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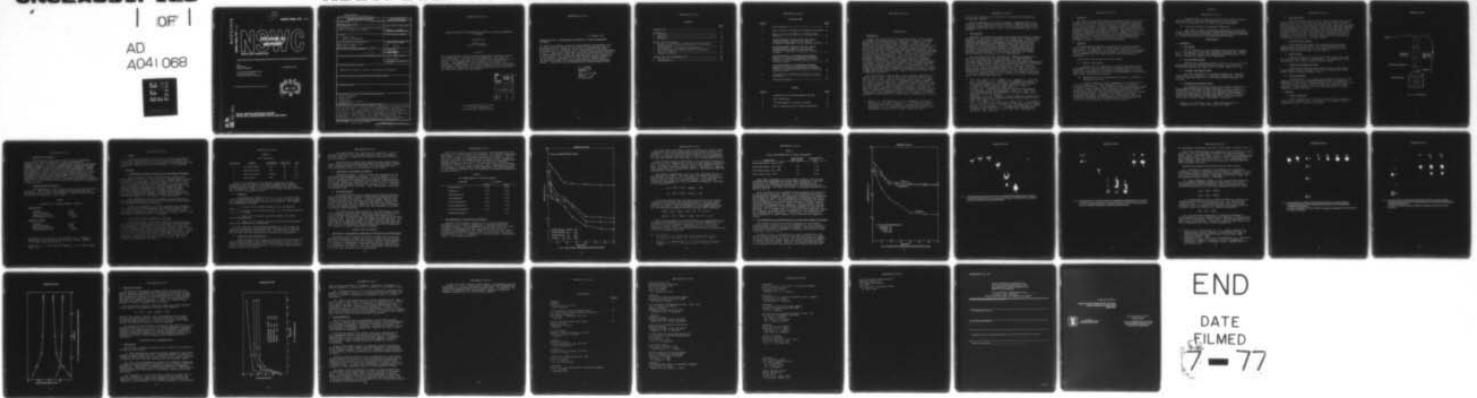
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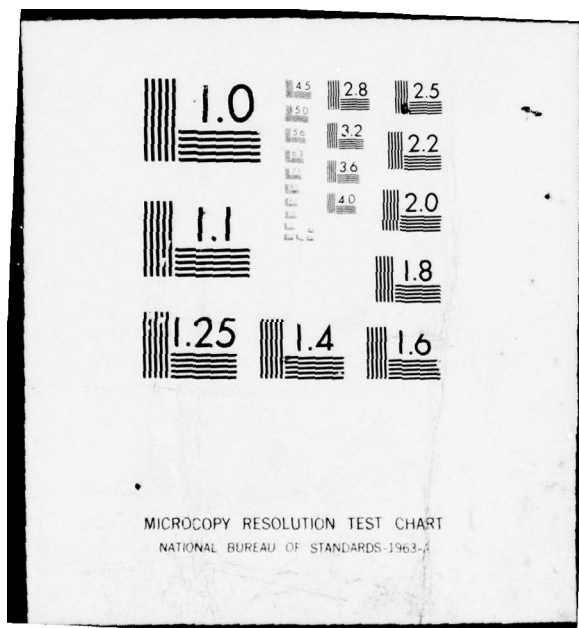
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# NSWC TECHNICAL REPORT C

WHITE OAK LABORATORY

IDENTIFICATION OF TRANSFORMATION PRODUCTS OF WHITE PHOSPHORUS IN WATER

BY  
Ming G. Lai  
David H. Rosenblatt

31 JANUARY 1977

NAVAL SURFACE WEAPONS CENTER  
WHITE OAK LABORATORY  
SILVER SPRING, MARYLAND 20910

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Prepared by:

Ming G. Lai  
David H. Rosenblatt

Abstract

Both suspended and soluble elemental phosphorus disappear rapidly in "phossey water". Initially the disappearance rate seems to follow the first order reaction with half-lives ranging from 3.5 to 6 hours. The disappearance is believed to be the result of chemical transformations. Four transformation products have been identified. These include only lower oxidation states of phosphorus. No significant quantities of condensed phosphates were detected in the solutions during the investigation.

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Naval Surface Weapons Center  
White Oak Laboratory  
Silver Spring, Maryland 20910

31 January 1977

IDENTIFICATION OF TRANSFORMATION PRODUCTS OF WHITE PHOSPHORUS  
IN WATER

In order to accurately assess the environmental consequences from the generation of "phossey water" wastes in loading operations at Pine Bluff Arsenal, Arkansas, there currently exists an urgent requirement for a thorough study of the chemistry of white phosphorus in water. This report identifies the major transformation products of white phosphorus in water and presents data on the kinetics of transformation. The information thus obtained appears sufficient for an accurate assessment of the pollution of "phossey water". The work was funded by the Army Medical Research and Development Command under Military Interdepartmental Purchase Request 5954.

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Commander

*Daniel L. Love*

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By direction

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## INTRODUCTION

1. Background

Concern has arisen over the deleterious effect on the aquatic environment of the discharge of "phossy water" wastes in loading operations at Pine Bluff Arsenal, Arkansas. "Phossy water" is defined as that water which comes in direct contact with large quantities of molten phosphorus, including dip-tank overflow, water used to flush white phosphorus from pipes, spray water used for wetting the dip-fill line conveyor and water from periodic cleaning of the dip-fill tank. "Phossy water," which is initially above the melting point of phosphorus ( $44.2^{\circ}\text{C}$ ), contains both suspended and dissolved elemental phosphorus. The rate of production of this phosphorus-laden water varies greatly, as does its elemental phosphorus concentration. The contained phosphorus undergoes continual reaction with dissolved oxygen, with atmospheric oxygen at the surface, and with water and hydroxide ion, to form phosphorus compounds in various oxidation states. Given adequate time, the unreacted suspended white phosphorus particulates settle out as a sludge and the dissolved phosphorus is gradually oxidized. However, streams containing "phossy water" remain noticeably polluted over considerable distances.

White phosphorus (the tetramer  $\text{P}_4$  of elemental phosphorus) is highly toxic to fish. The 96 hour  $\text{LC}_{50}$ 's are less than  $50 \mu\text{g}/\text{l}$  for all fish studied, and the incipient lethal level is probably less than  $1 \mu\text{g}/\text{l}$  for most fish.<sup>1</sup> Phosphorus poisoning appears to be cumulative and irreversible, though the cause of mortality has not been determined. While phosphorus is readily taken up by fish and other aquatic organisms directly from water, fish may also acquire lethal quantities of elemental phosphorus through the food chain, since the few macroinvertebrates studied have a much higher tolerance for white phosphorus than fish. Furthermore, elemental phosphorus can be passed on to humans since a considerable portion,

1. Dacre, J. C. and Rosenblatt, D. H., "Mammalian Toxicology and Toxicity to Aquatic Organism of Four Important Types of Waterborne Munitions Pollutants - An Extensive Literature Evaluation," U. S. Army Medical Bioengineering Research and Development Laboratory Tech. Report 7403, Mar 1974

25% or more, remains in the muscle of the fish after processing, storage and cooking.<sup>2</sup>

White phosphorus is so toxic to aquatic organisms that it is difficult to set maximum permissible levels. Based on the minimum incipient lethal level of 0.1  $\mu\text{g}/\text{l}$ , it would seem advisable to set a maximum permissible level of 0.01  $\mu\text{g}/\text{l}$  in the mixing zone of any outfall.

## 2. The Problem

Addison<sup>3</sup> has presented evidence indicating that aqueous elemental phosphorus is oxidized to phosphate in a single step. Likely intermediates, though stable under the reaction conditions, could not be isolated and identified. Blumbergs, et al,<sup>4</sup> on the other hand, reported that "phosy water" from Pine Bluff AAP contains lower phosphorus oxides other than phosphate. However, data were not available as to the oxidation states of the individual species. In order to establish a data base for the setting of pollutant guidelines and standards, it is essential that the Army Surgeon General identify the products of  $\text{P}_4$  transformation.

