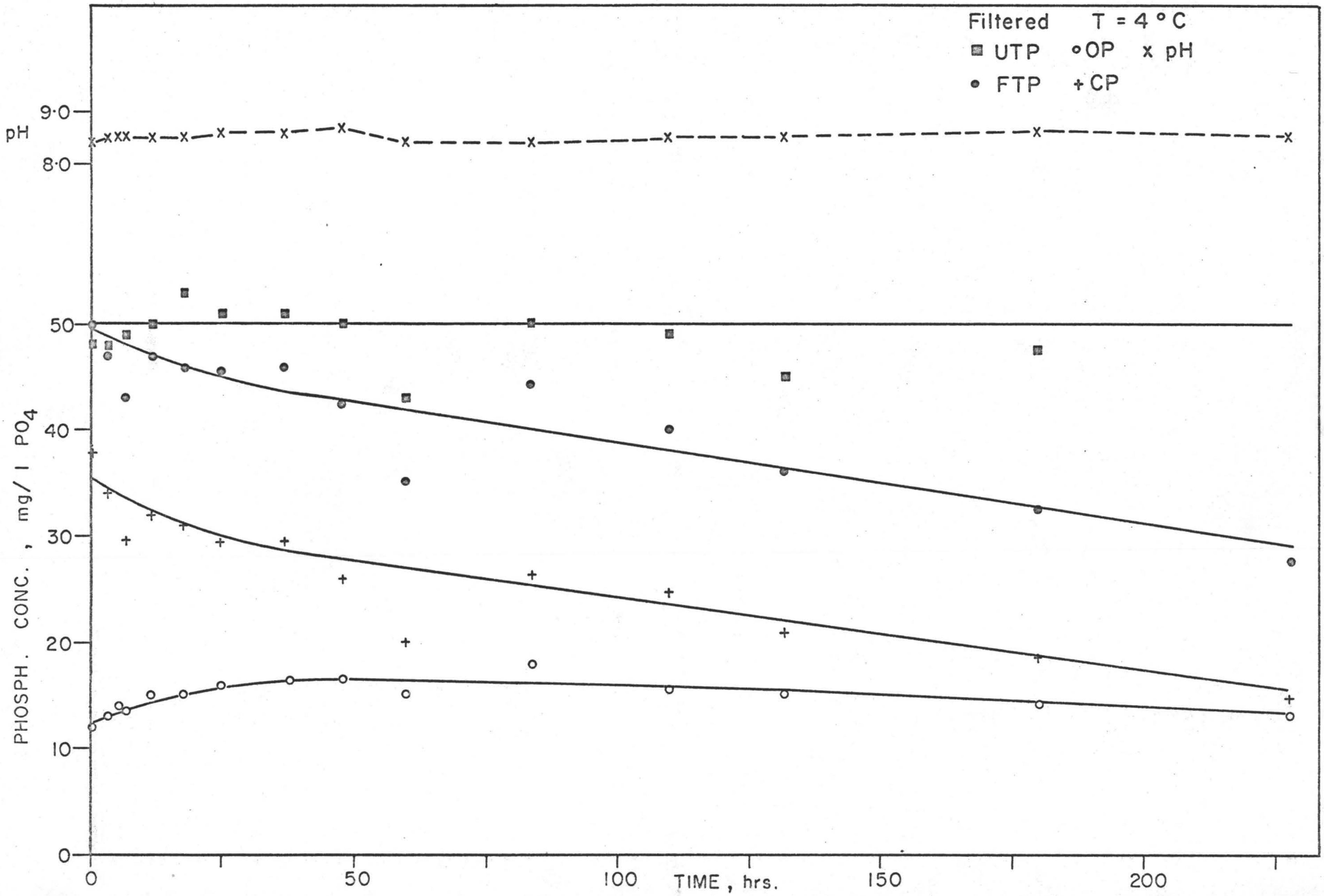


Figure 39-4. Experimental data for series VIII-4.



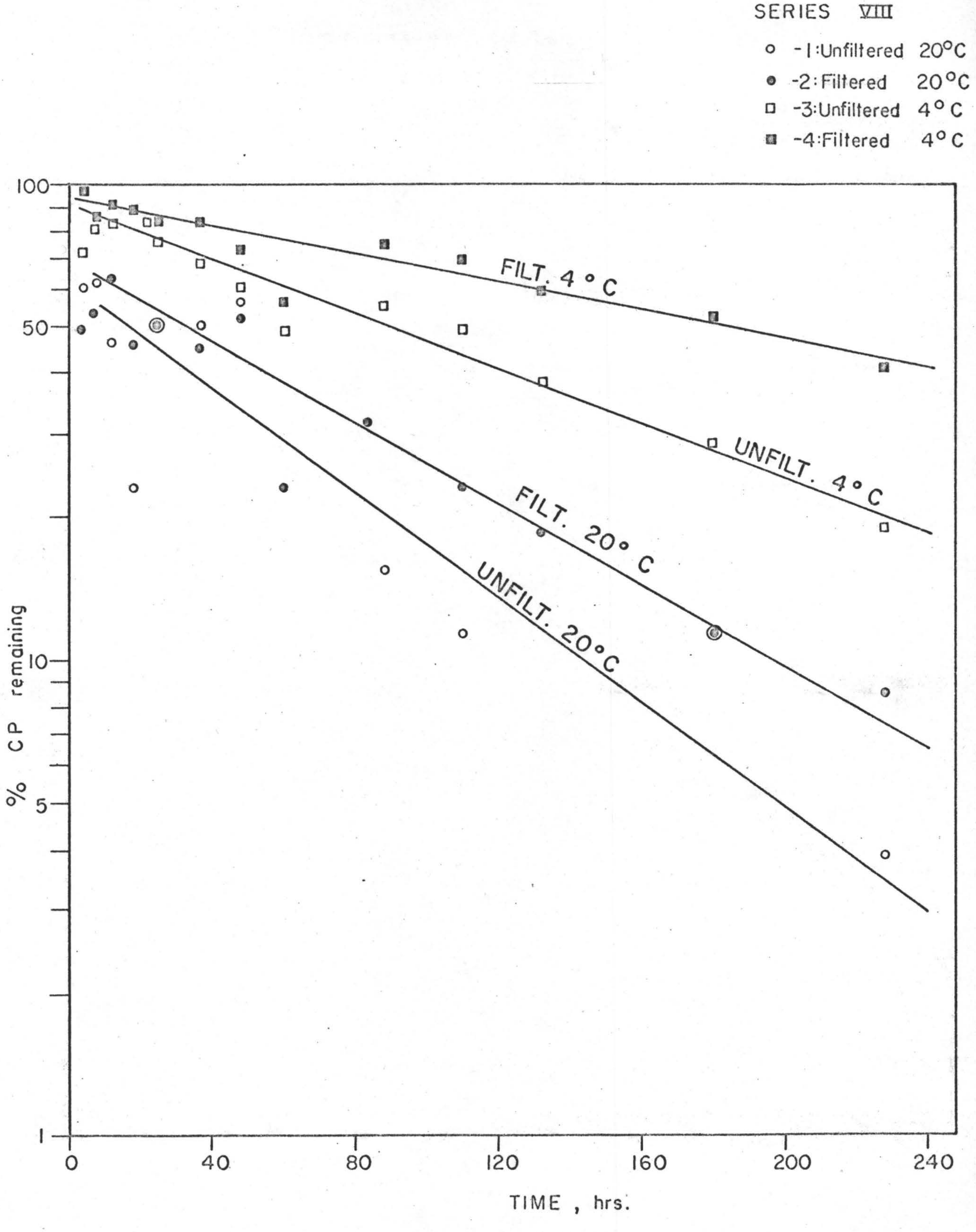


Figure 39-5. Experimental Data of Series VIII.

SERIES XV FIELD STUDY ON DUNDAS SEWAGE TREATMENT PLANT

The purpose of this series is to estimate the rate of hydrolysis of condensed phosphates in an activated sludge plant under winter conditions. (See Series V for summer conditions).

Field Conditions

Date: March 18, 1968

Flow rate: 2.2 MGD Temp. of wastewater: 8.3°C

Sampling Points: Primary Effluent
Final Effluent

Tests: FTP, OP, Percent OP, Percent PP, Percent TPP

Experimental Data:

	mg/l PO_4		Percent		
	FTP	OP	OP	PP	TPP
Primary Effluent	21.0	5.0	29.0	7.9	63.1
Final Effluent	12.0	9.5	80.2	7.5	12.3

Rate of Hydrolysis:

Detention Time in activated sludge tanks = 270 min.

PP + TPP in Primary Effluent = 15.5 mg PO_4/l

PP + TPP in Final Effluent = 2.5 mg PO_4/l

$k_{avg} = 7 \times 10^{-3}\ \text{min}^{-1}$

Percent Reduction in FTP = 43 percent.

SERIES XVI EFFECT OF pH ON RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN WASTEWATER

The purpose of this series is to establish what effect the variation of pH has on the rate of hydrolysis of tripolyphosphate in wastewater.

Experimental Conditions:

Date: March 1968

Medium: Primary Effluent, Dundas S.T.P.

FTP = 14.0 mg/l PO_4 (for XVI-2,-3) = 21.0 mg/l PO_4 (for XVI-1)
OP = 5.0 mg/l PO_4 " = 5.5 mg/l PO_4 "
pH = 7.9 = 7.9

Additions:

to XVI-1: pH ~ 5 Potassium Acetate-Acetic Acid Buffer
50 mg/l PO_4 of TPP
to XVI-2: pH ~ 7 Dilute Hydrochloric Acid to lower pH
30 mg/l PO_4 of TPP
to XVI-3: pH ~ 9 Sodium Carbonate buffer
30 mg/l PO_4 of TPP

Incubation Temperature = 20°C Mag.-Mix and Aeration

Day-Night Lighting

Tests: FTP, OP, UTP, Percent OP, Percent PP, Percent TPP, pH

Experimental Data: These are presented in Fig. 40-1, -2, -3.

Rate of Hydrolysis: The experimental data for all three series were replotted on a graph of logarithm (percent condensed phosphate remaining) versus time and rates calculated.

XVI-1: pH ~ 5.5 $k_{avg} = 3.3 \times 10^{-4}\ \text{min}^{-1}$
-2: pH ~ 7.5 $k_{avg} = 6.5 \times 10^{-4}\ \text{min}^{-1}$
-3: pH ~ 9.0 $k_{avg} = 1.2 \times 10^{-4}\ \text{min}^{-1}$

Microscopic Examination: (at t = 70 hours)

XVI-1: Mycelial Fungi, yeasts, few dispersed bacteria
-2: Bacteria, dispersed and in clumps, some flagelates
-3: Bacteria, dispersed and in clumps, many flagelates.

Figure 40-1. Effect of pH on rate of hydrolysis of TPP in wastewater.

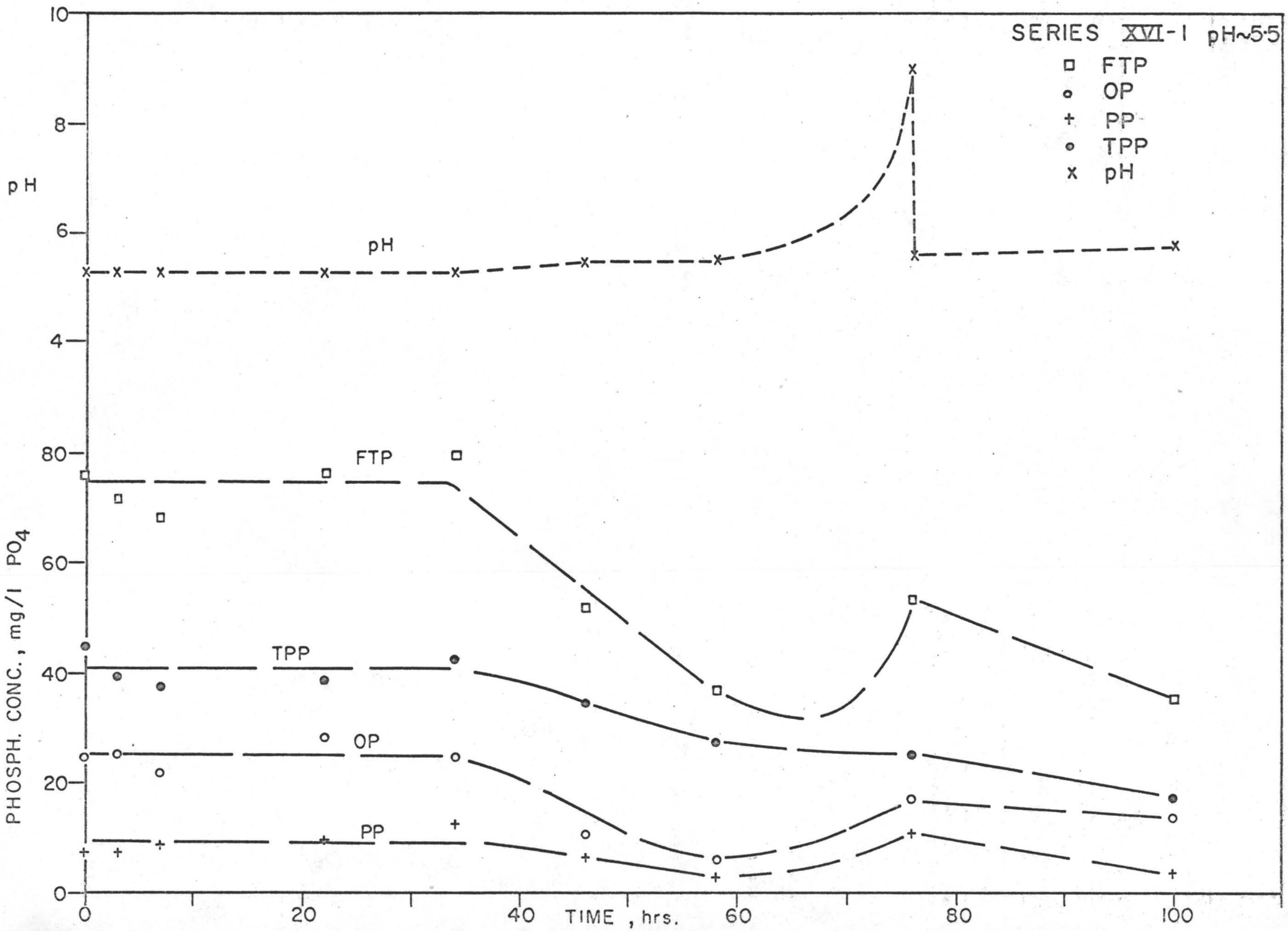


Figure 40-2. Effect of pH on rate of hydrolysis of TPP in wastewater.

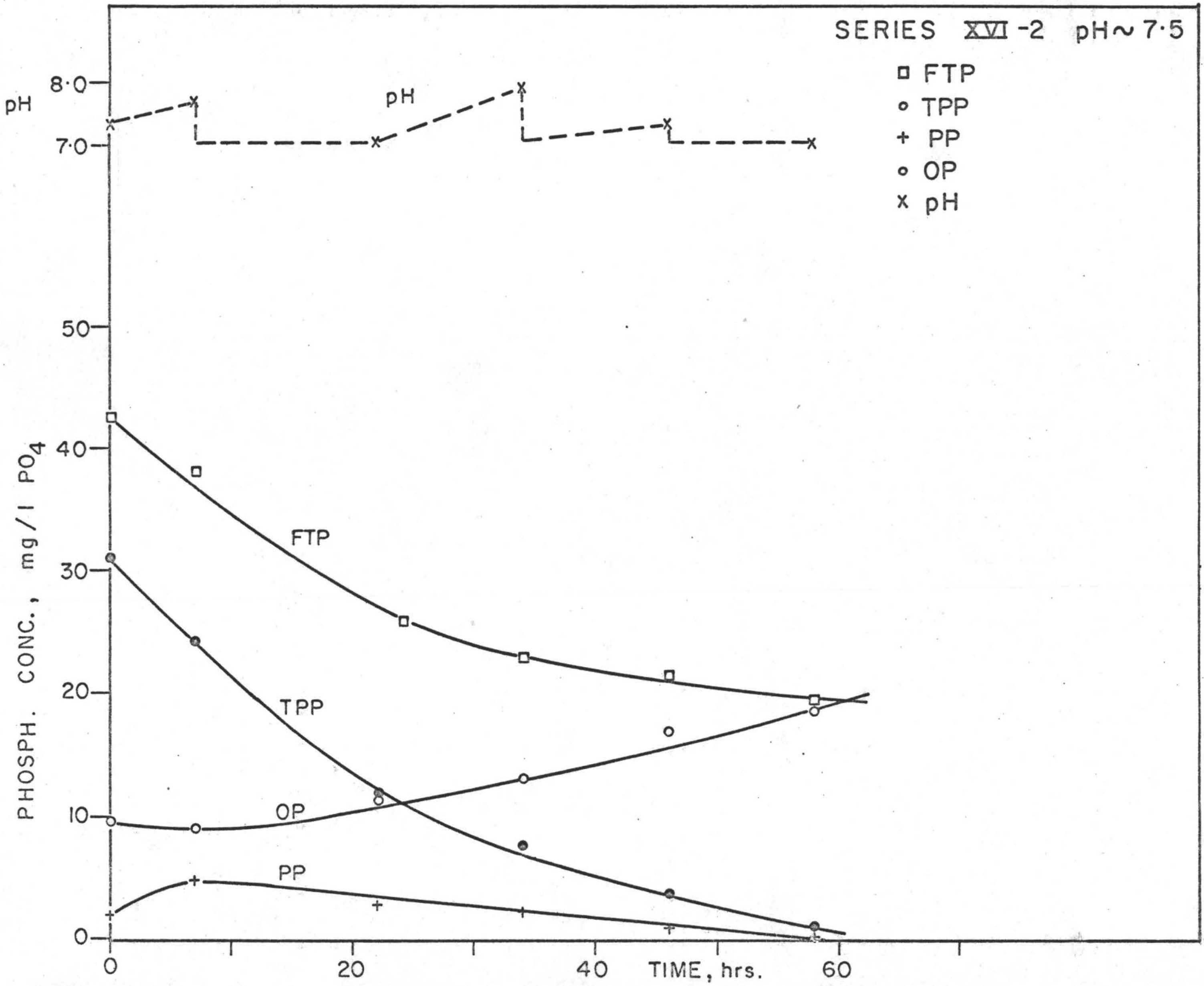
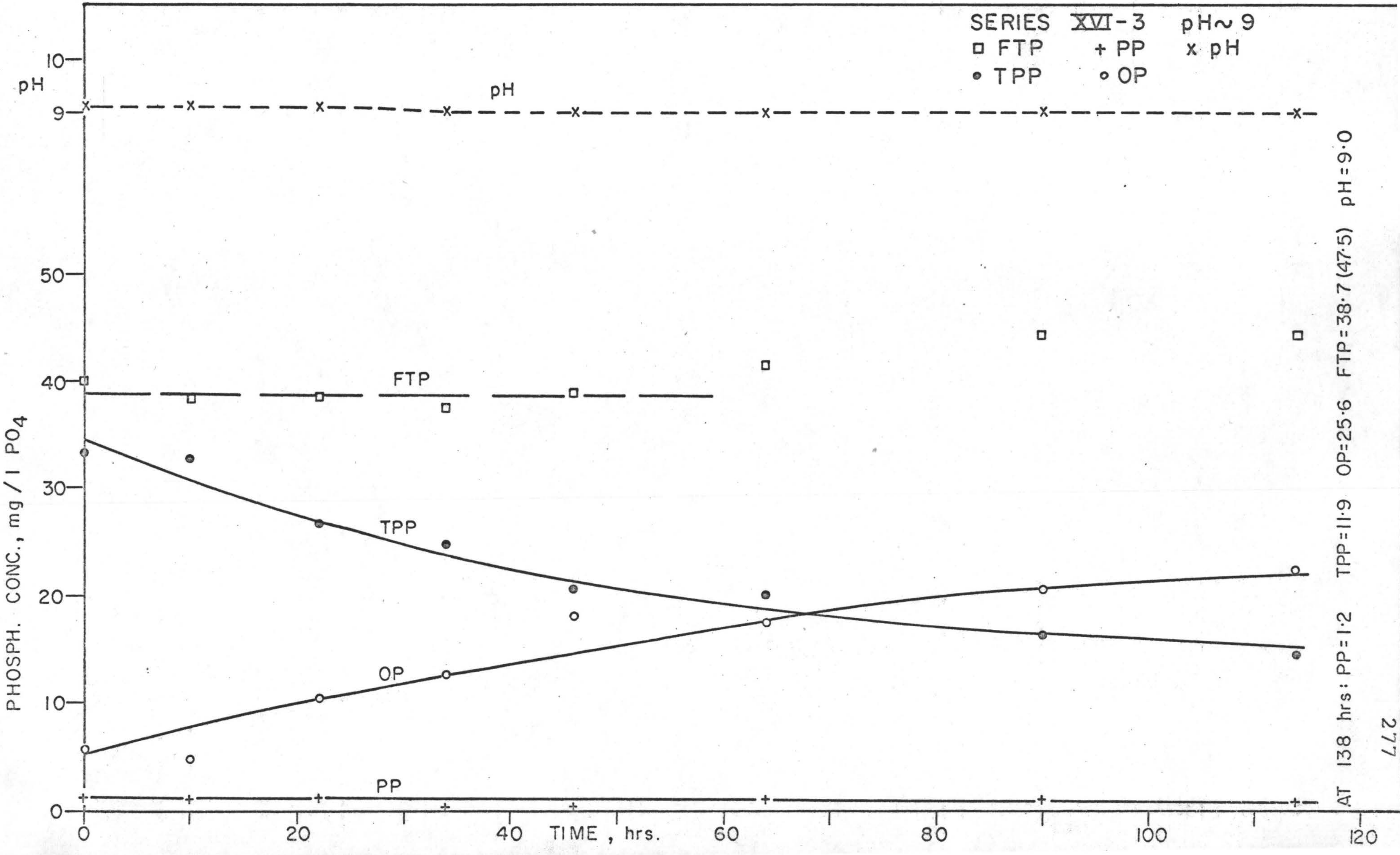


Figure 40-3. Effect of pH on rate of hydrolysis of TPP in wastewater.



SERIES XXI HUMBER SEWAGE TREATMENT PLANT STUDY - 24 HOUR SURVEY

The purpose of this study is to obtain data on the concentration and type of phosphorus compounds present in untreated wastewater, primary and secondary effluent. The data can then be used to estimate efficiencies of phosphorus removal and rates of hydrolysis of condensed phosphates.

Treatment Plant Information

The Humber Treatment Plant is located at the mouth of the Humber River in the Municipality of Metropolitan Toronto. It serves at present an estimated population of 425,000 people. Industrial wastes bring the population equivalent to about 607,000. The sewer system is partly combined, partly separate. The plant provides secondary treatment (Activated Sludge, Step Aeration) to a maximum flow of 54 MIGD. It can provide primary treatment only for an additional 6 to 8 MIGD. If the flow is still higher raw sewage must be bypassed after screening and chlorination. The effluent from the plant is discharged to Humber Bay, Lake Ontario, about 3000' from shore through a pipeline and diffusers. A schematic plant diagram is shown in Fig. 41-1.

Experimental Work and Data

The survey was carried out on May 29 and 30, 1968. All work was done in the laboratories of the plant, using autoanalyzer equipment. The cooperation of the staff of the laboratory and the plant is gratefully acknowledged. Every hour samples were obtained at the influent, and every two hours at the primary and secondary effluent. They were analyzed for unfiltered total phosphorus (UTP), filtered total phosphorus (FTP), filtered orthophosphate (OP), pH and temperature. Nineteen samples were also analyzed for differential condensed phosphates. Digestor supernatant and return sludge were analyzed for filtered total phosphorus and orthophosphate on two occasions.

The flow rates of influent wastewater, primary effluent and return sludge were recorded during the survey. Flow records of the week prior to the survey were obtained, since the flow rate during the survey was higher than normal due to rainfall on the two days preceding the survey. The information on flow rate and rainfall is shown in Fig. 41-2. The rainfall data were obtained from the Department of Transport, Meteorological Branch, for the gauging station at Toronto International Airport, which is at the upper reaches of the contributing sewer area. Fig. 41-2 clearly shows the increase in flow rate due to the rainfall.

Based on information received on the volume of the tanks, the detention times during the survey were calculated as follows:

	Detention Time, hours		
	Avg. Flow	Low Flow	High Flow
Primary Settling Tanks	0.9	1.5	0.7
Activated Sludge Tanks	5.3	7.2	5.3
Final Settling Tanks	1.9	2.9	1.9

In the presentation of phosphorus data in Fig. 41-3 to -5 the data on primary effluent were displaced by one hour, and on secondary effluent by eight hours relative to the influent data. This will allow direct visual examination on phosphorus removal and hydrolysis. Fig. 41-3 to -5 show the concentration of unfiltered total phosphorus (UTP), filtered total phosphorus (FTP), and filtered orthophosphate (OP), and condensed phosphates (CP) in the influent, primary and secondary effluent.

Table XXXIV gives information on other plant measurements.

TABLE XXXIV EXPERIMENTAL DATA FOR SERIES XXI - HUMBER S.T.P. SURVEY - MAY 29-30, 1968*

DATE	FLOW, MGD			RAW SEWAGE			PRIMARY EFFLUENT			SECONDARY EFFLUENT		
	Compl. Treatmt.	Prim.Treatment only	Bypassed	pH	BOD$_5$,mg/l	S.S.,mg/l	pH	BOD$_5$,mg/l	S.S.,mg/l	pH	BOD$_5$,mg/l	S.S.,mg/l
May 29	54.0	6.6	6.4	7.4	190	300	7.6	135	145	7.8	19	35
May 30	54.0	4.6	0.0	7.4	210	430	7.4	135	165	7.5	23	29
Avg. April 1968	45.6	2.4	.3	7.5	215	335	7.6	135	155	7.6	22	28
Avg. 1967	52.2	4.0	-	7.4	161	229	7.5	107	129	7.4	19	48

*Courtesy of Municipality of Metropolitan Toronto.

The data in Table XXXIV indicate that the plant achieves biochemical oxygen demand and suspended solids removals typical of well-operated conventional activated sludge plants. The variation in temperature and pH during the survey is shown below.

	Temperature, °C	pH
Influent	15.5 - 18.0	6.9 - 8.3
Primary Effluent	15.5 - 17.0	7.2 - 7.8
Secondary Effluent	15.5 - 16.5	7.2 - 7.7

The concentration of phosphorus in filtered digestor supernatant and return sludge was measured twice.

Digestor Supernatant: FTP = 130, OP = 130 mg/l PO_4

Return Sludge : FTP = 69, OP = 68 mg/l PO_4

Average and Range of Concentration of Phosphorus Compounds - mg/l PO_4

mg/l PO_4

Medium	UTP	PAP	FTP	OP	CP
Influent	21.7 (16.0-31.5) 23.0 (2.5-29.0)*	9.5 (3.5-25.0)	12.2 (1.0-20.5)	6.5 (0.5-12.0)	5.7 (0.5-10.5)
Primary Effluent	19.8 (14.5-25.0)	6.0 (4.0-7.5)	13.8 (9.5-17.5)	8.2 (5.0-11.0)	5.6 (2.5-9.5)
Secondary Effluent	7.6 (3.0-15.5) 16.0 (2.0-27.0)*	1.0 (0.5-2.0)	6.6 (2.0-14.5)	5.7 (1.5-13.5)	0.9 (0.0-2.5)

*For comparison the only available phosphorus data on the Humber Sewage Treatment Plant are shown. They were obtained on a weekly composite sample, and are the average values and range for 1967.

Average and Range of Concentration of Phosphorus Compounds - Percent

	Percent of UTP		Percent of FTP	
Medium	PAP	FTP	OP	CP
Influent	44(26-94)	56(6-74)	53(36-86)	47(14-64)
Primary Effluent	31(23-37)	69(63-77)	59(45-74)	41(26-55)
Secondary Effluent	17(6-50)	83(50-94)	86(71-100)	14(0-29)

Average and Range of Phosphorus Reduction

	Percent Reduction, based on influent concentration			
Medium	UTP	PAP	FTP	CP
Primary Effluent	9(0-48)	37(0-70)	<0(<0-14)	2(0-19)
Secondary Effluent	65(26-77)	90(75-100)	45(0-72)	84(78-100)

Rate of Hydrolysis

Avg. detention time in primary settling tanks = 53 min.

Avg. detention time in activated sludge tanks = 320 min.

Avg. Cond. Phosph. in influent = 5.7 mg/l PO_4

Avg. Cond. Phosph. in primary effluent = 5.6 mg/l PO_4

Avg. Cond. Phosph. in secondary effluent = 0.9 mg/l PO_4

Primary Settling Tanks : $k_{avg} = 3 \times 10^{-4}$ min^{-1}

Activated Sludge Tanks : $k_{avg} = 6 \times 10^{-3}$ min^{-1}

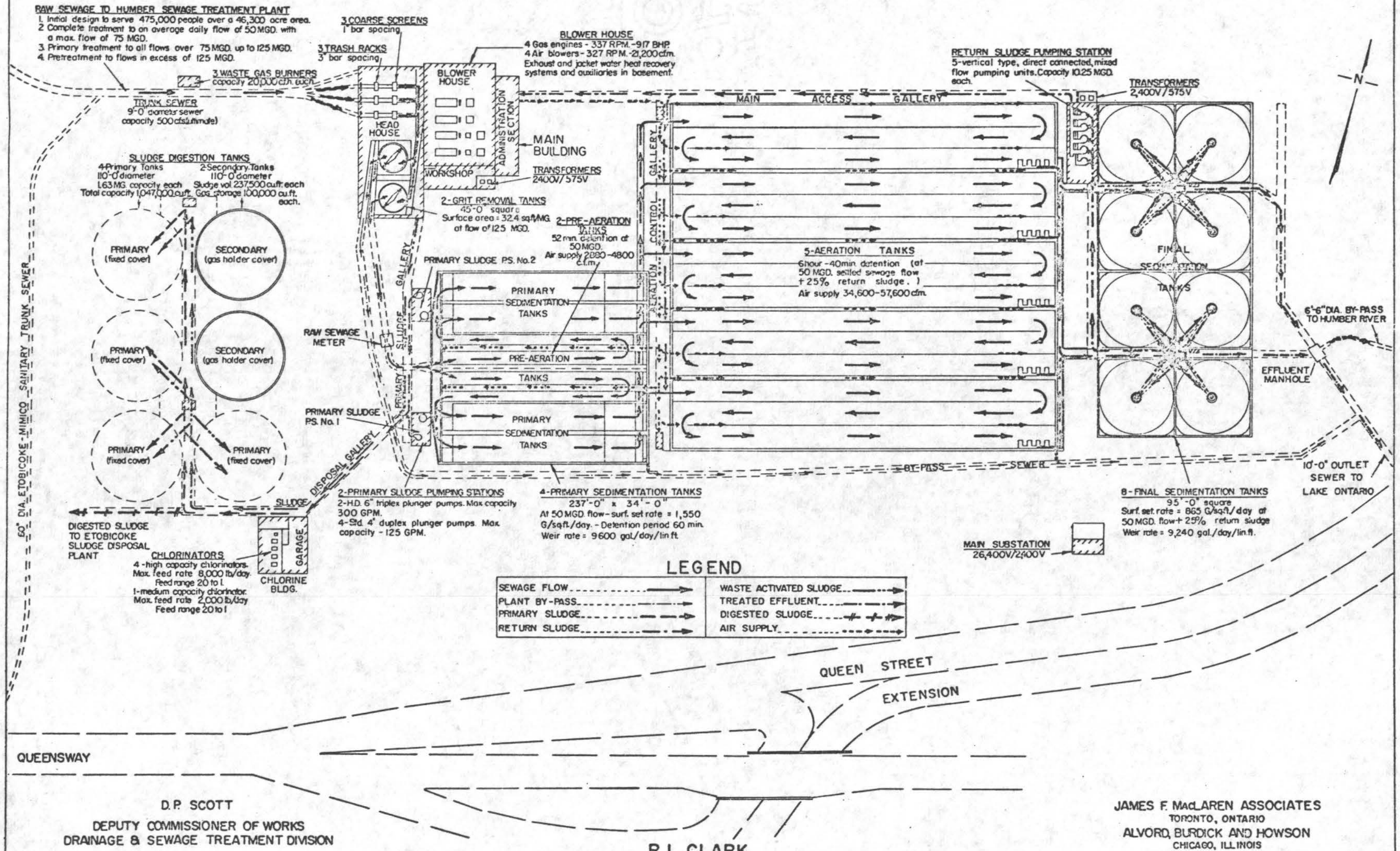
(It is assumed that the hydrolysis taking place in the final settling tanks can be neglected.)

Presence of Soluble Organic Phosphorus Compounds

Comparison of the results of the differential condensed phosphate analysis and direct analysis for orthophosphate shows that the values obtained by direct analysis in all cases were smaller, by about 10 to 20 percent, than the value obtained by applying the percentage for orthophosphate to the value for filtered total phosphorus (FTP). This could be explained partly by the presence of other soluble phosphorus compounds, such as higher condensed phosphates and soluble organic phosphorus compounds, which do not appear within the analysis time in the differential condensed phosphate analysis. On this basis the amount of soluble organic phosphorus compounds and higher condensed phosphates in the survey varied from 1 - 3.5 mg/l PO_4. It must be remembered that there could be considerable error in this estimate, since there will be a difference between the values for orthophosphate from direct and differential analysis simply due to error in each analysis, which has been arbitrarily eliminated in the procedure to obtain this estimate.