Data on the kinetics of oxidation of elemental phosphorus in water are available but not well defined. At concentrations (10  $\mu\text{g}/\text{l}$ ) well below the solubility limit of 3 mg/l, with the dissolved oxygen content unspecified, elemental phosphorus disappeared by a first order process with a half-life of two hours at 10°C<sup>5</sup> and 0.85 hour at 30°C.<sup>3</sup> At concentrations well above the solubility limit, with a dissolved oxygen content of 6 to 7 mg/l, the same reaction had a half-life of 80 hours at 30°C and 240 hours at 0°C.<sup>6</sup> No data have been presented on the kinetics of elemental phosphorus in water at concentrations of 0.01 to 0.001  $\mu\text{g}/\text{l}$ , where the maximum permissible levels have been set.

2. Dyer, W.J., Hiltz, D. F., Ackman, R. G., Hingley, J., Fletcher, G.L., and Addison, R.F., "Stability of Elemental Phosphorus in Edible Muscle Tissue of Cod During Processing, Incl. Icing, Freezing & Thawing, Frozen Storage, Salting & Cooking," J. Fish. Res. Bd. Canada 29, 1053 (1972)
3. Addison, R.F., "Analysis of Elemental Phosphorus and Some of its Compounds by Gas Chromatography," Proc. Int. Symp. Identification Measurement Environmental Pollutants, Ottawa, Ont., June 14-17, 1971, pp 386-390
4. Blumbergs, P., et al, "Chemical Process Studies for Commercially Unavailable Materials," Edgewood Arsenal Contract DAAA 15-69-C-0584, Final Report (1973)
5. Zitko, V., Aiken, D.E., Tibbo, S.N., Besch, K.W.T., and Anderson, J.M., "Toxicity of Yellow Phosphorus to Herring, Atlantic Salmon, Lobster, and Beach Flea," J. Fish. Res. Bd. Canada 27, 21 (1970)
6. Bullock, E. and Newlands, M.J., "Decomposition of Phosphorus in Water" Proc. Conf. Poll. Chem. Inst. Can., Halifax, N.S., Aug 24-26, 1969, pp 23-24

### 3. Objective

In order to assess the probable environment impact of the discharged "phossey water" from munitions plants without sufficient literature data on the aqueous chemistry of elemental phosphorus, it is first necessary to obtain, through a series of laboratory investigations, basic information regarding the characteristics of elemental phosphorus in aqueous solutions. The objective of this work is to quantitatively identify all the chemical species of phosphorus formed by the addition of white phosphorus to water and to determine the kinetics of oxidation of white phosphorus in aqueous solutions. This report also describes the analytical procedures used to accomplish the above purposes.

### 4. Approach

The experimental approach is based on the nuclear technique, which offers the advantages of being simple, rapid, and non-destructive. In addition, the sensitivity and accuracy of measurement in nuclear methods are far superior to those of other analytical techniques for the identification and determination of phosphorus.

The program was divided into three phases:

#### (1) Methods Development

Methods for the separation of various chemical species of phosphorus in water by thin-layer chromatography (TLC) were developed. The location and quantity of each species on the TLC plates were determined by the use of autoradiography in conjunction with liquid scintillation counting.

#### (2) Identification of Transformation Products of Elemental Phosphorus in Water

A small quantity of white phosphorus was irradiated in a nuclear reactor to produce phosphorus-32 ( $t_{1/2} = 14.3$  days, 1.71 MeV Beta emitter). The radioactive white phosphorus was added to various types of water under laboratory controlled conditions. A portion of each solution was examined periodically by the developed TLC methods. The identification of the chemical species in the "phossey water" was made by the comparison of known phosphorus standards. Concentrations of the species were quantitatively determined by the measurement of the phosphorus-32 activity of the individual spots on the TLC plates.

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Gaseous products from the reactions were passed through a tube containing silica gel impregnated with silver nitrate. Phosphine was absorbed and its quantities were determined.

## (3) Kinetics of Decay of Elemental Phosphorus

The rates of decay of elemental phosphorus in water were studied under various conditions. Radioactive elemental phosphorus in the solutions was first extracted with benzene and then measured in a liquid scintillation or gas proportional counter.

## EXPERIMENTAL

1. Apparatusa. TLC Plates

MN 300 cellulose (250  $\mu\text{m}$  thickness) pre-coated TLC plates (20 x 10 cm and 20 x 20 cm) were employed (Analtech, Inc., Newark, Del.). To minimize tailing the plates were pre-developed in one or two solvents and dried at room temperature.

b. TLC Developing Tank

Conventional developing tanks 4" x 12" x 9" (l x w x h) with ground edges on the rim and covers were used. Each tank can accommodate several TLC plates with a solvent volume of 100 ml.

c. Constant Temperature Bath

The bath consisted of a constant temperature circulator (HAAKE Model E52) mounted on a five gallon pyrex jar. The temperature range was from  $-30$  to  $150^{\circ}\text{C}$  with control accuracy to  $\pm 0.02^{\circ}\text{C}$ .

d. Phosphine Collection Tubes

The phosphine collection tubes were prepared according to the procedure described by Nelson and Milun:<sup>7</sup> To a solution containing 1.5g of  $\text{AgNO}_3$  in 100 ml of distilled water, add 76g of 16-to-28-mesh silica gel and stir the mixture for 15 minutes. Decant the excess  $\text{AgNO}_3$  solution, dry the silica gel at  $90^{\circ}\text{C}$  for three hours and sieve to 30-to-50-mesh size. Pack the treated silica gel in glass tubing, 18cm length x 0.5cm i.d.

7. Nelson, J.P. and Milun, A.J., "Rapid Determination of Phosphine in Air, "Anal. Chem. 29, 1665 (1957)

e. Test Apparatus

The test apparatus was a 350-ml pyrex cylinder with ground glass cap (Fig. 1). Two tubulations on the top of the cylinder served as the inlet and outlet for the test gas, either air or argon. The inlet tube had a fritted pyrex bubbler on the end that extended to the bottom of the pyrex cylinder. The outlet tube was connected to the phosphine collection tube which in turn exhausted to the atmosphere inside a hood. The inlet flow of the gas, either from an air or argon tank, was controlled by a regulator valve and a flowmeter, in that order. The test solution in the cylinder was continuously stirred with a magnetic mixer.

f. Scintillation Counter

A Nuclear Chicago Model 6853 coincidence-type liquid scintillation counter was used. The counting efficiency for phosphorous-32 was about 95% with the use of Aquasol counting cocktail (New England Nuclear, Boston, Mass.).

g. Beta Counter

A Beckman Widebeta II gas proportional counter was used for counting low levels of radioactivity. The background of the counter was of the order of two counts per minute.

h. Gamma Pulse-Height Analyzer

Pulse-height analysis was performed with a 4096-channel pulse-height analyzer (Nuclear Data, Inc.) coupled with a 30cc Ge(Li) detector (Nuclear Diodes, Inc.).

i. Autoradiography

Conventional 8" x 10" X-ray film holders were used for the exposure of X-ray films (Eastman Kodak Type AA) to radioactive components on thin-layer chromato-plates. The inner portion of the box was lined with a soft black felt material to ensure light-tightness. After exposure the films were developed in a Kodak Industrial X-Omat Processor.

2. Reagents

a. White Phosphorus

White phosphorus with a purity of 99.999% was supplied by Ventron Corp, Danvers, Mass. The material was packed in argon atmosphere inside a sealed pyrex ampule.