MUNICIPALITY OF METROPOLITAN TORONTO

FIG. 41-1 HUMBER SEWAGE TREATMENT PLANT



RAW SEWAGE TO HUMBER SEWAGE TREATMENT PLANT

1. Initial design to serve 475,000 people over a 46,300 acre area.
2. Complete treatment to an average daily flow of 50 MGD. with a max. flow of 75 MGD.
3. Primary treatment to all flows over 75 MGD. up to 125 MGD.
4. Pretreatment to flows in excess of 125 MGD.

3 COARSE SCREENS
1" bar spacing

3 TRASH RACKS
3" bar spacing

3 WASTE GAS BURNERS
capacity 20,000 cfh. each

TRUNK SEWER
9'-0" diameter sewer
capacity 500 cfs(ultimate)

BLOWER HOUSE
4 Gas engines - 337 RPM.-917 BHP.
4 Air blowers - 327 RPM.-21,200 cfm.
Exhaust and jacket water heat recovery systems and auxiliaries in basement.

RETURN SLUDGE PUMPING STATION
5-vertical type, direct connected, mixed flow pumping units. Capacity 10.25 MGD. each.

TRANSFORMERS
2,400V/575V

SLUDGE DIGESTION TANKS
4-Primary Tanks
110'-0" diameter
1.63 MG. capacity each
Total capacity 1,047,000 cu.ft.
2-Secondary Tanks
110'-0" diameter
Sludge vol. 237,500 cu.ft. each
Gas storage 100,000 cu.ft. each.

TRANSFORMERS
2400V/575V

2-GRIT REMOVAL TANKS
45'-0" square
Surface area = 32.4 sq.ft/MG. at flow of 125 MGD.

2-PRE-AERATION TANKS
52 min. detention at 50 MGD.
Air supply 2880-4800 c.f.m.

5-AERATION TANKS
6 hour-40 min. detention (at 50 MGD. settled sewage flow + 25% return sludge.)
Air supply 34,600-57,600 cfm.

2-PRIMARY SLUDGE PUMPING STATIONS
2-H.D. 6" triplex plunger pumps. Max capacity 300 GPM.
4-Std. 4" duplex plunger pumps. Max. capacity - 125 GPM.

4-PRIMARY SEDIMENTATION TANKS
237'-0" x 34'-0"
At 50 MGD. flow - surf. set rate = 1,550 G/sq.ft./day. - Detention period 60 min.
Weir rate = 9600 gal/day/lin ft.

8-FINAL SEDIMENTATION TANKS
95'-0" square
Surf. set. rate = 865 G/sq.ft./day at 50 MGD. flow + 25% return sludge
Weir rate = 9,240 gal./day/lin.ft.

CHLORINATORS
4-high capacity chlorinators.
Max. feed rate 8,000 lb/day.
Feed range 20 to 1.
1-medium capacity chlorinator.
Max. feed rate 2,000 lb/day
Feed range 20 to 1

MAIN SUBSTATION
26,400V/2400V

D.P. SCOTT
DEPUTY COMMISSIONER OF WORKS
DRAINAGE & SEWAGE TREATMENT DIVISION

R.L. CLARK
COMMISSIONER OF WORKS

JAMES F. MacLAREN ASSOCIATES
TORONTO, ONTARIO
ALVORD, BURDICK AND HOWSON
CHICAGO, ILLINOIS
CONSULTING ENGINEERS

OCTOBER 1957

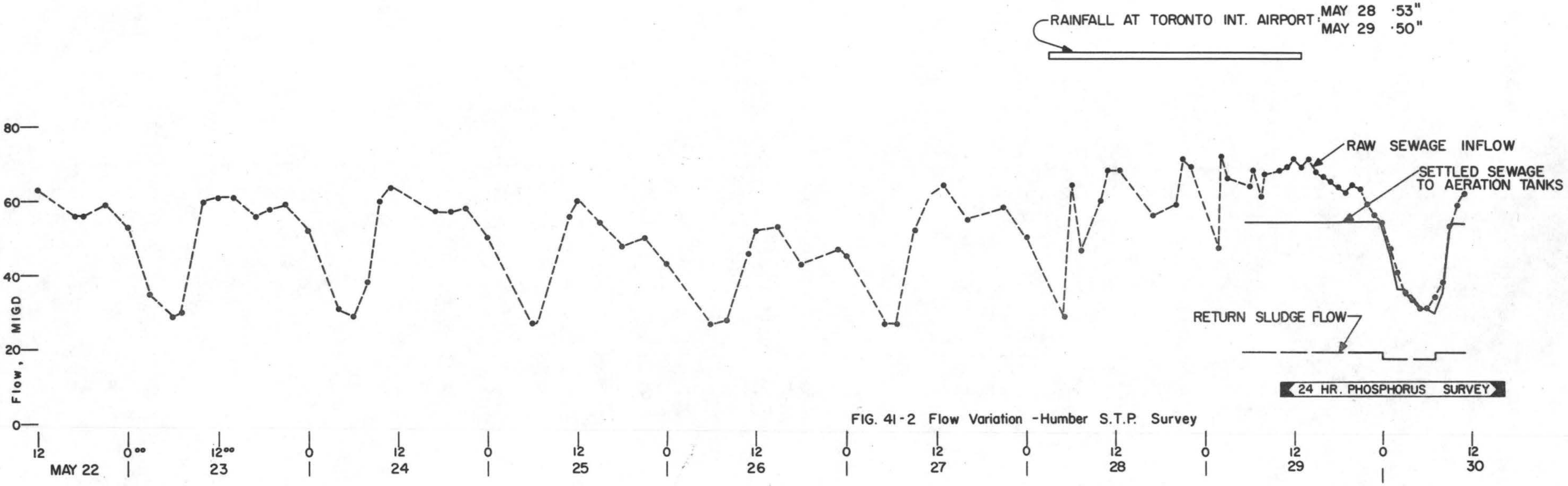


FIG. 41-2 Flow Variation -Humber S.T.P. Survey

Figure 41-3. Experimental data for series XXI - Humber S.T.P. survey.

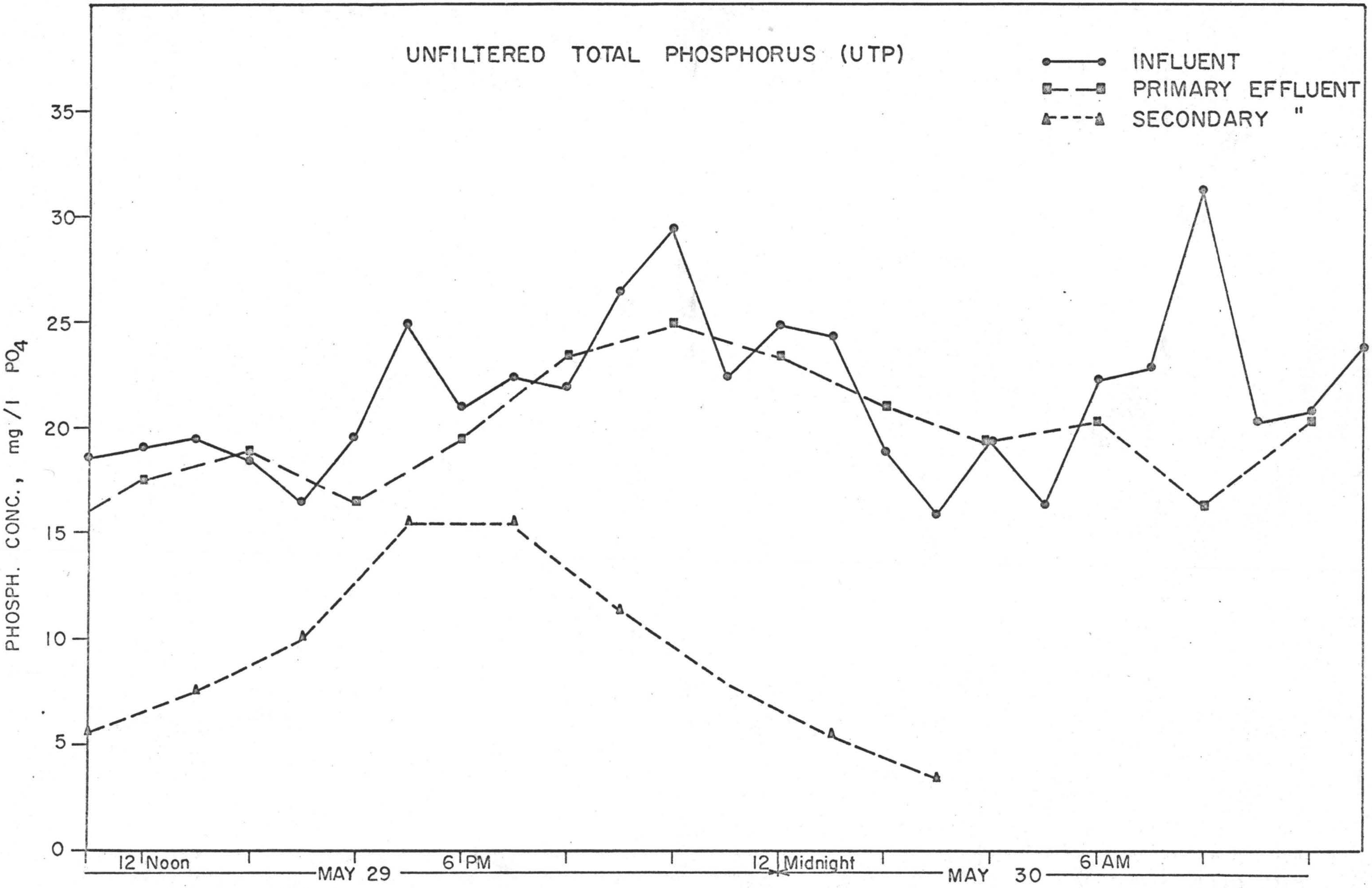


Figure 41-4. Experimental data for series XXI - Humber S.T.P. survey.

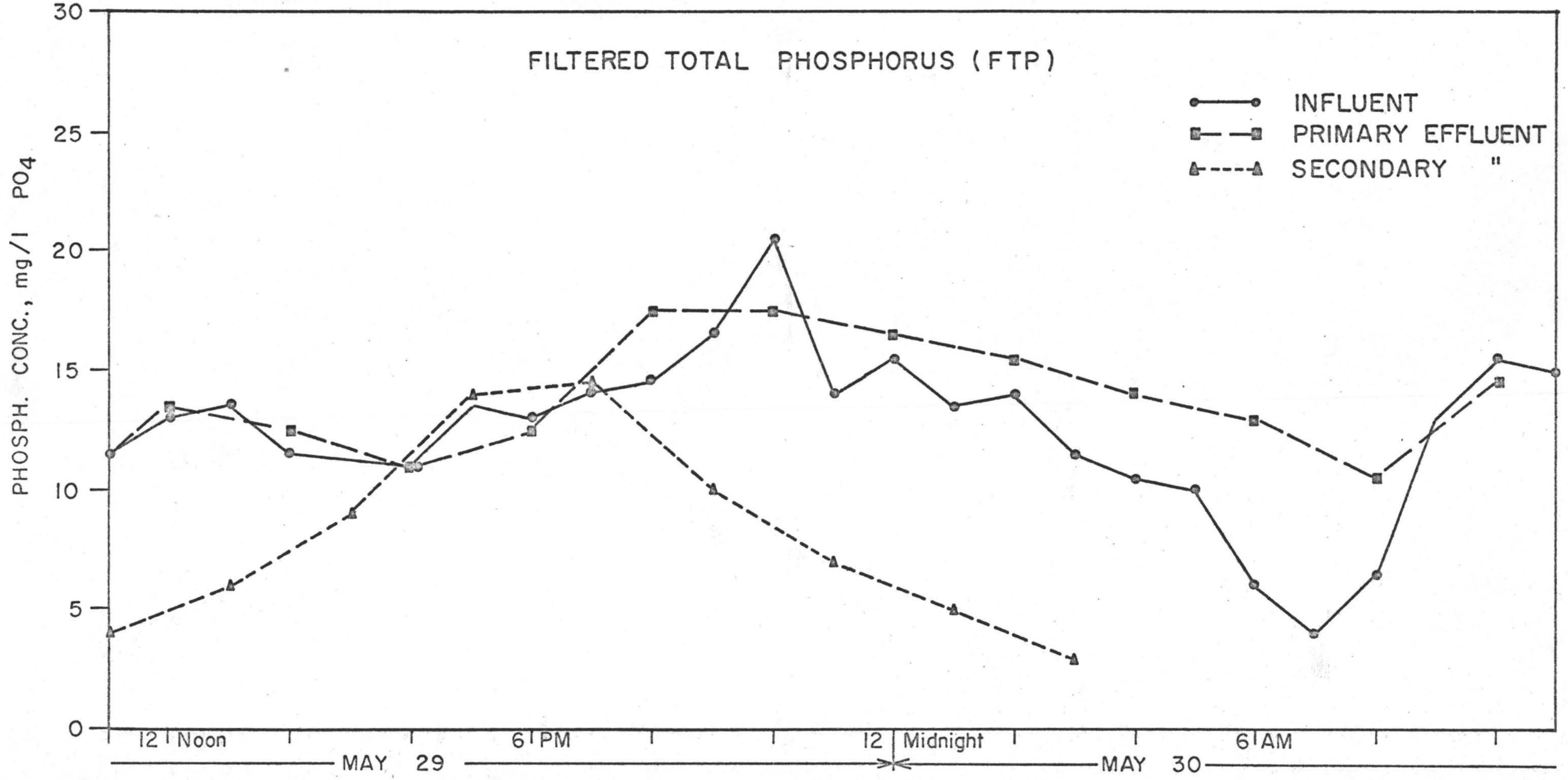
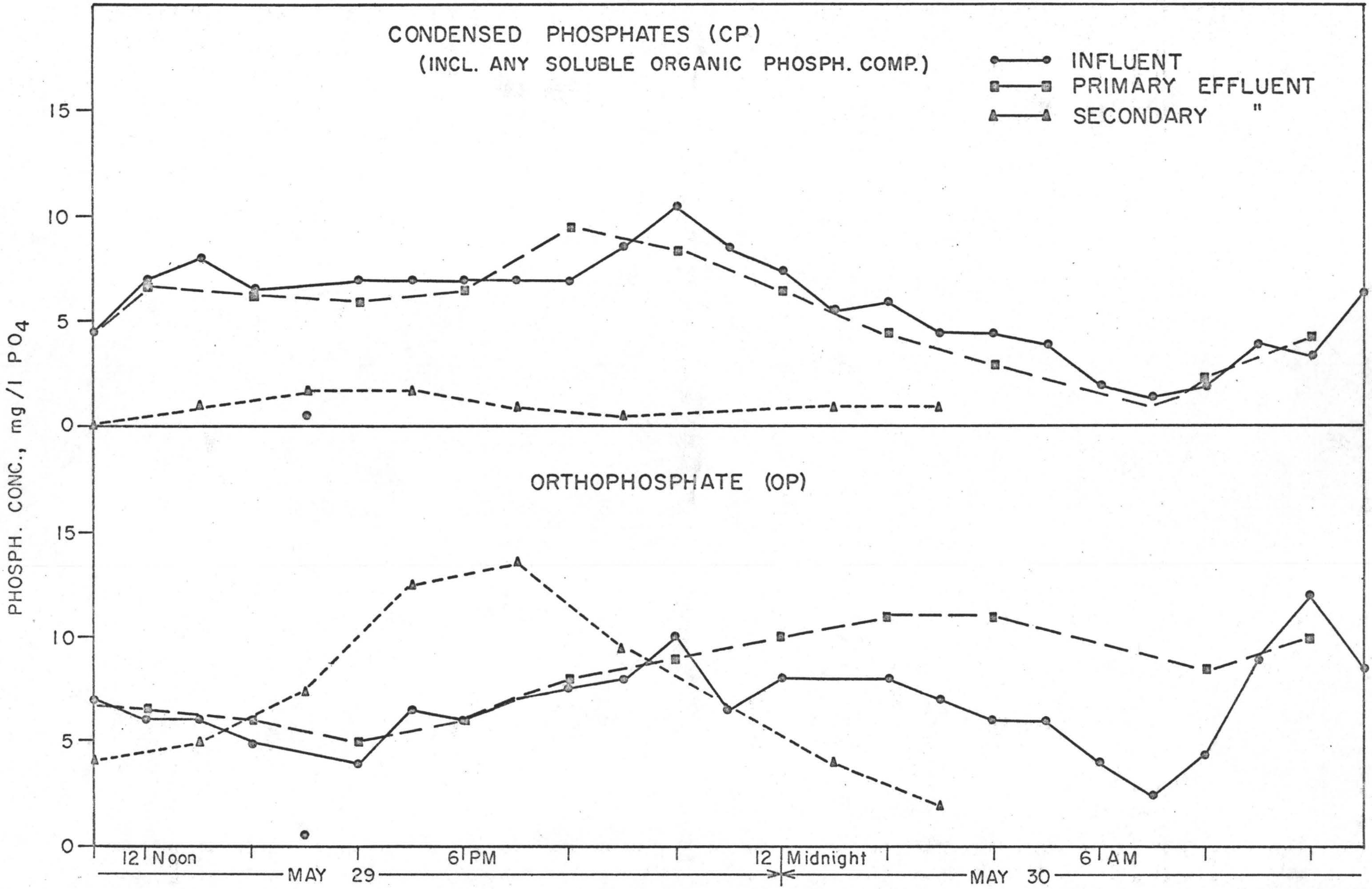


Figure 41-5. Experimental data for series XXI - Humber S.T.P. survey.