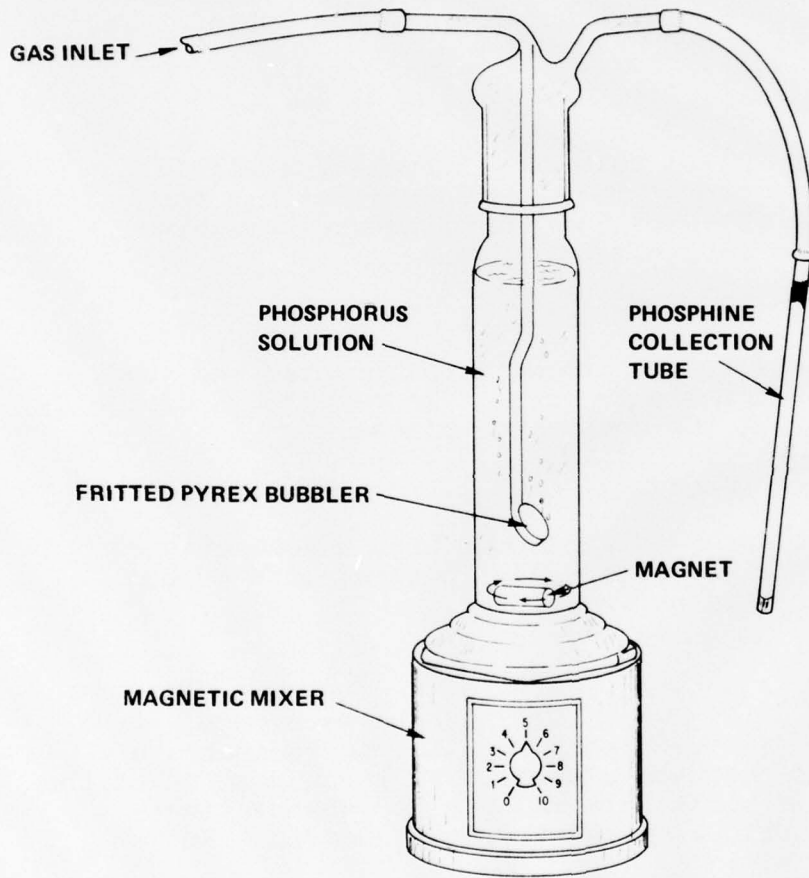


FIG. 1 TEST APPARATUS

b. Phosphorus Standards

The following sodium and potassium salts of phosphate compounds were used as standards. Sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ), sodium phosphite ( $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ ), potassium phosphate monobasic ( $\text{KH}_2\text{PO}_4$ ), and sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) were analytical reagent grade and standard items of commerce. Sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) and sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub> were supplied by Fisher Scientific Company, Fair Lawn, N.J., as purified grade. Sodium trimetaphosphate ( $\text{NaPO}_3$ )<sub>3</sub> and sodium tetrametaphosphate ( $(\text{NaPO}_3)_4 \cdot 4\text{H}_2\text{O}$ ) were prepared and purified in the laboratory using existing procedures.<sup>8,9</sup> All the standards were irradiated in the National Bureau of Standards reactor at a neutron flux of  $4.6 \times 10^{13} \text{ n/cm}^2/\text{sec}$  for one hour and dissolved in appropriate volumes of water.

c. Chromatographic Solvents

The composition of the solvents used in this work are given in Table 1. The solvents were prepared by dissolving the trichloroacetic acid in water, then adding the ammonium hydroxide and the dioxane or methanol, in that order.

TABLE 1

## Composition of Chromatographic Solvents

Acid Solvent

Dioxane	75 ml
Distilled Water	25 ml
Ammonium Hydroxide	0.25 ml
Trichloroacetic Acid	5 grams

Alkaline Solvent

Methanol	55 ml
Distilled Water	40 ml
Ammonium Hydroxide	5 ml
Trichloroacetic Acid	3 grams

8. Partridge, E. P., Hicks, V. and Smith, G. W., "A Thermal, Microscopic and X-ray Study of the System  $\text{NaPO}_3 - \text{Na}_4\text{P}_2\text{O}_7$ " J. Am. Chem. Soc. 63 454 (1941)
9. Griffith, E. J., "New Sodium Phosphates," J. Am. Chem. Soc 76 5892 (1954)

d. Water

Distilled water was obtained from a Corning MEGA-PURE all glass still, which produced water with resistivity higher than 1.0 meg ohm. River water was collected from the Potomac River near Great Falls, Maryland, and filtered through a 0.45  $\mu\text{m}$  membrane filter.

3. Procedurea. Irradiation of White Phosphorus and Phosphorus Standards

Ten milligrams of white phosphorus were loaded into a quartz ampule (6 mm i.d., 8.5 mm o.d., 4 cm length) under an argon atmosphere in a glove box. The ampule was sealed under vacuum and placed in an air-tight aluminum capsule (1.2 cm i.d., 1.0 cm o.d., 5 cm length), which in turn was placed in a polyethylene capsule supplied by the National Bureau of Standards (NBS). The capsule was then transported into the NBS reactor through a pneumatic tube and irradiated at a thermal neutron flux of  $4.6 \times 10^{13}$  n/cm<sup>2</sup> sec for one hour. Several milligrams of each phosphorus standard were wrapped in aluminum foil, placed in the polyethylene capsule and irradiated in the same manner.

The temperature during the irradiation was measured by temperature sensing color indicators and the neutron flux profile was monitored by the cobalt flux wire.

After the irradiation the white phosphorus and standards were cooled for two weeks to permit the decay of possible interfering activities (e.g., <sup>24</sup>Na, <sup>42</sup>K, etc.). The purity of the samples was established by gamma pulse-height analysis and the decay measurements of the activity in the samples.

b. Reaction of White Phosphorus with Water

The quartz ampule containing radioactive white phosphorus was broken in a glove box under argon atmosphere and the contents were immediately transferred into 60 ml of distilled water in a 100-ml Erlenmeyer flask with a ground glass stopper. The flask was placed in an ultrasonic cleaner and shaken for ten minutes. After a short period to allow some coarse unsuspended materials to settle out, ten ml of the aqueous suspension were added to each of the 280-ml test solutions in the test vessels. The initial white phosphorus concentration was found to be 205  $\mu\text{g/l}$ . The test conditions are described in Table 2.

TABLE 2

## Test Conditions

<u>Experiment</u>	<u>Medium</u>	<u>Atmosphere</u>	<u>Temp. (°C)</u>	<u>pH</u>
1	Distilled water	Air	22	6.1
2	Distilled water	Air	40	6.1
3	Distilled water	Argon	22	6.8
4	River water	Air	22	7.5

Prior to the addition of the aqueous suspension of white phosphorus, the test waters were either aerated (air purged) or deaerated (argon purged). During the experiments the gas flow was maintained at a rate of 0.1 liter per minute, and the solutions were stirred with magnetic mixers.

d. Sampling

At successive intervals of 1, 1, 3, 4, 4, 7, 8 and 7 days (total elapsed reaction times 1, 2, 5, 9, 13, 20, 28 and 35 days) 4-ml samples were withdrawn from each test solution. The samples were processed as follows:

1. Filter 2 ml of sample through a 0.45  $\mu$ m membrane filter
2. Extract 1 ml of unfiltered and 1 ml of filtered samples with 1 ml of benzene
3. Pipet 0.5 ml aliquot from each extract for radioactivity measurements
4. Pipet 0.1 ml aliquot from each filtered and unfiltered sample for radioactivity measurements

For the sampling of the absorbed phosphine in the silica gel tubes, the tubes were removed from the test apparatus at periodic intervals and replaced with fresh ones. The section of the color band in each tube was separated for radioactivity measurement.

e. Radioactivity Measurements

Sample aliquots with relatively high levels of phosphorus-32 activity were counted in the liquid scintillation counter. The sample solutions were pipetted into counting vials, each containing 15 ml of the scintillation cocktail. The resulting solutions were shaken, cooled, and counted.

For samples with very low levels of activity, a gas proportional counter with a low background was used. The sample solutions were first evaporated to dryness in aluminum planchets and then counted.

The silica gel samples were counted in the liquid scintillation counter using the similar procedure described above, except that a suspension material, CAB-O-Sil, (0.5 to 1.0g) was mixed with the cocktail prior to the addition of the sample.

f. Separation of Phosphorus Species

Phosphorus species in the solution were separated by the thin-layer chromatographic technique. In the procedure, 4  $\mu$ l of filtered sample solution were spotted on the TLC plates and air dried. The plates were developed in development tanks containing the solvent system to a depth of about 0.5 cm (100 ml of solvent). The solvent was allowed to ascend to a height of 10 cm. The time of development was about one hour. After development, the plates were dried in air.

g. Autoradiography

Each developed TLC plate containing radioactive chromatograms was covered with a piece of sheet plastic (Handi-Wrap) and placed in an X-ray film holder. A piece of Kodak type AA X-ray film was laid on top of the plastic-covered plate. Spring locks of the film holder held the plate and the X-ray film firmly together. The X-ray film was exposed to the thin-layer chromatogram for periods between three to seven days and developed in a Kodak Industrial X-Omat Processor.