SERIES XXIII LABORATORY BATCH STUDY ON RATE OF HYDROLYSIS OF TRIPOLYPHOSPHATE IN ACTIVATED SLUDGE

The purpose of this series is to establish the rate of hydrolysis of tripolyphosphate in the presence or absence of activated sludge organisms.

Experimental Conditions

Date: June 17-19, 1968

Medium: Activated Sludge, Humber S.T.P.,

FTP = 65 mg/l PO_4

OP = 63 mg/l PO_4

pH = 7.7

Sample preparation: XXIII-1 Unfiltered

XXIII-2 Filtered

50 mg/l PO_4 of TPP were added to the two flasks.

Incubation Temperature: 22°C

Samples were mixed by magnetic stirrer and by aeration.

Tests: FTP, OP, Percent OP, Percent PP, Percent TPP, pH

Experimental Data:

XXIII-1 Unfiltered

		mg/l PO_4			Percent	
Time, hrs.	pH	FTP	OP	OP	PP	TPP
1	7.7	115	112.5	91.0	T	9.0
3	7.7	120	117.5	100.	T	T

XXIII-2 Filtered

		mg/l PO_4		Percent		
Time, hrs.	pH	FTP	OP	OP	PP	TPP
1	7.7	120	72	62.4	T(race)	37.6
20	7.7	105	67	66.5	T	33.5
28	7.7	95	80	not measured		
44	7.8	70	66	94.1	T	5.9
68	7.8	50	47.5	100	T	T

Bacterial growth occurred after about 20 hours, and as a result FTP decreased.

Comparison between differential and direct orthophosphate data is good.

Rate of Hydrolysis: The data for condensed phosphates, ie. the sum of PP and TPP were plotted in Fig. 42 as logarithm (percent condensed phosphate remaining) versus time and rates of hydrolysis calculated for both runs as the slope of the straight line. As there are only few data points, no comment can be made on the reasonableness of the fit. The filtered sample showed a lag period of about 20 hours, after which time bacterial growth was evident in the flask. Correspondingly, the rate of hydrolysis increased sharply.

XXIII-1: Unfiltered Activated Sludge, 22°C: $k_{avg} = 1.7 \times 10^{-2}\ min^{-1}$

-2: Filtered Activated Sludge, 22°C:

- Lag period, no growth: " $= 2.5 \times 10^{-4}\ min^{-1}$
- Bacterial growth : " $= 1.6 \times 10^{-3}\ min^{-1}$

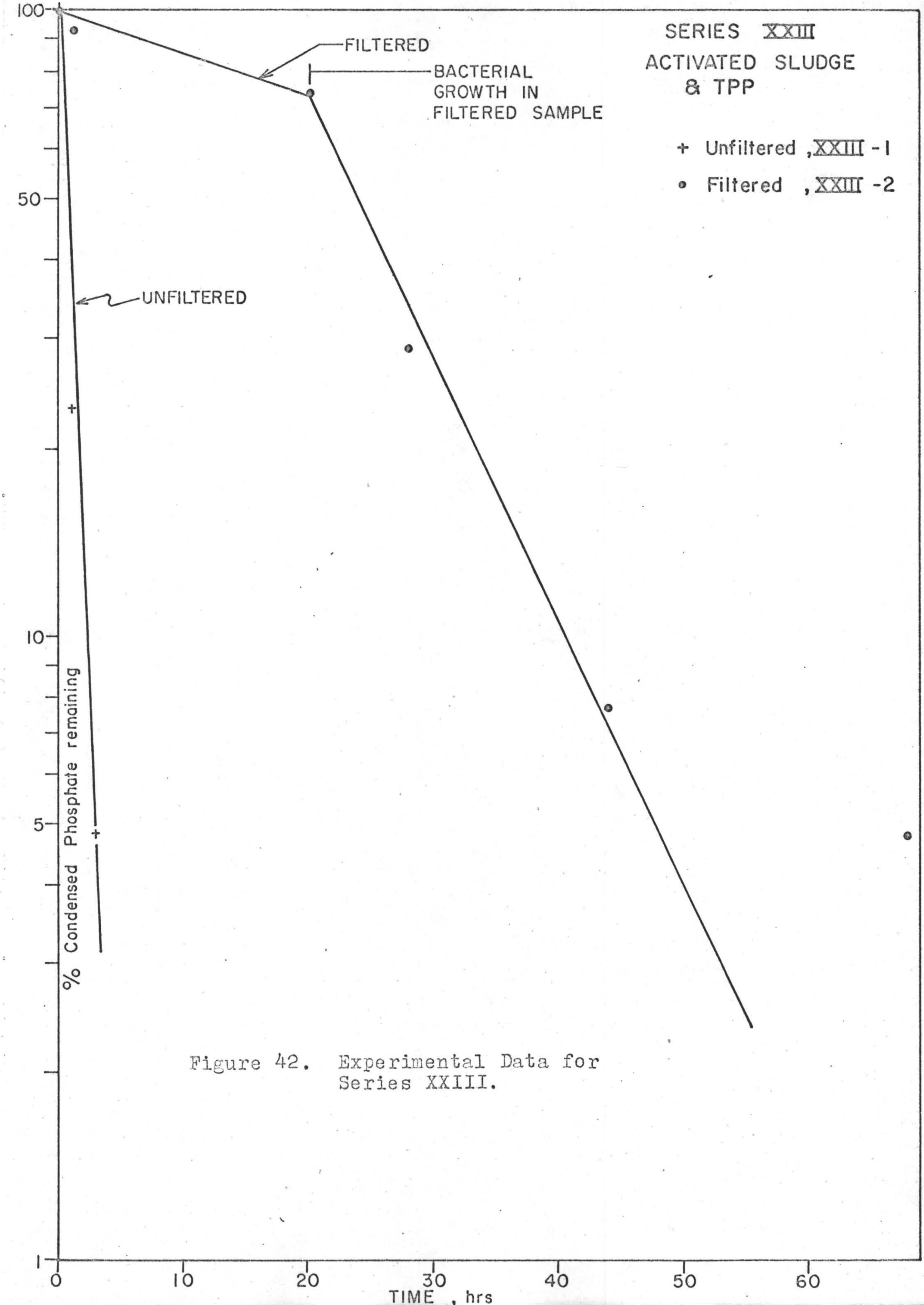


Figure 42. Experimental Data for Series XXIII.

V-5 DISCUSSION AND SUMMARY OF RESULTS

Discussion of the experimental results is presented under several headings. Where applicable phenomena studied and results obtained in various aqueous media are discussed under one heading.

Effect of variation in pH on the Rate of Hydrolysis of Tripolyphosphate

The following experimental series apply:

-- Distilled Water (low concentration): Series XVII

-- Lake water: Series XVIII

-- Wastewater: Series XVI

Distilled Water

	Low Concentration		High Concentration (From Fig.13)	
pH	k_1, mg PO_4/l-min	Ratio	k_1, min^{-1}	Ratio
4.3	1.6×10^{-4}	67	1.2×10^{-6}	17
6.9	1.7×10^{-5}	7	3.0×10^{-7}	4.3
9.9	2.4×10^{-6}	1	7.0×10^{-8}	1

The results indicate that at low concentrations of tripolyphosphate (0.5 mg PO_4/l) the effect of pH is in the same direction as at high concentration, ie. a faster rate at lower pH values. The magnitude of the effect may be increased. However the data at pH = 4.3 are too few to be reliable. By plotting the above rate constants on Fig. 13 one could see that the slope of the curve is similar to Griffith's nomograph line. There is good agreement with the data of Shannon (S-12), although it must be remembered that Shannon's rate constant is a k_{avg} value, rather than k_1. Experimental studies on low concentrations of tripolyphosphate in distilled water in this work were carried out at pH values close to 7. This series shows that it is reasonable to use Griffith's nomograph at low levels of concentration for conversion of rate constants from experimental pH values to pH = 7. Although no experiment was done on the pH dependence of pyrophosphate at low concentrations, Griffith's nomograph will be used.

Lake water

pH	TPP k_1, mg PO_4/l-min	PP k_2, mg PO_4/l-min
5	3.5×10^{-5}	7.1×10^{-6}
7	1.6×10^{-5}	3.7×10^{-6}
9	1.8×10^{-5}	4.9×10^{-6}

There is little difference between the rates of hydrolysis of tripolyphosphate and pyrophosphate at pH levels of 7 and 9. It is reasonable to expect that the fastest rate would occur at natural pH levels of about 7.5 to 8. In a narrow range each side of it, there appears to be little change in rate. At the lower value of pH 5 there are too few data points to rely on the rate constant shown. It does, however, indicate a doubling of the rate constant. Since all the experiments on lake water were carried out at the natural pH level, there is no need for pH adjustment of experimental data in this work. Tripolyphosphates hydrolyzed faster than pyrophosphate in lake water.

Wastewater

pH	k_{avg}, min^{-1}
5.5	3.3×10^{-4}
7.5	6.5×10^{-4}
9.0	1.2×10^{-4}

The fastest rate of hydrolysis occurred at natural pH levels of 7.5. Filtered total phosphorus decreased due to uptake by organisms. Orthophosphate level increases due to hydrolysis and decreases due to uptake, resulting in a net slow increase. Little growth of organisms occurred at pH of 9. Filtered total phosphorus stayed relatively constant, showing little or no uptake. Orthophosphate increased due to hydrolysis.

The experiment at a pH level of 5.5 p.275 shows qualitatively very interesting results, although too few data points are available to rely on the rate constant. The change of pH level from 7.5 to 5.5 must have caused a change in predominant organisms. For the first day and a half no uptake of phosphorus, nor hydrolysis of condensed phosphates is evident. By then fungi and yeast organisms have taken over, as could be seen by microscopic examination at 70 hours. During this period filtered total phosphorus decreased sharply, indicating uptake by organisms. At the same time tripolyphosphate hydrolyzed. During this entire time the pH stayed constant. Between 60 and 75 hours the pH rose to 9, presumably due to exhaustion of the buffer. This arrested uptake and hydrolysis. The pH was adjusted to pH 5.5 at 77 hours.

Since, there are only two data points available in this time period which differ widely, nothing definite can be said about this portion of the experiment.

Effect of Concentration of Condensed Phosphates on the Rate of Hydrolysis and the Order of Response

The following series apply:

-- Distilled Water: Series XX - at concentration of 500 and 100 mg/l PO_4 of TPP and PP.
Series IX, X, XI - at concentrations of 0.5 to 50 mg/l PO_4 of TPP.
Series XIV - at concentrations of 0.5 to 50 mg/l PO_4 of PP.
-- Lake water: All series at concentration of 0.5 mg/l PO_4 of TPP.
-- Wastewater: All series at concentration of 30-50 mg/l PO_4 of TPP.

Distilled Water

See Fig. 11A and 12A.

All rate constants obtained in the experimental work are added to the literature data of Fig. 11 and 12. The results of Series XX provide data points in that range of high concentration in which no literature data were available. Together these data indicate that a first-order response in hydrolysis of tripolyphosphate and pyrophosphate occurs at concentrations higher than about 15 to 50 mg/l PO_4. The data of Series IX, X and XI show that at low concentrations the data can be fitted better by a zero-order response. At the experimental conditions used at the level of 50 mg/l PO_4 so little hydrolysis occurs, that any order fit may be reasonable. At levels of 15, 2.5 and 0.5 mg/l PO_4 a zero-order fit is much more reasonable than a first-order fit. If the rate of hydrolysis is independent of concentration at this low level (10^{-5} to 10^{-6} moles/l) then the rate constants found should be the same. The variation that is indicated is probably primarily due to the effect of organisms present during the course of some experiments, and is discussed further under that heading. Variations in rates during the lag period, which may be equated to sterile conditions, are of one order of magnitude, but due to the few data points available and the small extent of hydrolysis taking place this is not significant. The constants are of the same order of magnitude as Shannon (S-12) and Karl-Kroupa et al (K-3). Under non-sterile conditions the agreement between the rate constants at concentrations from 0.5 to 50 mg/l is reasonably close, allowing for any difference between the experiments in the extent of non-sterility. Pyrophosphate hydrolyzes slower than tripolyphosphate over the entire range of concentration, but the difference appears to be smaller at low concentrations.

Lake water   See Fig. 11B and 12B.

All experiments on lake water were run at an initial concentration of about 0.5 mg/l PO_4. All individual experimental data were best fitted by zero-order response, and k_1 and k_2 values were obtained. The rate constants obtained were added to the literature data of Fig. 11 and 12, with the difference in experimental conditions noted. The rate constants range over slightly more than one order of magnitude, with the sterile lake water having the lowest rate, and about equal to rates in sterile distilled water. The rates for lake water samples in this work are in the same order of magnitude as literature data shown.

Wastewater   See Fig. 11 B.

The initial concentration of tripolyphosphate added to wastewater was about 30 mg/l PO_4. The experimental data were best fitted by a first-order curve. The rate constants obtained were used in plotting the rate of hydrolysis on Fig. 11 B. Comparison between the rates obtained in this work and the data by Sawyer (S-6) is good.

Figure 11A. Concentration dependence of the rate of hydrolysis at 20°C and pH = 7. Experimental data on distilled water added.

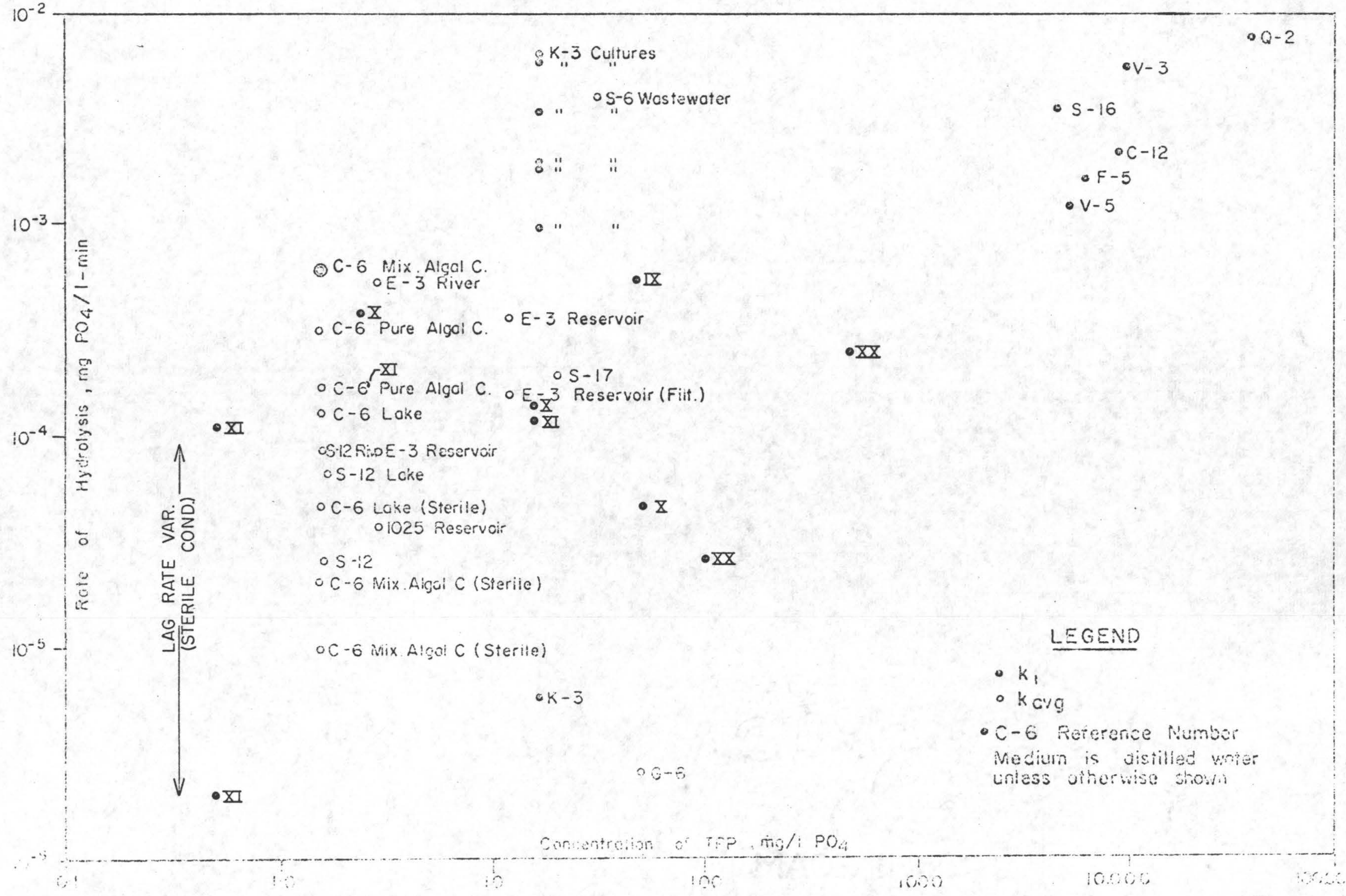


Figure 11B Concentration dependence of the rate of hydrolysis of tripolyphosphate at 20°C and pH = 7. Experimental data on lake water and wastewater added.

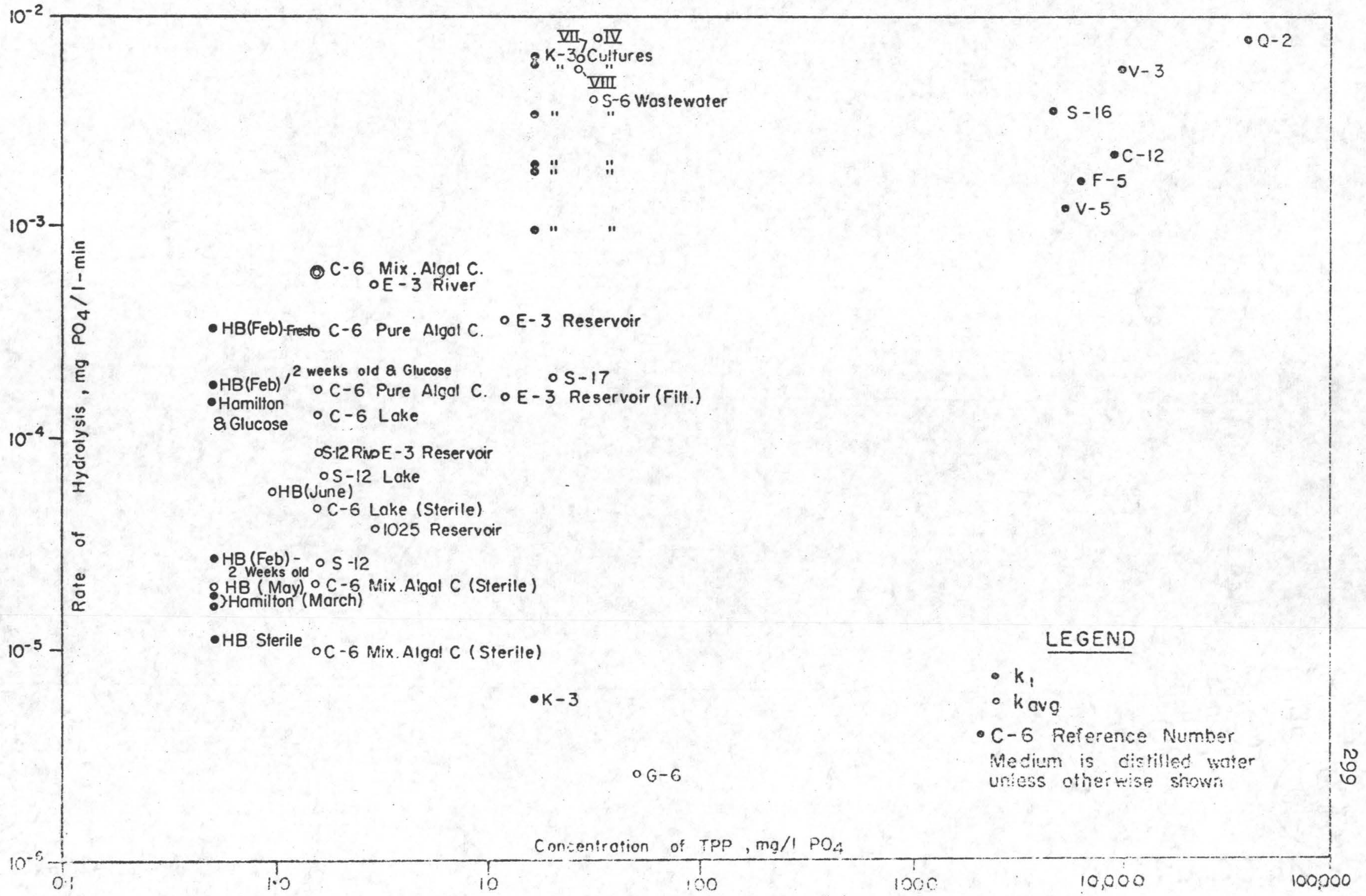


Figure 12A. Concentration Dependence of the Rate of Hydrolysis of Pyrophosphate at 20°C and pH = 7. Experimental Data on Distilled Water added.

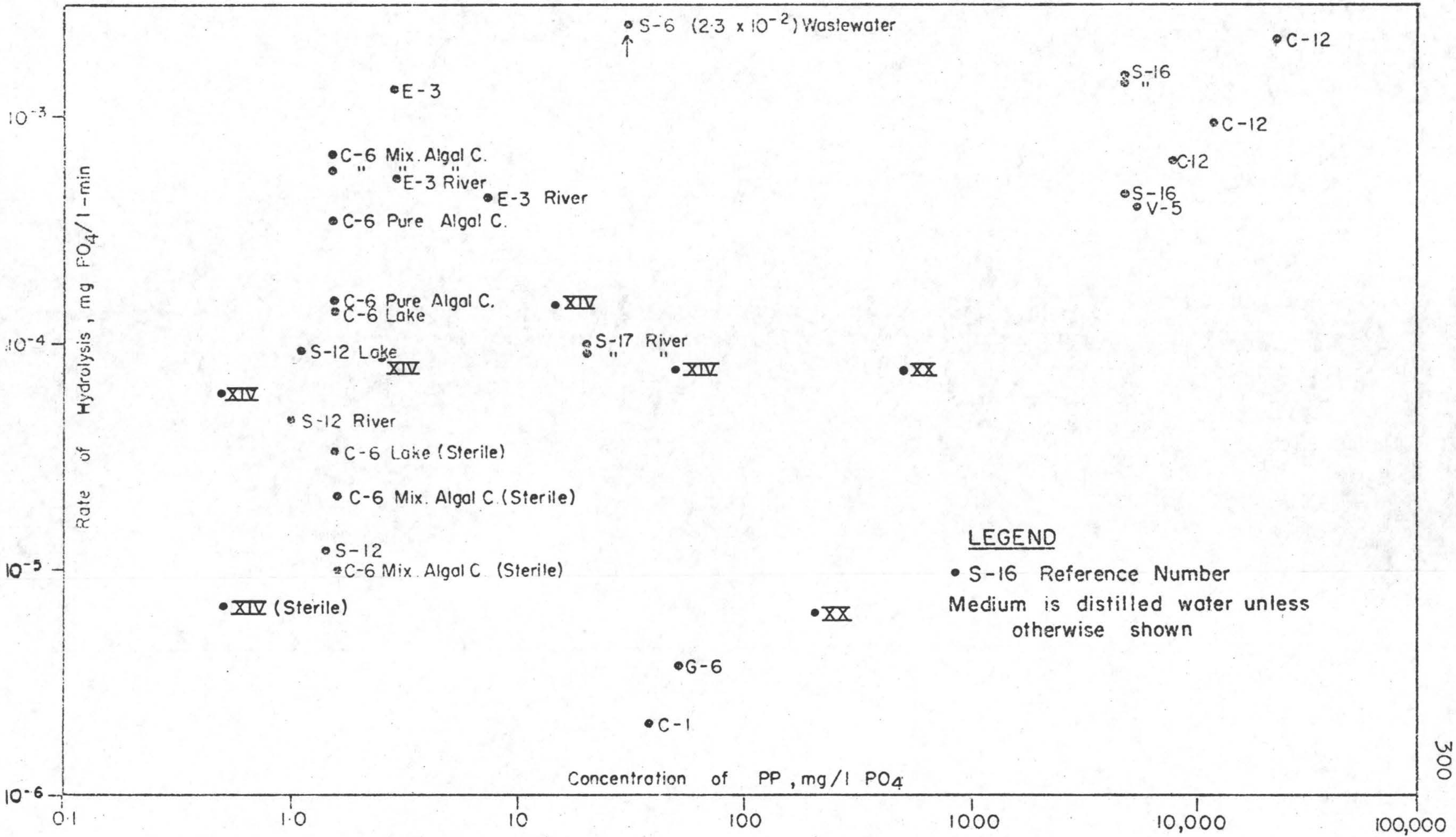
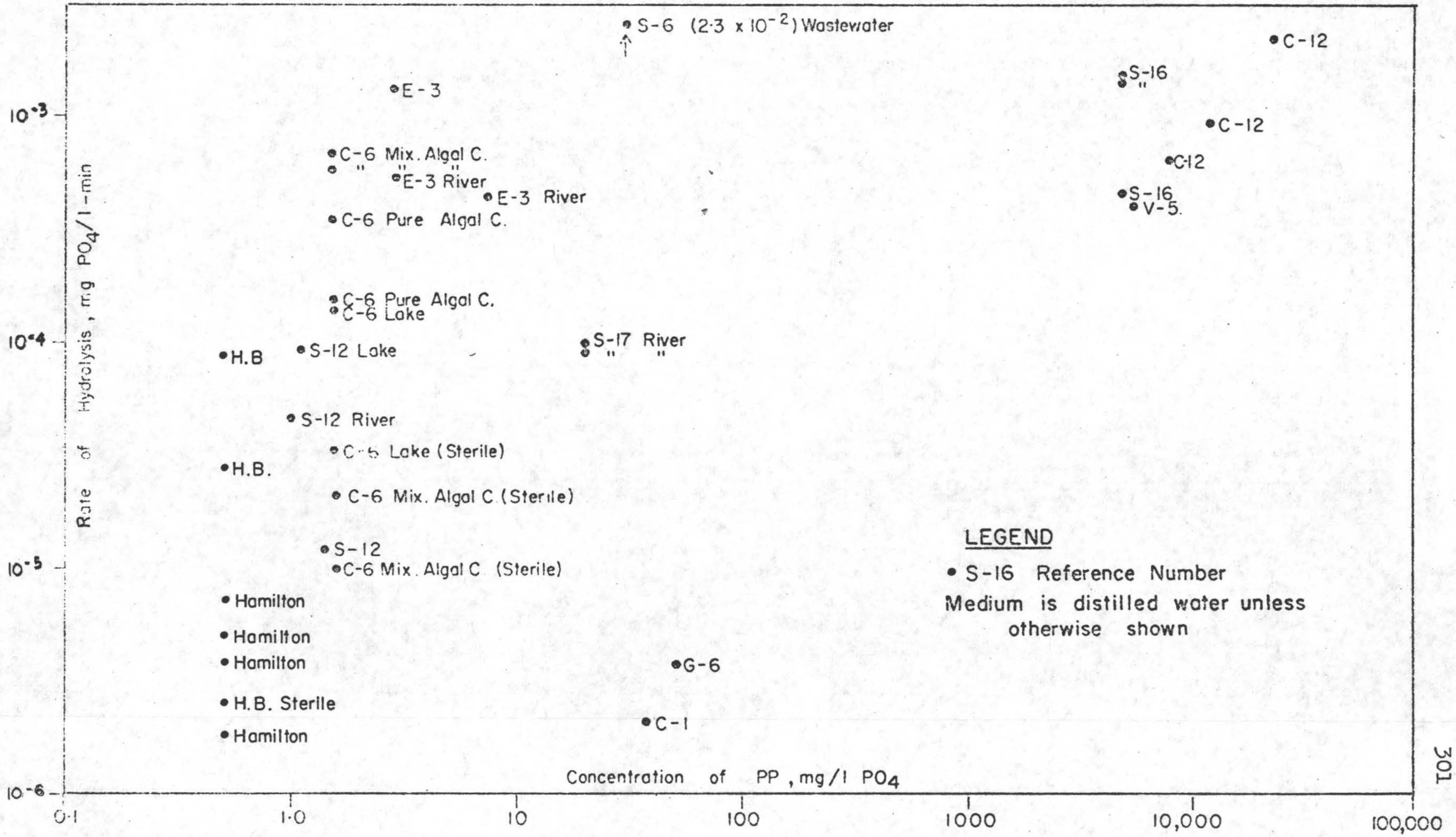


Figure 12B. Concentration Dependence of the Rate of Hydrolysis of Pyrophosphate at 20°C and pH = 7. Experimental Data on lake water added.



Effect of Variation in Temperature on the Rate of Hydrolysis of Condensed Phosphates

The following series apply:

-- Distilled water:	none
-- Lake water:	Series I, XIII
-- Wastewater:	Series IV, VII, VIII

The above series on lake water were carried out at temperatures of 20°C and 4°C. An estimate of the activation energy was obtained by comparing rates at these two temperatures. It would have been desirable to run experiment at three or four temperatures within the range of 4°-30°C. This would have allowed a much more definite conclusion on the value of activation energy for the media used. However, this was not possible due to time constraints. The results on activation energies obtained are shown below.

Lake Ontario water

Series I:	Humber Bay (May),	TPP,	E = 22.2 k cal/mole
Series XIII:	Hamilton W.T.P. (March),	TPP	E = 19.1 "
		PP	E = 14.7

It appears that for Lake Ontario water the activation energy may be as high as 22 k cal/mole. This means that condensed phosphates would persist about seven times as long under average winter conditions (4°C) than under summer conditions (20°C). The activation energy estimated for Lake Ontario water is higher than the values calculated in this work based on data of Smith, Cohen and Walton (S-17) and Shannon (S-12) and shown in Table XVIII. This could be explained by the probably lower microbial activity in Lake Ontario water than in Lake Mendota or Ohio River water.

Wastewater

Series IV, unfiltered, TPP, E = 9.8 k cal/mole
" VII, " , " , E = 10.0 "
" VIII, " , " , E = 6.5 "

The estimated values for the activation energy for the hydrolysis of tripolyphosphate in wastewater agree well with the value calculated in this work from the data of Sawyer (S-6) of 8.6 k cal/mole. This means that the rate of hydrolysis in wastewater will be about three times faster under summer conditions (20°C) than under winter conditions (4°C).

Independence in Rate of Hydrolysis of Condensed Phosphates

Crowther and Westman (C-12)report the following:

> "Whether or not tripolyphosphate and pyrophosphate hydrolyze independently of each other can be ascertained from an examination of the course of hydrolysis of sodium tripolyphosphate and the corresponding first-order rate constants for pyrophosphate and tripolyphosphate."

They present data from which they conclude that pyrophosphate and tripolyphosphate do hydrolize independently.

The results of Series XX on distilled water support this conclusion. Series XX-1 and 2 are experiments at concentrations of 500 mg/l PO_4 of tripolyphosphate and pyrophosphate respectively. Fig. 25 shows the comparison of experimental data to the calculated first-order model based on rate constants obtained from XX-1 for k_1, and XX-2 for k_2. The close comparison between the experimental data and calculated curve for pyrophosphate in Fig. 25-1 and -2 shows that pyrophosphate hydrolized at the same rate whether tripolyphosphate was present or not. The results of Series XX-3 and -4 show the same trend, but the comparison is not as good. This is primarily due to the relatively poor first-order fit of the tripolyphosphate data.

Influence of Dissolved Oxygen on the Rate of Hydrolysis of Condensed Phosphates in Lake Water

The results of Series III show that there is little or no difference in the rate of hydrolysis of condensed phosphates in lake water, which has been maintained under aerobic and anaerobic conditions. The small difference in pH between the two samples should not have any effect on this conclusion in light of results of Series XVIII on pH effects. However, lake water obtained from regions of zero or low dissolved oxygen levels in the lake will have a different micro-organism environment than saturated surface water, and the above conclusion may not apply in this case.

Effect of Length of Storage of Lake Water on the Rate of Hydrolysis of Condensed Phosphates

In general lake water was obtained within one or two days from the start of an experiment. However, it was certainly possible that at times it might be more convenient to obtain the sample when the vessel, Pt. Dauphine, was near the sampling station for other reasons. Series XII investigated what effect a two-week storage period has. Fig. 32-1 and -2 show the results on a fresh sample (2 days old) and a two-week old sample. Fig. 32-3 shows the result on sterile lake water.

XII-1: Fresh sample $k_1 = 3.2 \times 10^{-4}$, $k_2 = 2.7 \times 10^{-5}$ mg PO_4/l-min

XII-2: Two week old sample $k_1 = 2.8 \times 10^{-5}$, $k_2 = 8.3 \times 10^{-6}$ "

XII-3: Sterile sample $k_1 = 1.2 \times 10^{-5}$, $k_2 = 2.4 \times 10^{-6}$ "

The two-week old sample shows a large reduction in the rate of hydrolysis, tenfold for tripolyphosphate, over the fresh sample. Its rate is only slightly more than twice the rate in a sterile sample. Most workers do not report the time lapse between sampling and start of experiment. This series shows that this difference alone may account for some of the difference in rates obtained by various workers.