For quantitative determination of the chromatogram, radioactive areas on the plate were located by placing it over the film on a horizontal X-ray viewer. These areas were marked with a needle and then transferred from the plate into liquid scintillation counting vials. For this a steel flat-blade scraper was used. The blade was 13 mm wide and tapered to a sharp edge to facilitate the rapid removal of adsorbent from the plate. The adsorbent was mixed with 15 ml of scintillation cocktail containing 0.5 g of CABO-Sil and counted in a liquid scintillation counter.

## RESULTS AND DISCUSSION

1. Separation of Phosphorus Compounds by Thin-Layer Chromatography

Preliminary work involved a qualitative comparison of various adsorbent materials of commercial origin. Avicel, Cellulose DEAE, PEI Avicel, Cellulose MN 300, and Cellulose MN300 HR were compared with respect to separation, form of spots, tailing, and adhesion of the layer to the support. The best results were obtained with Cellulose MN300 on glass. On this basis precoated Cellulose MN300 TLC plates were selected for the experiments.

Two solvent systems, acid and alkaline, were developed for the separation of several phosphorus compounds. The solvent compositions that seemed to give the best results are given in Table 1. The  $R_f$  values for a number of phosphorus compounds are listed in Table 3. The data indicated that hypophosphite, phosphite, and orthophosphate separate poorly in the acidic solvent but that the condensed phosphates separate quite well. On the other hand, in an alkaline solvent the reverse is true. Therefore, with a combination of these two systems, it seemed possible that separation and identification of the oxidation products from the oxidation of elemental phosphorus could be effected.

TABLE 3

## TLC PERFORMANCE OF SOLVENT SYSTEMS

COMPOUND	$R_f$ VALUES	
	Acidic	Basic
Hypophosphite	0.93	0.80
Phosphite	0.92	0.65
Orthophosphate	0.91	0.48
Pyrophosphate	0.78	0.18
Tripolyphosphate	0.44	0.26
Trimetaphosphate	0.22	0.24
Tetrametaphosphate	0.12	0.15
Hexametaphosphate	-	0.10

## 2. Transformation of Elemental Phosphorus

Results of the kinetic studies (Fig. 2) confirm previous observations that elemental phosphorus in aqueous suspensions disappears rapidly. The disappearance is believed to be the result of chemical transformations such as oxidation and reduction. Initially the disappearance rate seems to follow the first order reaction with half-lives ranging from 3.5 to 6 hours. The results suggest that the rate is dependent on dissolved oxygen, temperature, and pH of the aqueous solutions.

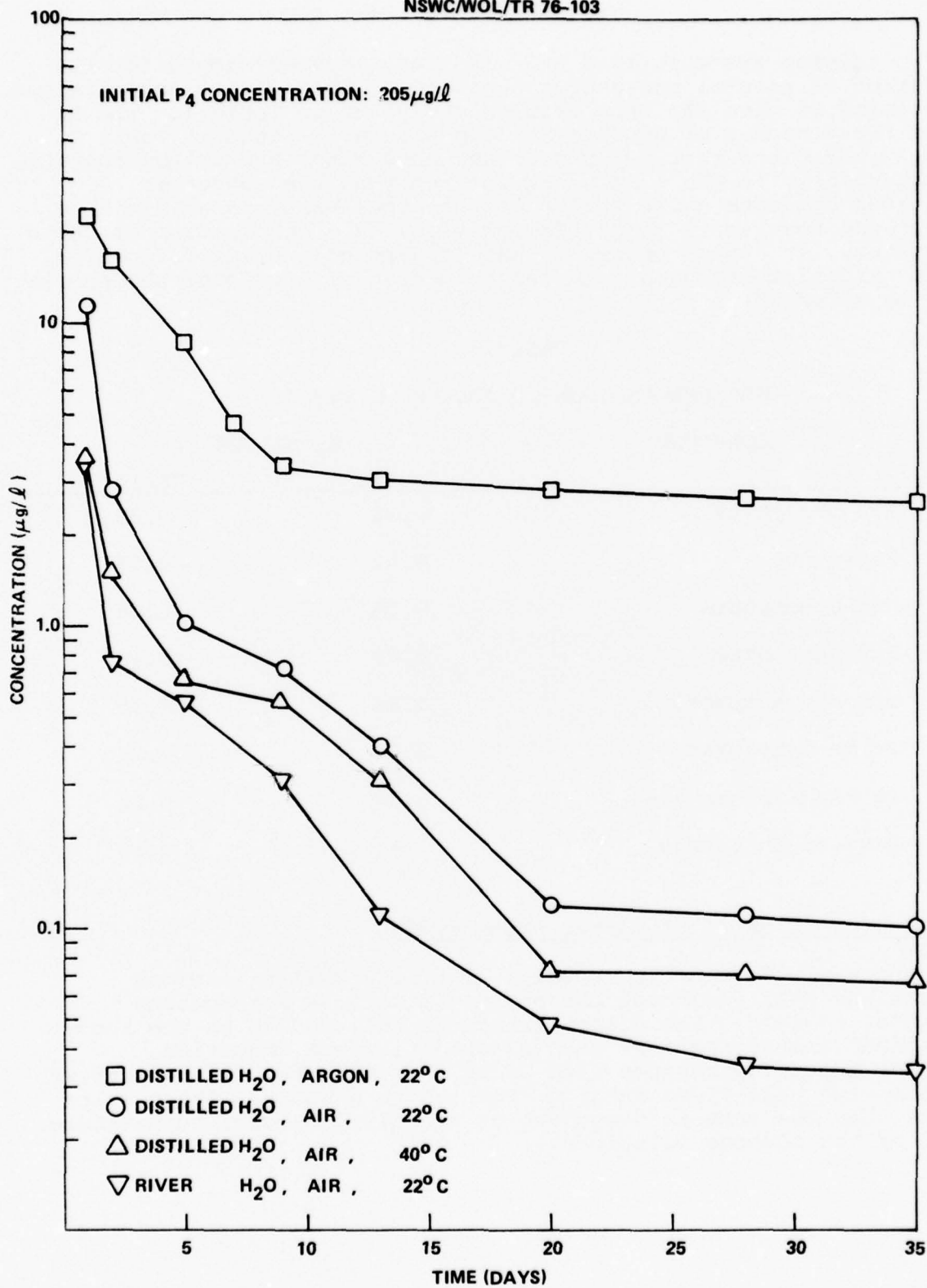
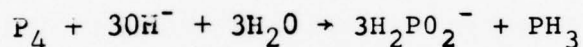
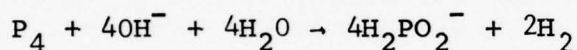


FIG. 2 DECAY OF WHITE PHOSPHORUS IN AQUEOUS SOLUTIONS

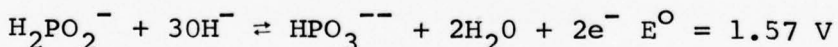
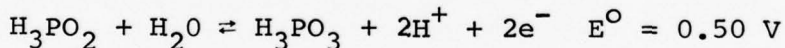
The principles of chemical kinetics predict that higher oxygen concentration and higher temperature should enhance the rate of oxidation. Since the dissolved oxygen contents of the air-purged and the argon-purged solutions were 8.9 and 1.5 mg/l respectively, the rate of oxidation was much lower in the argon-purged solution.

The dissolved oxygen concentration of the aerated solutions at 40°C was 5.9 mg/l, compared to 8.9 mg/l for the aerated solutions at 22°C. However, the latter solution had a lower oxidation rate in spite of a higher dissolved oxygen content. Therefore, it appears that temperature has a predominant effect on the kinetics under the experimental conditions.