Effect of Addition of Glucose on the Rate of Hydrolysis of Condensed Phosphates in Lake Water

In Series XII-2 glucose was added to the sample part way through the experiment to see if this would stimulate microbial activity and thus increase the rate of hydrolysis. Fig. 32-2 shows the dramatic effect. The rate increased to about 2 x 10^{-4} mg PO_4/1-min, which is almost as fast as the rate in the fresh sample. In Series XIX this effect was checked a second time, and the results showed a ten-fold increase in rate due to the addition of glucose, $k_1 = 1.5 \times 10^{-4}$ mg PO_4/1-min. In a lake a continuous supply of food would be available, although not as high and available as the amount of glucose added. It is therefore likely that in situ rates would be higher than in batch experiments without addition of food, and probably lower than rates with the addition of glucose.

Effect of Organisms (Enzymatic Activity) on the Rate of Hydrolysis of Condensed Phosphates

Figures 11 and 12 show the literature data on the effect of organisms in giving comparative rates in various aqueous media of sterile or nonsterile condition. Under the heading of effect of concentration in this chapter, data obtained in this work were added to these figures and generally showed reasonable agreement. Rate constants for distilled water (Series IX and X) and lake water (Series XII) show a decrease of about one order of magnitude in the rate of hydrolysis of sterile sample versus a nonsterile sample. Series X, XI and XIV on distilled water, which were supposedly sterile samples at the start of the experiment, show a slow rate of hydrolysis for a lag period of several days, followed by an increased rate which is several fold faster and ascribed to the loss of sterile conditions. Although several attempts were made in Series IV, VII and VIII to obtain sterile wastewater, this was never achieved. The membrane filtered wastewater samples showed a marked lower rate of hydrolysis than the unfiltered wastewater samples. However, after about twenty-four hours growth occurred again in the filtered samples, which increased the rate to values close to the unfiltered samples.

Concentration and Type of Phosphorus Compounds in Wastewater

A comparison of the data of Series V and XV (Dundas S.T.P. survey), Series XXI (Humber S.T.P. survey), and literature data of Table IX shows the following:

1. The average concentration of unfiltered total phosphorus (UTP) in untreated wastewater of the Humber S.T.P. survey (21.7 mg/l PO_4) and Dundas S.T.P. survey (36 mg/l PO_4) fall well within the range of literature values in Table IX. The relatively low values of the Humber survey are caused by the rainfall preceding the survey.

2. The range of measurements on the Dundas S.T.P. wastewater is generally wider than at the Humber plant because of the small size of the Dundas system.

3. Soluble phosphorus (FTP) in the untreated wastewater accounted for slightly more than half (56 percent) at the

Humber plant, and for four-fifth (81 percent) at the Dundas plant. In the final effluent soluble phosphorus constituted 83 percent at the Humber plant and 97 percent at the Dundas plant.

4. Condensed phosphates in the untreated wastewater accounted for 63 percent of soluble phosphorus at the Dundas plant, and for 47 percent at the Humber plant. This could be due partly to the much longer time of flow in the sewer system at the Humber plant with its opportunity for hydrolysis in the sewer system. In the secondary effluent condensed phosphates accounted for only 4 percent of the soluble phosphorus at the Dundas plant and 14 percent at the Humber plant. These figures indicate the extensive hydrolysis that takes place in an activated sludge treatment plant, and are in general agreement with values of 19 percent given by Finstein and Hunter (F-3) as the average for several activated sludge plants. Comparable values for the primary effluent show that relatively little hydrolysis takes place during primary treatment, and that therefore contact with activated sludge organisms is responsible for the rapid hydrolysis during secondary treatment.

5. Total phosphorus (UTP) removal by primary treatment was small (9 percent at Humber plant, 12 percent at Dundas plant), but primary and secondary treatment reduced total phosphorus considerably (65 percent at the Humber plant,

48 percent at the Dundas plant). This latter conclusion is in disagreement with Finstein and Hunter (F-3) who found little reduction in total phosphorus by aerobic biological treatment.

6. Examination of Fig. 41-5 (Humber S.T.P. survey p.288) shows that for part of the survey orthophosphate values in the effluent were considerably higher than in the influent and primary effluent. Fig. 41-4 shows that in the same time period filtered total phosphorus in the effluent approximately equalled the concentration in the influent and primary effluent, showing apparently little or no reduction during this time. The explanation for this may lie in the method of returning digestor supernatant at the Humber plant. Under normal operations the digestor supernatant is pumped intermittently from the digestors to holding tanks and is continuously added to the activated sludge tanks. The flow rate is not measured but is estimated at about 260,000 gal/day. During the survey major construction was carried out in this part of the plant and the supernatant was added to the activated sludge tanks irregularly. The exact timing and amount of addition could not be established and therefore a mass balance cannot be made. However, the explanation holds true in qualitative terms. Similarily the concentration of filtered total phosphorus and orthophosphate in the primary effluent is higher than in the influent for part

of the survey due to return of waste activated sludge to the head of the primary settling tanks. These two cases point out the importance of measuring the flow rate and concentration in all streams, when attempting to carry out a mass balance.

Comparison of Laboratory Batch Rates of Hydrolysis of Condensed Phosphates in Wastewater and Activated Sludge to Rates Obtained in Treatment Plant Studies

Rate constants of hydrolysis in batch experiments of Series IV, VII and VIII agree closely with each other and give an average value of $k_{avg} = 2.3 \times 10^{-4}\ \text{min}^{-1}$. Batch experiments on activated sludge in Series XXIII indicate that the rate constant may be as high as $1.7 \times 10^{-2}\ \text{min}^{-1}$. In the filtered sample with no growth $k_{avg} = 2.5 \times 10^{-4}$, and about 1.6×10^{-3} when growth occurred again. This indicates the dramatic effect of contact with activated sludge organisms in increasing the rate of hydrolysis. Hurwitz _et al_ (H-17) reported "that condensed phosphates were degraded at a rapid rate during activated sludge treatment". Finstein and Hunter (F-3) carried out a short term experiment with activated sludge, filtered and unfiltered. The unfiltered sample showed a marked decrease in condensed phosphates, whereas the filtered sample did not. Although only three data points are available, an estimate of the rate constant gives $k_{avg} = 3 \times 10^{-3}\ \text{min}^{-1}$. This checks quite well with results in this work, and supports the argument that the hydrolysis takes place at the surface of microbial organisms rather than in the solution phase.

Series V, XV and XXI provide estimates of rates in plant operation.

Series V: (20°C) Primary Settl. Tanks: $k_{avg} = 6x10^{-3}$ min^{-1}
XXI: (16°C) " " " " $= 3x10^{-4}$ "
V: (20°C) Activated Sludge Tanks: " $= 1x10^{-2}$ "
XV: (8°C) " " " : " $= 7x10^{-3}$ "
XXI: (16°C) " " " : " $= 6x10^{-3}$ "

Rate constants in the activated sludge tanks are close to the values obtained in batch experiments. Value obtained at 8°C in Series XV is only about 1/3 lower than the value at 20°C, rather than about 1/2 to 2/3 lower as would be predicted from activation energies on wastewater. However, it would be likely that the temperature influence on activated sludge would not be as great as in wastewater, which could explain the result. The rate constant for wastewater in primary settling tanks of Series XXI agrees closely with batch results; the value of Series V is about one magnitude faster for unknown reasons.

Humber Bay Field Studies

Series XXII achieved only one of the purposes of the investigation, namely to establish levels of concentration and form of phosphorus in lake water in the vicinity of a major sewage treatment plant outlet. It did not achieve its second purpose, namely to measure rates of hydrolysis of condensed phosphates in lake water in situ. The main reasons for the failure to be able to achieve this, and suggested changes for a future attempt are as follows:

1) The flow pattern in Humber Bay is complex. This makes it difficult to separate the effect of diffusion and dilution from the effect of hydrolysis of condensed phosphates in lowering the concentration of condensed phosphates with distance from the source. It would be much preferable to carry out the experiment again in an area of simple flow pattern.
2) The 2000 lbs of sodium tripolyphosphate added in a 2-hour period should have been sufficient to give a marked increase in phosphorus concentration, and in particular in condensed phosphate concentration, in the effluent and the bay. It compares to an average discharge of about 8000 lbs of phosphorus per day, 15 percent of which may be in the condensed form. The decision to dry-feed the material proved to be a wrong one, due to the previously mentioned problem of hydration and caking of the powder. For a repeat experiment dosing of a concentrated solution of tripolyphosphate will rectify this situation.

Other comments on the data are:

-- The concentration of unfiltered and filtered total phosphorus, orthophosphate and condensed phosphates within a distance of three miles from a major sewage treatment plant outlet were reduced to levels generally found in near shore areas of Lake Ontario.

-- The flow of the Humber River, in which only few samples were taken should be considered as an additional input of pollutants. This applied particularly to the measurements of conductivity and turbidity, less in the case of phosphorus.

VI CONCLUSIONS AND RECOMMENDATIONS

1. The ascorbic acid method, as outlined in detail in Appendix A, should be used for the analysis of phosphorus in wastewater. It is apparently free of interferences that do occur with the stannous chloride method.

2. The sulfuric acid-persulfate digestion method for the analysis of total phosphorus is superior to other methods. Further work will be necessary to show that it is sufficiently strong to be used in the analysis of sludges.

3. The differential analysis of condensed phosphates in aqueous media at low concentrations can be achieved by a combination of ion-exchange with gradient elution and subsequent automatic orthophosphate analysis. At times some interferences occurred in the analysis of lake water. Further work is required to identify the causes of these interferences and their elimination.

4. The stannous chloride method for the automatic analysis of phosphorus in lake water allows the determination of phosphorus at very low levels. The precision at the level of 0.05 mg/l PO_4 is ± 5 percent. Further work is required

to show if the ascorbic acid method may be equal to or superior to the stannous chloride method.

5. The aminonaphtholsulfonic acid method for the automatic analysis of phosphorus in wastewater has a precision of ± 2.5 and 10 percent in the range 100 to 5 mg/1 PO_4. Further work is required to adapt the manual ascorbic acid method to automatic analysis, which may be superior to the aminonaphtholsulfonic acid method.

6. The rate of hydrolysis of tripolyphosphate and pyrophosphate in aqueous media is strongly dependent on the hydrogen ion concentration. The rate is faster in acidic media. This effect is of the same order of magnitude at very low concentrations of phosphorus investigated in this research as it is at higher concentrations reported in the literature. In a narrow range each side of the pH of natural water or wastewater there is little effect on the rate due to variations in hydrogen ion concentration.

7. First-order response in the rate of hydrolysis of condensed phosphates at concentrations higher than about 15 to 50 mg/1 PO_4 is well documented in the literature and supported by work done in this research. At lower concentrations a zero-order response is indicated by experimental work in this investigation.

8. The effect of temperature on the rate of hydrolysis in aqueous media can be estimated by use of Arrhenius

temperature dependence. Work in this research indicates that the rate of hydrolysis in Lake Ontario water is about seven times faster in summer than in winter. In wastewater the rate at summer temperatures is about three times the winter rate. Further work is required to obtain more accurate estimates of this effect.

9. Rates of hydrolysis in wastewater and activated sludge check well with the few available literature data. Rates in lake water are of the same order of magnitude as reported by others.

10. The presence of micro-organisms greatly affects the rate of hydrolysis. The rate is highest in the presence of activated sludge organisms, and decreases in order in wastewater, lake water and distilled water. Sterile distilled water and sterile lake water show approximately the same rate, which is about one order of magnitude lower than under nonsterile conditions. At these low concentrations the systems are unpoised and conditions such as length of storage of lake water and addition of food in the form of glucose affect the organism activity and thus the rate of hydrolysis.

11. Work done in this research supports the findings of a few workers that tripolyphosphate and pyrophosphate hydrolyze independently of each other. Pyrophosphate hydrolyzes slower than tripolyphosphate.

12. Waste treatment plant studies show that condensed phosphates account for about fifty percent of soluble phosphorus at the influent. Extensive hydrolysis occurs in the activated sludge tanks. The effluent contains about fifteen percent condensed phosphates. Estimates for the rate of hydrolysis through the primary settling tanks and the activated sludge tanks were in reasonable agreement with the rates obtained in laboratory batch experiments on wastewater and activated sludge.

13. For future studies on the rate of hydrolysis of condensed phosphates in lake water in situ, an area of less complex flow patterns than Humber Bay should be chosen.

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APPENDIX A: INSTRUMENTAL METHODS OF ANALYSIS

1. MANUAL ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE)
    - (a) Ascorbic Acid Method - Lake water
    - (b) Ascorbic Acid Method - Wastewater
2. AUTOMATIC ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE)
    - (a) Stannous Chloride Method - Lake water
    - (b) Aminonaphtholsulfonic Acid Method - Wastewater
3. MANUAL AND SEMI-AUTOMATIC ANALYSIS FOR TOTAL PHOSPHORUS
    - (a) Lake water application
    - (b) Wastewater application
4. DIFFERENTIAL ANALYSIS OF CONDENSED PHOSPHATE MIXTURES BY ION EXCHANGE CHROMATOGRAPHY COUPLED WITH AN AUTOANALYZER
    - (a) Stannous Chloride Method for Differential Phosphate Analysis
    - (b) Aminonaphtholsulfonic Acid Method for Differential Phosphate Analysis

1. MANUAL ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE)

(a) Ascorbic Acid Method - Lake water

Major References:

Murphy, J., and Riley, J. P., (M-16)
Stephens, K., (S-19)
Strickland, J.D.H., and Parsons, T.R., (S-20)
Kramer, J. R., (K-9)

General: For lake water analysis the ascorbic acid method without extraction is used in the range of 0.1 to 1.0 mg/l PO_4, and with extraction from 0.005 to 0.1 mg/l PO_4. The filtered water sample reacts with a mixed reagent, containing ammonium molybdate, sulfuric acid, potassium antimony tartrate and ascorbic acid. A blue colour results in the presence of phosphate, which is measured at 880 mμ. Extraction with isobutanol may be used, in which case the optical density is measured at 690 mμ.

A. Capabilities

1. Range: with extraction 0.005 - 0.100 mg/l PO_4
   without extraction 0.100 - 1.000 mg/l PO_4
2. Precision: At the 95 percent confidence level the correct value will lie in the range of
   at 0.02 mg/l PO_4 level: 0.020 ± 0.004 mg/l PO_4
   at 0.10 mg/l PO_4 level: 0.10 ± 0.005 mg/l PO_4
   at 0.50 mg/l PO_4 level: 0.50 ± 0.04 mg/l PO_4

B. Apparatus: Bausch and Lomb Spectronic 20 with 1" cuvettes. 250 ml globe-type Separatory funnels.

C. Reagents: (1) 5 N Sulphuric Acid, Dilute. 140 ml of conc. H_2SO_4 (95.5 percent, S.G. = 1.84) with double distilled water to one litre.

(2) Ammonium Molybdate Solution: Dissolve 15 g. ammonium molybdate (M.W. 1236) in double distilled water and dilute to 500 ml.

(3) Potassium Antimony Tartrate: Dissolve 0.34 g Potassium Antimony Tartrate in double distilled water and dilute to 500 ml.

(4) Ascorbid Acid: Dissolve 5.40 g Ascorbic Acid in double distilled water and dilute to 100 ml.

(5) Mixed Reagent: Mix in the prescribed order

50 ml of (1)
20 ml of (2)
10 ml of (3)
20 ml of (4)

The mixed reagent is stable only for a few hours. The above quantity is sufficient for a batch run of eight samples. Discard any unused portion.

(6) Isobutyl Alcohol

(7) 95 percent Ethyl Alcohol

(8) Double Distilled Water

Note: i) Ammonium Molybdate Solution and Potassium Antimony Tartrate solution are reported by Strickland and Parsons as stable for several weeks. In this work they are prepared weekly.

ii) Ascorbic Acid is stable only in dry form.

D. Procedure (Extraction Method):

1. Filter sample through membrane filter, 0.45 μ.
2. Allow samples to come to room temperature (15-25°C).
3. Measure 100 ml of sample in a graduated cylinder and pour into 250 ml separatory funnel.
4. Add 10 ml of mixed reagent with pipette and mix immediately by shaking for 60 seconds.
5. Continue step 4 for other samples in batch run. Usually eight samples are done in one run.
6. Add 20 ml of isobutyl alcohol about 15 minutes after addition of mixed reagent and shake vigorously for 60 seconds. Continue in the same way for all samples.
7. Reshake all funnels vigorously for 60 seconds.
8. Add 1 ml of Ethyl Alcohol (95 percent) to 1" cuvettes.
9. Separate aqueous phase by draining funnel to waste.
10. Drain organic layer directly into 1" cuvettes containing ethyl alcohol. Fill to mark (10 ml). Mix by swirling to insure mixing of extract and ethyl alcohol.

11. Measure optical density by Spectronic 20 at 690 mμ. Reference Sample (100 percent transmission) is to be made up daily by mixing 1 ml ethyl alcohol and 9 ml isobutanol in a 1" cuvette. Optical density reading on reagent blank, double distilled water, subjected to steps 2-10, is to be subtracted from all sample optical density readings. Obtain orthophosphate concentration from the equation: mg/l PO_4 = 0.285 x optical density.