The highest disappearance rate for white phosphorus occurs in the aerated river water. The pH of the river water solution at equilibrium was found to be 7.6 compared to 4.2 for the distilled water solutions (both air and argon purged). The higher pH apparently accelerated the loss of elemental phosphorus according to the reactions<sup>10, 11</sup>



It is also possible that the above reaction could be further enhanced by some anions and cations present in the river water because of the strong reducing property of the hypophosphorous acid and its salts. This is indicated by the standard potentials for the reactions represented by the following half reactions:



Under the conditions in the experiments, the disappearance rate decreased monotonically with time, and the white phosphorus concentrations in the solutions approached certain final values, which are listed in Table 4. Significantly, the final white phosphorus content of the argon-purged solution was much higher than that of the aerated solutions.

10. Van Wazer, J. R., Phosphorus and its Compounds, Vol I," Interscience Publishers, Inc., New York, N. Y. (1953)
11. Sneed, M. C., and Brasted, R. C., "Comprehensive Inorganic Chemistry, Vol V," D. Van Nostrand Co., Princeton, N. J. (1956)

TABLE 4

## FINAL CONCENTRATIONS OF WHITE PHOSPHORUS

CONDITIONS	EQUILIBRIUM TIME (DAYS)	CONCENTRATION $\mu\text{g}/\text{l}$
Distilled water, Argon, 22°C	9	2.9
Distilled water, Air, 22°C	20	0.10
Distilled water, Air, 40°C	20	0.06
River water, Air, 22°C	25	0.04

When white phosphorus was first added to water, each mixture contained both suspended and soluble white phosphorus. The concentrations of suspended and soluble white phosphorus were determined from the benzene extractions of the filtered and unfiltered samples. The ratio of soluble to suspended phosphorus was found to be 2.2.

After one day all the suspended white phosphorus had dissolved in the aerated solutions. However, in the argon-purged solution suspended white phosphorus was observable throughout the experiment, even though the initial white phosphorus concentration was below the solubility limit. The concentrations of suspended and soluble white phosphorus in the argon-purged solution at various elapsed times are presented in Fig. 3. After an initial decrease the concentration of suspended white phosphorus remained fairly constant, while the concentration of soluble white phosphorus continued to decrease. It is evident that in a solution of low dissolved oxygen, the oxidation of soluble white phosphorus has the preference over the suspended white phosphorus. Furthermore, the solubility of white phosphorus in water appears to be a function of dissolved oxygen.

### 3. TLC Separation and Identification of Dissolved Reaction Products

The oxidation products of white phosphorus in the aerated distilled water solution (22°C) were separated by the thin-layer chromatographic method previously developed. They were identified by parallel migration of phosphorus standards and located by autoradiography (Figs. 4 and 5).

As shown by Fig. 4, essentially one spot is observed on the autoradiogram developed in the acid solvent system for the sample with an elapsed time of two days. The possible oxidation products are  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$ , which have almost the same  $R_f$  values in the acid solvent system. However, the autoradiogram developed in the alkaline solvent system reveals that  $\text{H}_3\text{PO}_2$  and  $\text{H}_3\text{PO}_3$  are

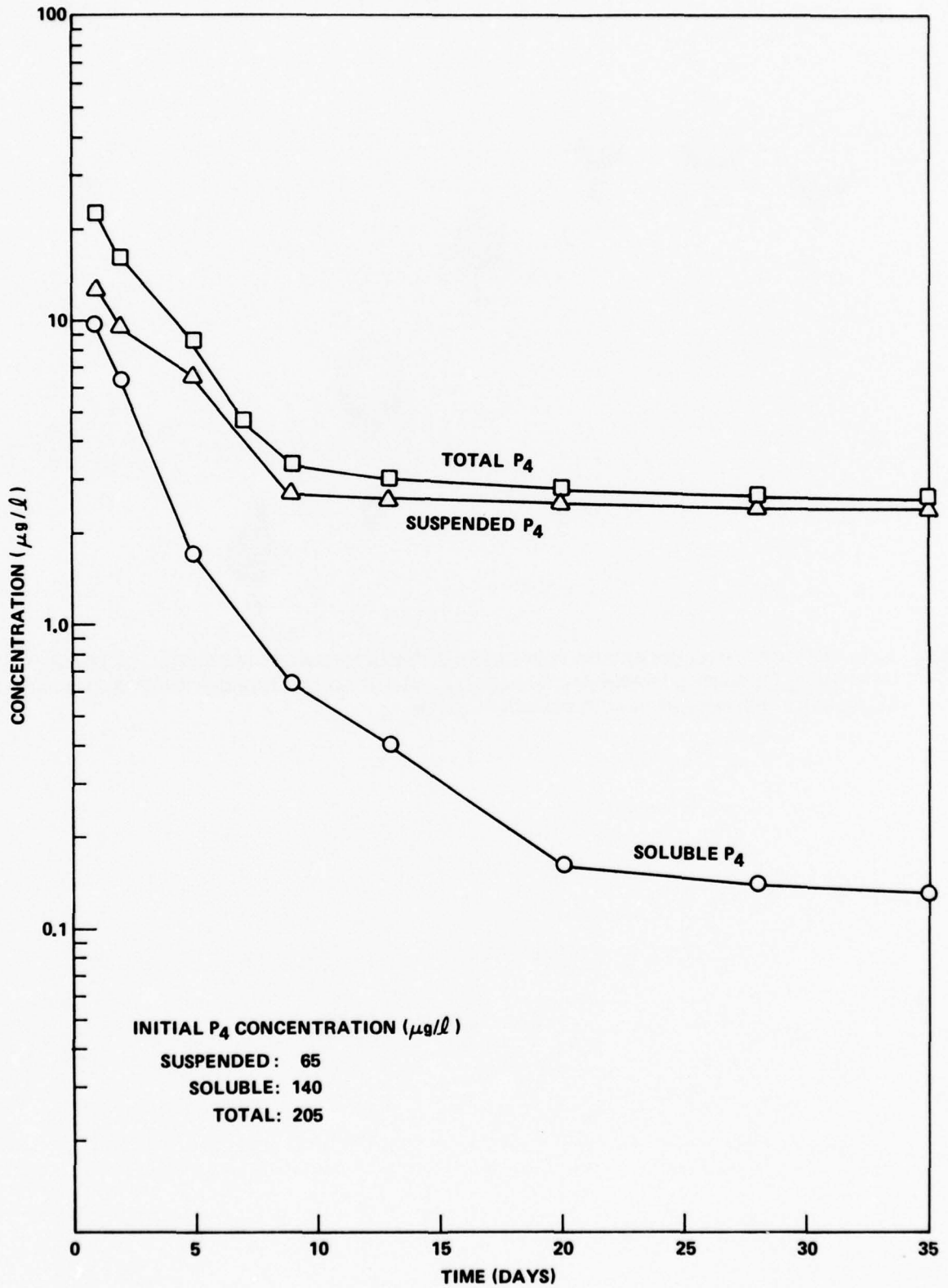


FIG. 3 DECAY OF WHITE PHOSPHORUS IN ARGON PURGED SOLUTION

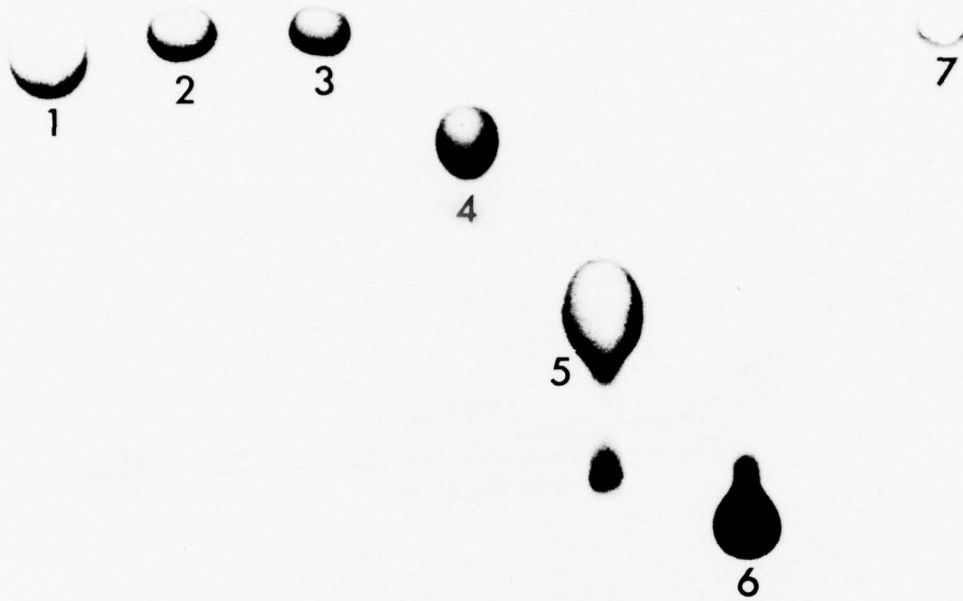


FIG. 4 AUTORADIOGRAPH ILLUSTRATING THIN-LAYER CHROMATOGRAPHIC MIGRATION OF (1)  $\text{NaH}_2\text{PO}_2$ , (2)  $\text{Na}_2\text{HPO}_3$ , (3)  $\text{KH}_2\text{PO}_4$ , (4)  $\text{Na}_4\text{P}_2\text{O}_7$ , (5)  $\text{Na}_5\text{P}_3\text{O}_{10}$ , (6)  $(\text{NaPO}_3)_6$ , (7) ONE-DAY SAMPLE OF AQUEOUS ELEMENTAL PHOSPHORUS IN ACID SOLVENT SYSTEM.

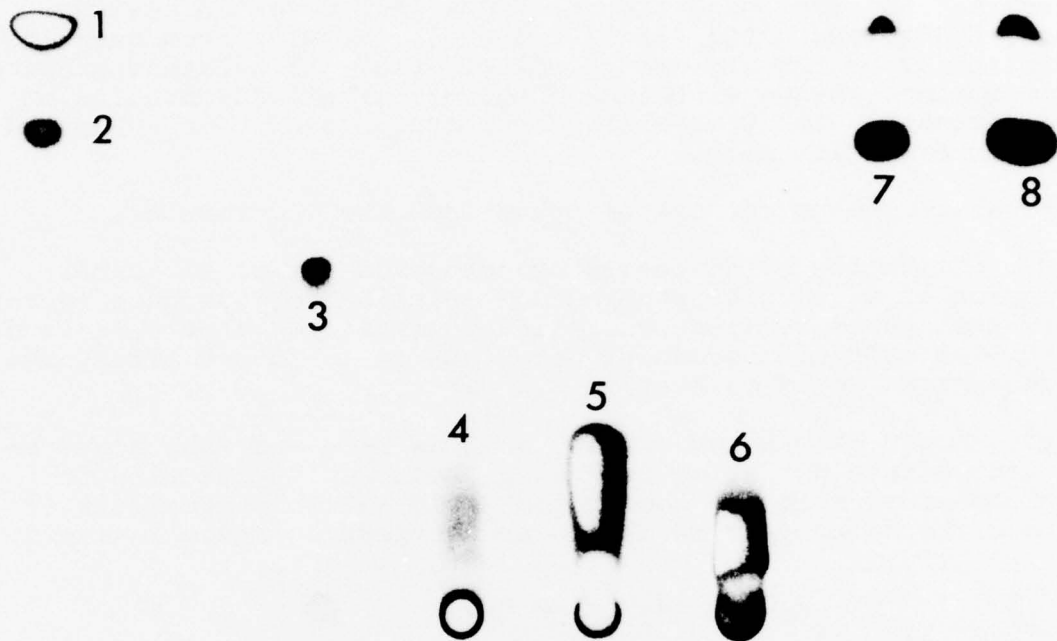


FIG. 5 AUTORADIOGRAPH ILLUSTRATING THIN-LAYER CHROMATOGRAPHIC MIGRATION OF (1)  $\text{NaH}_2\text{PO}_2$ , (2)  $\text{Na}_2\text{HPO}_3$ , (3)  $\text{KH}_2\text{PO}_4$ , (4)  $\text{Na}_4\text{P}_2\text{O}_7$ , (5)  $\text{Na}_5\text{P}_3\text{O}_{10}$ , (6)  $(\text{NaPO}_3)_6$ , (7) AND (8) ONE-DAY SAMPLES OF AQUEOUS ELEMENTAL PHOSPHORUS IN ALKALINE SOLVENT SYSTEM.

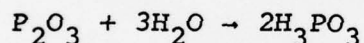
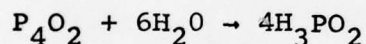
the predominant components and very little  $H_3PO_4$  is present (Fig. 5).

Thin-layer chromatography was repeated on the solution at various intervals. No other oxidation products were observed besides  $H_2PO_2$ ,  $H_3PO_3$ , and  $H_3PO_4$  (Figs. 6 and 7). Results from quantitative determination of the TLC spots indicate that the relative amounts of each component change with time (Fig. 8). The concentration of  $H_3PO_4$  increases with time while concentrations of both  $H_3PO_2$  and  $H_3PO_3$  decrease with time.

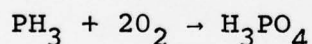
Several conclusions can be drawn from the TLC results:

(1) Oxidation by dissolved or contacted air of elemental phosphorus in aqueous suspension and solution to phosphate is not a single-step process, since the evidence indicates that  $P_2O_5$  is not the initial oxidation product. Were  $P_2O_5$  to be formed first, the polyphosphates would be seen in abundance.

(2) Lower phosphorus oxides, such as  $P_4O_2$  and  $P_2O_3$  might be the intermediate oxidation products; these could give rise to hypophosphorous acid and phosphorous acid through hydrolysis,<sup>12</sup> provided the hydrolysis of the lower phosphorus oxides is rapid.



(3) Orthophosphoric acid is formed through the oxidation of hypophosphorous acid and phosphorous acid. The reactions are relatively slow. It is also possible that part of the orthophosphoric acid is formed by the oxidation of phosphine which is produced during the oxidation of elemental phosphorus.



(4) No significant quantities of condensed phosphates - polyphosphates or cyclic phosphates were detected in the solutions during the investigation. This, again, indicates the absence of  $P_2O_5$ , which on hydrolysis is believed to undergo conversion to the cyclic phosphates and then to small fragments.<sup>13</sup>

12. Meyer, R. J., and Pietsch, E. G.E., "Gmelins Handbuch Der Anorganischen Chemie, Phosphor, System-Number 16, Teil C," Eighth Completely Revised Edition, Verlag Chemis GMBH, Weinheim, Germany (1965)
13. Rosenblatt, D. H., Small, M.J., and Barkley, J.J., "Munitions Production Products of Potential Concern as Waterborne Pollutants - Phase 1," Edgewood Arsenal, USAMEERU Rpt. No. 37-07, June 1973

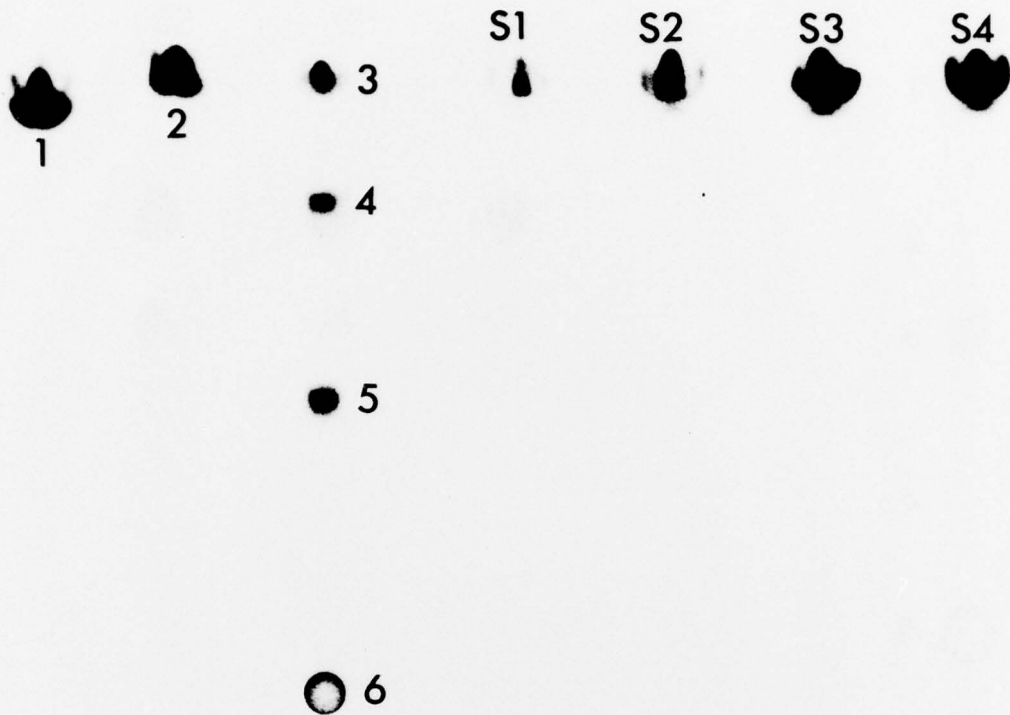


FIG. 6 AUTORADIOGRAPH OF CHROMATOGRAM SHOWING MIGRATION OF AQUEOUS ELEMENTAL PHOSPHORUS SAMPLES OF VARIOUS ELAPSED TIMES IN ACID SOLVENT SYSTEM COMPARED TO PHOSPHORUS STANDARDS.