E. Procedure (Non-Extraction Method)

Omit Steps 6, 7, 9, 10 and 11 of D.

Measure optical density at 880 mμ instead of 690 mμ. Correct for reagent blank and obtain orthophosphate concentration from the equation:

$$\text{mg/l } PO_4 = 2.10 \times \text{optical density}$$

(b) Ascorbic Acid Method - Wastewater

The ascorbic acid method without extraction is used. The wastewater sample is filtered, suitably diluted and contacted with the mixed reagent, and the resulting colour measured after ten minutes or more at a wavelength of 880 millimicrons.

A. Range: 1-100 mg/l PO_4

Beer's Law is followed up to approximately 50 mg/l PO_4 (See Fig. 22, Chapter IV)

B. Apparatus: Bausch and Lomb Spectronic 20 with ½" cuvettes, at 880 mm.

Membrane Filtration Setup.

C. Reagents: See 1) to 5) of a) Ascorbic Acid Method

Lake water.

D. Procedure:

1) Filter 20 ml of wastewater through 0.45 micron filter.
2) Dilute 5 ml of filtrate to 100 ml with distilled water in Nessler tube.
3) Put 20 ml of mixed reagent in 100 ml tube. All diluted sample to mark and mix. Wait ten minutes (or more) for colour development.
4) Measure optical density at 880 millimicron, using ½" cuvettes. Determine orthophosphate concentration of wastewater sample from a previously prepared calibration curve.

2. AUTOMATIC ANALYSIS FOR REACTIVE PHOSPHATE (ORTHOPHOSPHATE)

(a) Stannous Chloride Method - Lake water

Major Reference: Gales, M.E., Jr. and Julian, E.C., (G-2)

A. Capabilities

1. Range: 0.010 to 1.0 mg/l PO_4 with 50 mm flow cell

1 x Range Expansion: 0.1 to 1.0 mg/l PO_4

2 x Range Expansion: 0.05 to 0.3 mg/l PO_4

4 x Range Expansion: 0.01 to 0.1 mg/l PO_4

2. Precision:

at 0.05 mg/l PO_4 level: The correct value will be in the range of 0.05 ± 0.0025 mg/l PO_4 at the 95 percent confidence level.

At 0.50 mg/l PO_4 level: The correct value will be in the range of 0.50 ± 0.02 mg/l PO_4 at the 95 percent convidence level.

B. Apparatus and Flow Diagram

Sampler,
Proportioning Pump
Heating Bath
Colorimeter, 650 m Filters, 50 mm flow cell
Recorder with Range Expander

C. Reagents

Ammonium Molybdate Solution - Dissolve 12.5 g of $(NH_4)_6MO_7O_{24}.4H_2O$ in 175 ml of distilled water. Add 137.5 ml of concentrated sulfuric acid slowly and with stirring to 400 ml of distilled water and cool. Add the molybdate solution to the acid solution and dilute to one liter.

Stannous Chloride Solution - Dissolve 2.5 grams of fresh $SnCl_2.2H_2O$ in 20 ml of hydrochloric acid. Warming on a hot plate will aid in dissolving this material. Dilute to 400 ml.

Acid Wash Water - Add 40 ml of concentrated sulfuric acid slowly and with stirring to about 400 ml of distilled water. Dilute to two liters.

Phosphate Standards - Prepared in desired strength from KH_2PO_4.

D. Operating Procedure

1. Sample cups of 10 ml are filled with phosphate standards, filtered (0.45) samples or acid wash water. Place the cups in the sampler and separate each standard or sample with a wash cup. Be sure sample cups are acid washed.
2. A set of standards is run at the beginning and end of each day. When 4 x range expansion must be used, standards may be run more often.
3. All analysis are run in duplicate. Reproducibility is generally good, but at times erratic results are obtained.
4. A calibration curve is made up on the chart from the set of standards at the beginning and end of the run. Linear interpolation is used between standards.
5. The baseline is set at zero optical density. The drift if any, appears to be always in the direction of increasing optical density. When it exceeds 0.03 a fast wash is used to return it to the original baseline.
6. The rate selected is 30 per hour. Due to the need for an acid wash between samples, actually only fifteen phosphate analysis per hour can be done.
7. Once the samples are set up it is not necessary to leave an operator there at all times, but frequent checks on sensible output are required.

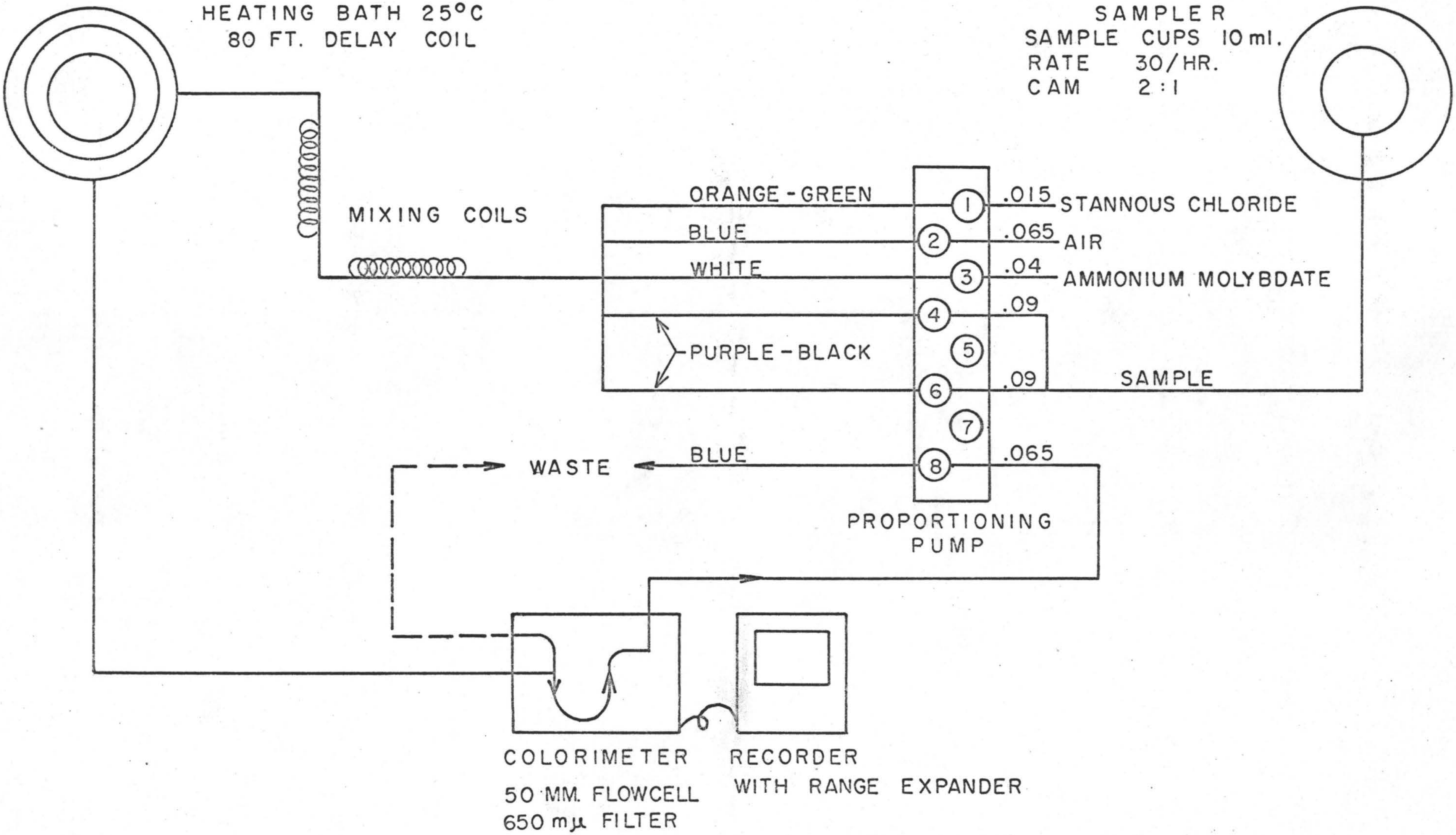

Figure 43. Autoanalyzer flow diagram - Stannous chloride method.

(b) Aminonaphtholsulfonic Acid Method - Wastewater

Major Reference: Standard Methods (A-3)

A. Range: 1-100 mg/l PO_4 with 15 mm flowcell

1 x Range expansion: 10 - 100 mg/l PO_4

2 x Range expansion: 1 - 25 mg/l PO_4

B. Apparatus and Flow diagram

Sampler
Proportioning Pump
Heating Bath
Colorimeter, 650 mμ Filters, 15 mm flowcell
Recorder with Range Expander

C. Reagents: Ammonium Molybdate Stock

Dissolve 31.4 g $(NH_4)_6 Mo_7 O_{24} \times 4H_2O$ in about 200 ml. distilled water. Cautiously add 252 ml conc. H_2SO_4 to 400 ml distilled water, cool, add 3.4 ml HNO_3, add the molybdate solution and dilute to 1 liter.

Ammonium Molybdate Reagent

Dilute 50 ml of Ammonium Molybdate Stock to 1 liter with distilled water. This will be good for several weeks.

Aminonaphtholsulfonic Acid Stock

Weigh out separately 0.75 g 1 - amino - 2 naphthol - 4 - sulfonic acid; 42 g anhydrous sodium sulphite, Na_2SO_3; and 70 g sodium metabisulfite, $Na_2S_2O_5$. Thoroughly mix the sulfonic acid with a small portion of the $Na_2S_2O_5$ powder.

Dissolve the remaining salts in about 900 ml distilled water: dissolve the mixed sulfonic acid powder in this mixture and dilute to 1 liter. Store in a glass container away from light at temperatures not exceeding 30°C.

Aminonaphtholsulfonic Acid Reagent

Dilute 50 ml of Aminonaphtholsulfonic acid stock to 1 liter with distilled water. Make this solution every few days.

Stock Phosphate Solution

Dissolve in distilled water 0.7165 g anhydrous potassium dihydrogen phosphate, KH_2PO_4 and dilute to 1000 ml. 1.00 ml = 0.500 mg PO_4.

Standard Phosphate Solution

Dilute 100.0 ml stock phosphate solution to 100 ml with distilled water. 1.0 ml = 50 µg PO_4

Acid Wash water

Add 40 ml of concentrated sulfuric acid slowly and with stirring to about 400 ml of distilled water. Dilute to two liters.

D. Operating Procedure and Notes

As in a) Stannous Chloride Method.

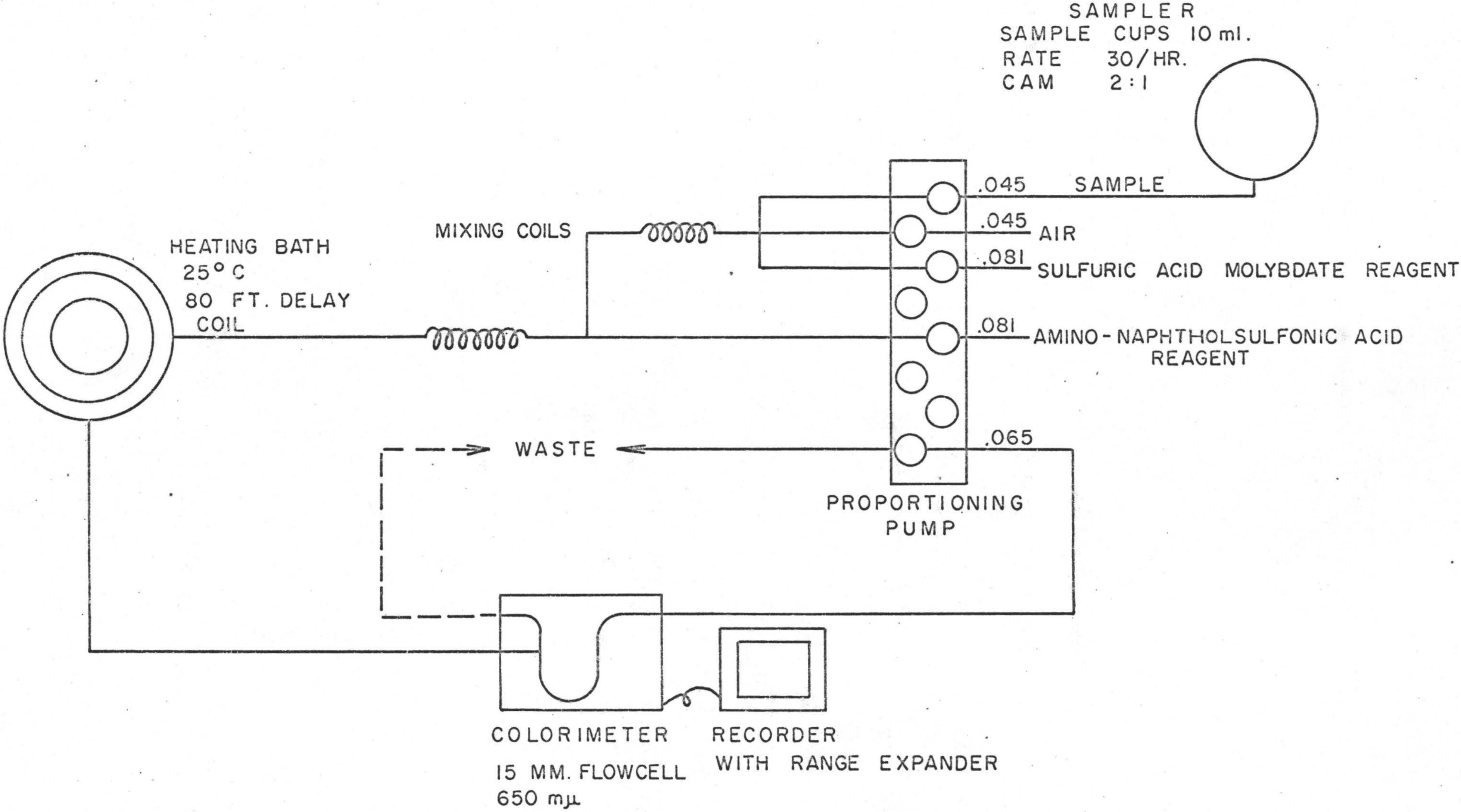

Figure 44. Autoanalyzer flow diagram - Aminonaphtholsulfonic acid method.

3. MANUAL AND SEMI-AUTOMATIC ANALYSIS FOR TOTAL PHOSPHORUS

Major Reference: Gales, M.E., Jr., Julian, E.C., and Kroner, R.C., (G-1)

General: The digestion step is carried out manually using potassium persulfate. This can be followed by either manual or automatic analysis for orthophosphate.

(a) Lake water Application

Digestion Step

1. Add 0.6 ml of sulfuric acid solution to a 30 ml sample in a 50 ml beaker.
2. Add 0.4 g of potassium persulfate.
3. Boil gently for 30 minutes.
4. Cool and dilute the sample with double distilled water to 30 ml. The sample is now ready for either manual analysis (see Method 1) or automatic analysis (Method 2) of orthophosphate.
5. Standards must be subjected to the digestion procedure for calibration purposes to obtain correct results.

Reagents for Digestion Step

1. Sulfuric Acid Solution: Add 310 ml of concentrated sulfuric acid slowly and with stirring to about 600 ml of distilled water. Cool and dilute to 1 liter.
2. Potassium persulfate, reagent grade.

Reagent for Automatic Analysis

1. Ammonium Molybdate Solution:

Replace the Ammonium Molybdate Solution specified in Method 2), by the following: Dissolve 12.5 g of $(NH_4)_6 MO_7O_{24}.4H_2O$ in 175 ml of distilled water. Add 77.5 ml of concentrated sulfuric acid slowly and with stirring to 400 ml of distilled water and cool. Add the molybdate solution to the acid solution and dilute to 1 liter.

(b) Wastewater Application

i) Manual Analysis - Ascorbic Acid Method

Digestion Step:

1) Add 2 ml of 5N Sulfuric Acid Solution (see Method 1a) to a 10 ml well-stirred wastewater sample in a 50 ml beaker.
2) Add 0.8 g of potassium persulfate. Dilute with 25 ml of distilled water.
3) Boil gently for about 30 minutes.
4) Cool and dilute to 500 ml.
5) Analyze for orthophosphate by steps 3 and 4 of Method 1b. Standards must be subjected to the digestion procedure for calibration purposes to obtain correct results.

ii) Automatic Analysis - Aminonaphtolsulfonic Acid Method

Digestion Step:

1) Add 2 ml of 5N sulfuric acid solution (see Method 1a) to 30 ml of well-stirred wastewater sample in a 50 ml beaker.
2) Add 1.2 g of potassium persulfate.

3) Boil gently for about 30 minutes.
4) Cool and dilute the sample with double distilled water to 30 ml. The sample is now ready for automatic analysis (Method 2b)
5) Standards must be subjected to the digestion procedure for calibration purposes to obtain correct results.