(1)  $\text{NaH}_2\text{PO}_2$ , (2)  $\text{Na}_2\text{HPO}_3$ , (3)  $\text{KH}_2\text{PO}_4$ , (4)  $\text{Na}_4\text{P}_2\text{O}_7$ , (5)  $\text{Na}_5\text{P}_3\text{O}_{10}$ , (6)  $(\text{NaPO}_3)_6$ , (S1) 2 DAYS, (S2) 6 DAYS, (S3) 12 DAYS, (S4) 20 DAYS.

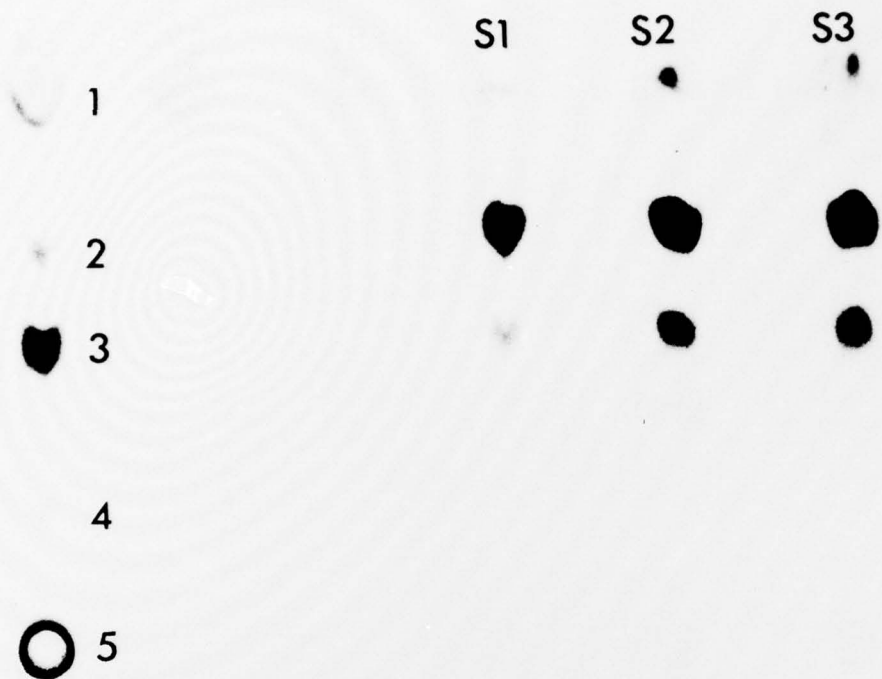


FIG. 7 AUTORADIOGRAPH OF CHROMATOGRAM SHOWING MIGRATION OF AQUEOUS ELEMENTAL PHOSPHORUS SAMPLES OF VARIOUS ELAPSED TIMES IN ALKALINE SOLVENT SYSTEM COMPARED TO PHOSPHORUS STANDARDS.

(1)  $\text{NaH}_2\text{PO}_2$ , (2)  $\text{Na}_2\text{HPO}_3$ , (3)  $\text{KH}_2\text{PO}_4$ , (4)  $\text{Na}_4\text{P}_2\text{O}_7$ , (5)  $(\text{NaPO}_3)_6$ , (S1) 6 DAYS (S2) 12 DAYS (S3) 20 DAYS.

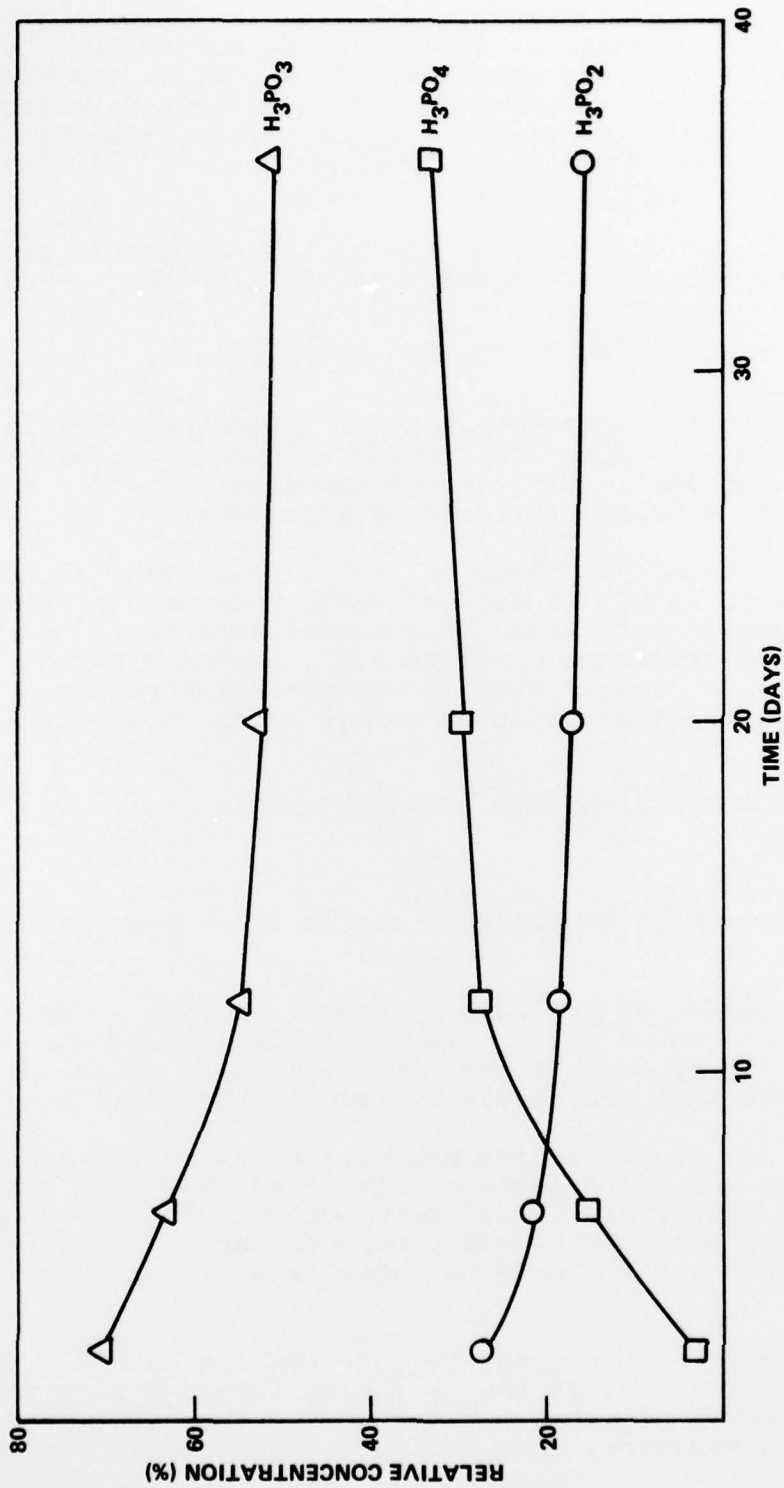
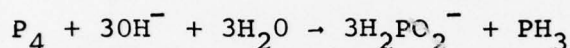


FIG. 8 DISTRIBUTION OF OXIDATION PRODUCTS OF WHITE PHOSPHORUS

#### 4. Phosphine Release

The quantity of phosphine released during the oxidation of aqueous elemental phosphorus was determined by collecting the gas with a tube containing silica gel impregnated with silver nitrate and subsequently counting the absorbed activity in a beta counter. The results are presented in Fig. 9. Under the experimental conditions, the release of phosphine is rapid; 80 to 90% of total phosphine release is reached within two days.

The river water solution, which has higher pH, should produce larger quantity of phosphine according to the reaction



However, the results indicate that more phosphine was collected in the argon purged solution. This could be due to the higher dissolved oxygen content in the aerated river water, which might oxidize the phosphine before it could be released.

The amounts of total phosphine collected range from 77 to 112  $\mu$ g, which are equivalent to 6.0 to 8.8% of white phosphorus initially present in the aqueous solutions. The actual amounts of phosphine released during the oxidation of elemental phosphorus cannot be accurately determined because part of the phosphine produced could undergo conversion to other products before escaping from the solutions.

### CONCLUSIONS AND RECOMMENDATIONS

#### 1. Conclusions

The following general conclusions can be drawn from the results presented in this report:

(1) Both suspended and soluble elemental phosphorus deteriorate rapidly in aerated aqueous media. The concentration of elemental phosphorus after twenty days is less than 0.1  $\mu$ g/l, which represents a reduction of more than two thousand times the original amount.

(2) The initial decomposition products of elemental phosphorus in aerated aqueous solutions include only lower oxidation states of phosphorus. The oxides are immediately converted to hypophosphorous acid, phosphorous acid, and phosphoric acid. These products are considered much less toxic to the aquatic organism than white phosphorus.

(3) Phosphine is a toxic gas (NPC 0.3 PPM for humans) with a low water solubility. Most of the phosphine formed during the oxidation of elemental phosphorus escapes from the solution and disperses in the atmosphere. The residual phosphine in the solution

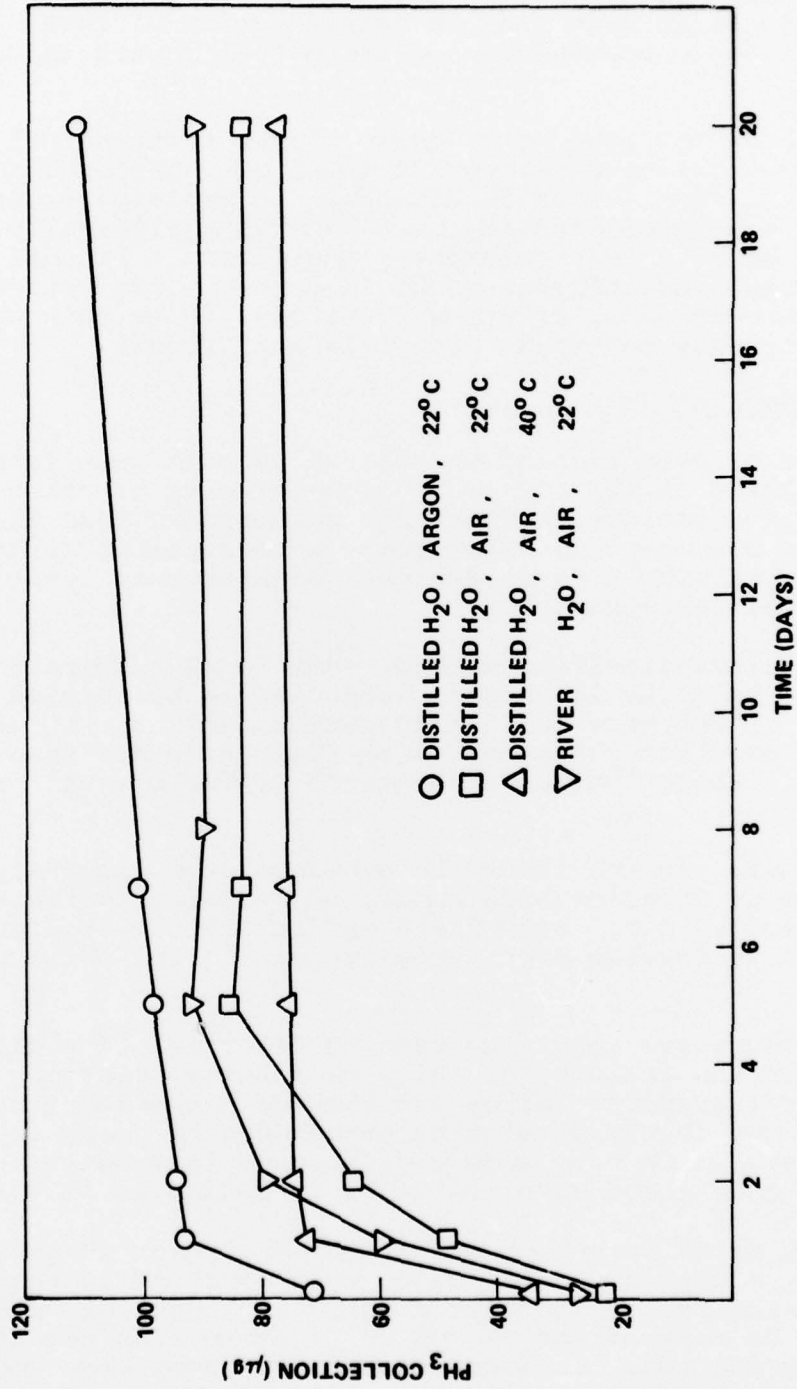


FIG. 9 PHOSPHINE RELEASE

can be further degraded by oxidation. Therefore, the amount of soluble phosphine in "phossy water" is expected to be extremely small.

(4) The appearance of a 6-9% yield of phosphine indicates that phosphine release is important in consideration of mass balance and may have a hitherto unsuspected environmental impact in current operations.

(5) Each of the phosphorus decay curves flattens out at some point to give a relatively constant level of phosphorus for a period of at least ten days. This is difficult to explain unless one postulates a low-level impurity that behaves analytically (but not kinetically) as if it were elemental phosphorus. If this is so, low-level phosphorus analyses might lead to concern over the presence of a toxic concentration of white phosphorus in certain water samples when, in fact, only non-toxic materials are present.

## 2. Recommendations

The limit of detection of phosphorus in this work is about 0.05  $\mu\text{g}/\text{l}$ . Based on the extremely high toxicity of white phosphorus to the aquatic organisms, a discharge standard of less than 0.01  $\mu\text{g}/\text{l}$  has been recommended. Therefore, an analytical method for the determination of elemental phosphorus, sensitive at least to that level should be developed.

With the ultra-sensitive method, additional examinations of white phosphorus decay in aerated water should be carried out, particularly in the very low concentration regions. In addition, interactions of white phosphorus with lake sediments should be investigated. These include adsorption, diffusion, and biodegradation.

Actual field samples should be examined, and the analyses of these samples by other methods should be compared to the analyses by the proposed method. Both field and laboratory studies should be undertaken to develop procedures for monitoring white phosphorus in water.

Aquatic bioassays should be used to determine if a difference exists between the toxicity of white phosphorus solutions near the threshold level prepared (a) by dilution of high-concentration preparations and (b) by permitting phosphorus to decay in water to a constant level. In case such a difference is demonstrated, the chemistry of this phenomenon should be investigated in detail.

The decay of white phosphorus in water at high pH should be investigated, along lines similar to those pursued in the present work. A possibility exists that high-pH treatment of "phossy water" would be more effective for white phosphorus removal than aeration or ozonation. In such a treatment, provision would have to be made for absorption and destruction of the considerable amounts of phosphine that would be evolved.

In the event that treated "phossy water" is discharged into the environment, it will be necessary to investigate the environmental hazard posed by hypophospite and phosphite ions. In addition, the release of phosphine from "phossy water" operations should be examined carefully for its environmental impact.

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