4. DIFFERENTIAL ANALYSIS OF CONDENSED PHOSPHATE MIXTURE BY ION EXCHANGE CHROMATOGRAPHY COUPLED WITH AN AUTOANALYZER

Major References: Czech and Hrycyshyn (C-17)
Lundgren and Loeb (L-10)

Principle: A mixture of ortho-, pyro- and tripolyphosphate is injected onto the top of an ion exchange column containing are anionic exchange resin. The individual phosphate species are separated and eluted by gradient elution with Potassium Chloride. The effluent of the column is continuously monitored by an Autoanalyzer, which performs hydrolysis, development, measurement and recording of the colour complex formed by methods given under 2.) The species appear in the crder of ortho-, pyro- and tripolyphosphate. The Aminonaphtosulfonic Acid Method is used for samples of higher phosphate concentration; the Stannous Chloride Method for samples of low phosphate concentration. As the procedures are somewhat different, they are written up separately.

4 (a) Stannous Chloride Method for Differential Phosphate Analysis

A. Range and Sample Size:

About 30 - 40 µg PO_4 gives full scale deflection on the recorder with the equipment as shown on the flow diagram. The volume of the sample is therefore adjusted from about 1 to 60 ml depending on the concentration of phosphorus in the sample. With this system the range of concentration can be from 0.5 to 30 mg/l PO_4 of the largest phosphate compound in the mixture.

B. Apparatus and Flow Diagram

Ion Exchange Column: 165 mm long borosilicate glass tube, inside dia. 11 mm, resin bed height 120 mm, supported on glass wool plug, rubber stoppers with glass connectors both ends.

All apparatus required for 2a)

Extra Heating Bath, 95°C.

Flow Diagram as per Fig.

C. Reagents

1. Stock buffer solution: Dissolve 78.5 g potassium acetate in 800 ml distilled water and buffer at pH 5.0 with glacial acetic acid. Dilute to 1 liter with distilled water.
2. Buffered Potassium Chloride solution (1M): Add 75 ml of Stock buffer solution to 225 g of K Cl, and dilute the dissolved mixture to 3 liters with distilled water.

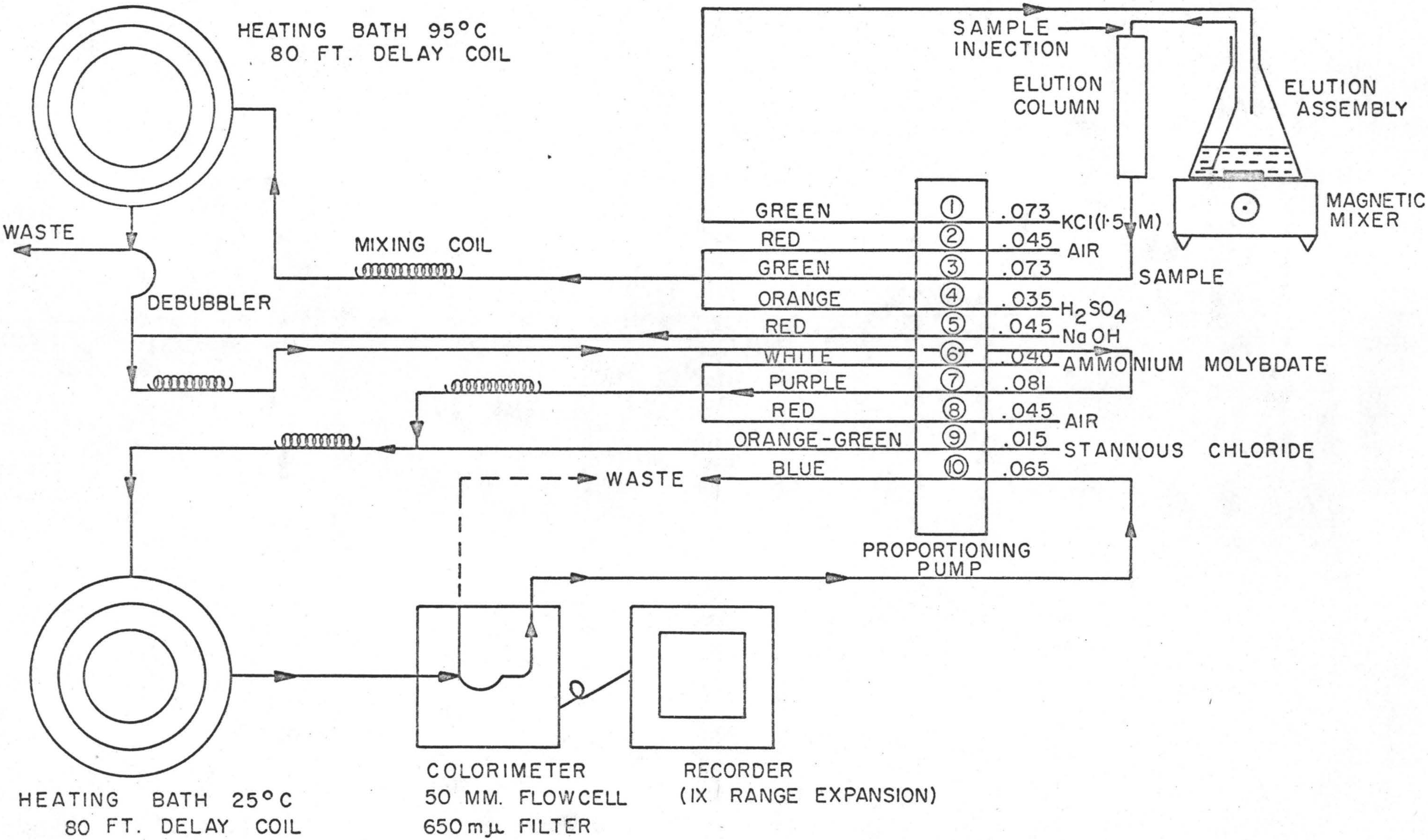

Figure 45. Autoanalyzer flow diagram.- Differential phosphate analysis by Stannous chloride method.

3. Buffered Potassium Chloride Solution (0.2M): Add 50 ml of stock buffer solution to 400 ml of buffered 1 M KCl solution and dilute to 2 liters with distilled water.
4. Buffered Potassium Chloride Solution (1.5M): Add 25 ml of stock buffer solution to 112.5 g of K Cl and dilute the dissolved mixture to 1l with distilled water.
5. Sulfuric Acid Solution: Add slowly 740 ml concentrated sulfuric acid to 1000 ml distilled water. Let cool and make up to two liters with distilled water.
6. Sodium Hydroxide Solution: Add 400 g NaOH to 1500 ml of distilled water. Let cool and make up to two liters with distilled water.

All necessary reagents for Method 2a)

Ion Exchange Resin: Anion Exchange Resin AG1 - XB,
200 - 400 mesh, chloride form (supplied by Canlab, Toronto).

D. Operating Procedure

Before introducing a sample, the column is washed and recharged by pumping 1 percent HCl for three minutes followed by 0.2 M KCl for ten minutes through the column. A sample volume is selected which will contain approximately 30 µg PO_4. It is introduced onto the top of the column. When the sample has gone through the column the elution assembly is started and eluant pumped through the column. The different phosphate peaks appear in the order of ortho-, pyro-, tripoly- and any higher ones if present. About 30 - 50 minutes elapse between start of elution and appearance of peaks. After the appearance of the tripolyphosphate peak the elution assembly is cut off and the HCl - KCl washing recharging cycle is restarted.

E. Analysis and Correction of Data

The area under each curve (Gaussian) is obtained as the product of the peak absorbance and the width of half peak height, and is expressed in arbitrary units of absorbance-millimeters. The relative distribution of each phosphate species can be expressed as a percentage of the total area. A correction factor must be applied as per Computer Program in Appendix B or as per Chapter IV, Figs. 20 and 21. To obtain absolute values it is necessary to determine the total phosphorus content of the sample by Method 3) and to apply the corrected percentages of ortho-, pyro- and tripolyphosphate to it.

4 (b) Aminonaphtholsulfonic Acid Method for Differential Phosphate Analysis

A. Range and Sample Size

About 500 ug PO_4 gives full-scale deflection on the recorder. The volume of the sample is therefore adjusted from 1 to 20 ml, depending on the concentration of phosphorus in the sample. With this system the range of concentration can be from 25 - 500 mg/l PO_4 of the largest phosphate compound in the mixture.

B. Apparatus and Flow Diagram

Ion Exchange Column: 165 mm long borosilicate glass tube, inside diameter 11 mm, resin bed height 120 mm, supported on glass wool plug, rubber stoppers with glass connectors both ends.

All apparatus required for 2b)

Extra Heating Bath, 95°C.

Flow Diagram as per Fig.

C. Reagents

1. to 4.: as per Method 4 a)

5. Sulfuric Acid Solution: Add slowly 370 ml of concentrated sulfuric acid to approximately 1500 ml of distilled water. Dilute to two liters with distilled water.

All necessary reagents for Method 2B)

Ion exchange Resin: as per Method 4 a)

D. Operating Procedure

As for method 4 a), but with a sample size of about 500 µg PO_4.

E. Analysis and Correction of Data

The area under each curve (Gaussian) is obtained as the product of the peak absorbance and the width at half peak height, and is expressed in arbitrary units of absorbance-millimeters. The relative distribution of each phosphate species can be expressed as a percentage of the total area.

No correction factor is necessary in this method. To obtain absolute values it is necessary to determine the total phosphorus content of the sample by Method 3) and to apply the corrected percentages of ortho-, pyro-, and tripolyphosphate to it.

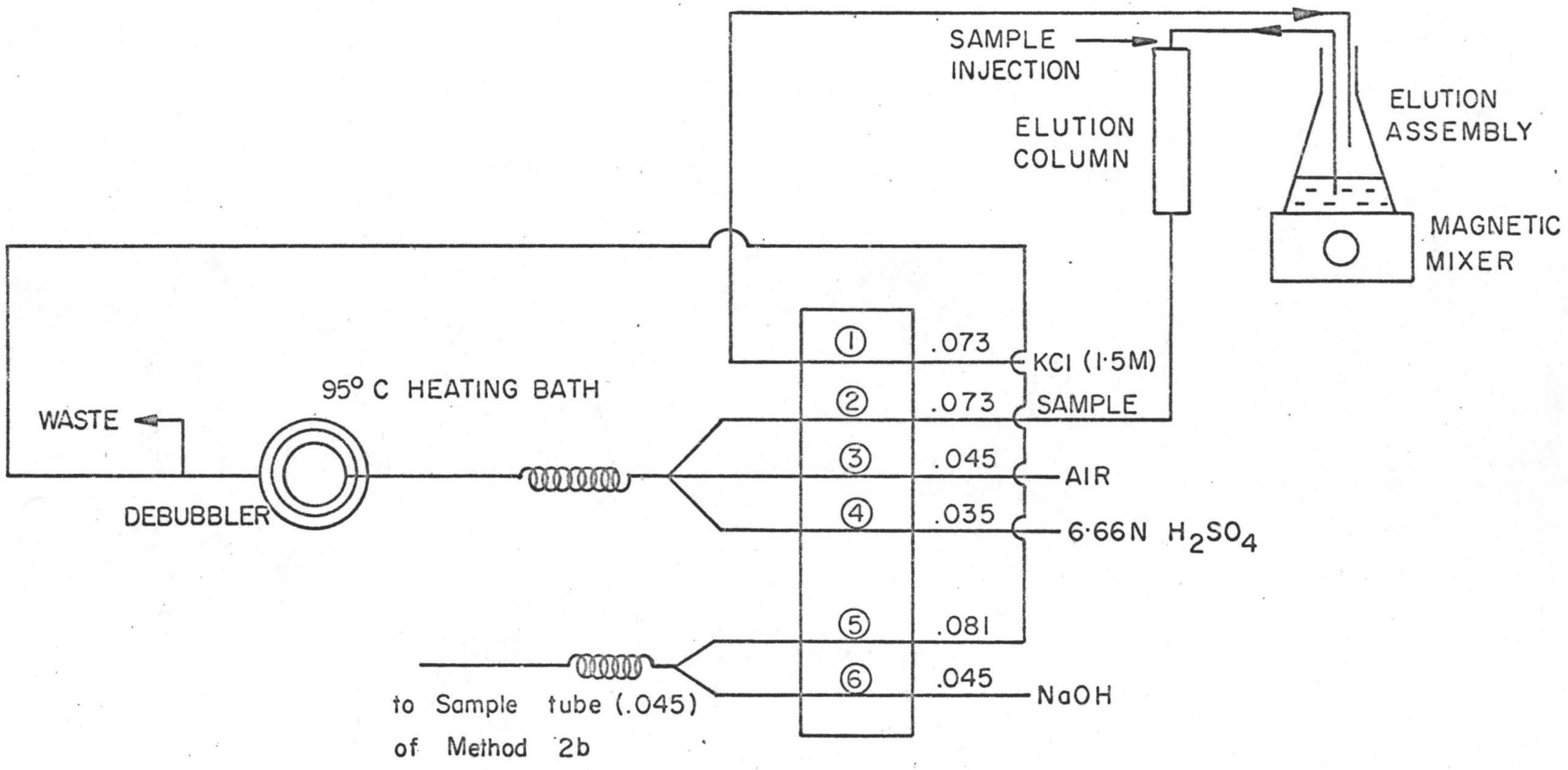

Figure 46. Autoanalyzer flow diagram - Differential phosphate analysis by aminonaphthol sulfonic acid method.

APPENDIX B: THEORY OF CONSECUTIVE REACTIONS

FIRST-ORDER

The hydrolysis of tripolyphosphate to orthophosphate can be described as follows:

$$\text{I} \quad TPP + H_2O \xrightarrow{k_1} PP + OP$$

$$\text{II} \quad PP + H_2O \xrightarrow{k_2} 2\ OP$$

The differential rate equations are

$$\frac{d\ (TPP)}{dt} = -\ k_1\ (TPP)$$

$$\frac{d\ (PP)}{dt} = k_1\ (TPP) - k_2\ (PP)$$

$$\frac{d\ (OP)}{dt} = k_1\ (TPP) + 2\ k_2\ (PP)$$

The integrated equations are

$$(TPP) = (TPP)_o\ e^{-k_1 t}$$

$$(PP) = (TPP)_o\ \frac{k_1}{k_2-k_1}\ (e^{-k_1 t} + a\ e^{-k_2 t})$$

$$\text{and } a = \frac{(PP)_o\ (k_2 - k_1)}{(TPP)_o\ k_1} - 1$$

$$(OP) = -(TPP)_o \left[e^{-k_1 t} + \frac{2}{(k_2-k_1)}\ (k_2\ e^{-k_1 t} + a\ k_1\ e^{-k_2 t}) \right] +$$

$$(TPP)_o \left[1 + \frac{2}{(k_2-k_1)}\ (k_2 + a\ k_1) \right] + (OP)_o$$

The terms are as follows:

$(TPP), (PP), (OP)$ = concentrations (moles/l) of tripolyphosphate, pyrophosphate and orthophosphate at time t.

$(TPP)_o, (PP)_o, (OP)_o$ = concentrations (moles/l) of tripolyphosphate, pyrophosphate and orthphosphate at time $t = 0$.

t = time, (minutes)

k_1, k_2 = first order rate constant for the hydrolysis of tripolyphosphate and pyrophosphate respectively, (minutes^{-1})

ZERO-ORDER

The equations I and II are as for first-order kinetics. The differential rate equations are:

$$\frac{d\,(TPP)}{dt} = -\,k_1$$

$$\frac{d\,(PP)}{dt} = +\,k_1 - k_2$$

$$\frac{d\,(OP)}{dt} = +\,k_1 + 2\,k_2$$

The integrated equations are

$$(TPP = (TPP)_o - k_1\,t$$

$$(PP) = (PP)_o + (k_1 - k_2)t \quad \text{from } t = 0 \text{ to } t = \frac{(TPP)_o}{k_1}$$

$$= (PP)_o + \frac{k_1 - k_2}{k_1} (TPP)_o - k_2 t \quad \text{from } t = \frac{(TPP)_o}{k_1} \text{ to } t$$

$$(OP) = (OP)_o + (k_1 + 2 k_2)t \quad \text{from } t = 0 \text{ to } t = \frac{(TPP)_o}{k_1}$$

$$= (OP)_o + \frac{k_1 + 2 k_2}{k_1} (TPP)_o + 2 k_2 t \text{ from } t = \frac{(TPP)_o}{k_1} \text{ to } t = t$$

The terms are as follows:

(TPP), (PP), (OP) = concentrations (moles/l) of tripolyphosphate, pyrophosphate and orthophosphate at time t.

$(TPP)_o$, $(PP)_o$, $(OP)_o$ = concentrations (moles/l) of tripolyphosphate, pyrophosphate and orthophosphate at time t = 0.

t = time, (minutes)

k_1, k_2 = zero-order rate constants $\left(\frac{\text{moles}}{\text{l-min}}\right)$ for the hydrolysis of tripolyphosphate and pyrophosphate respectively.