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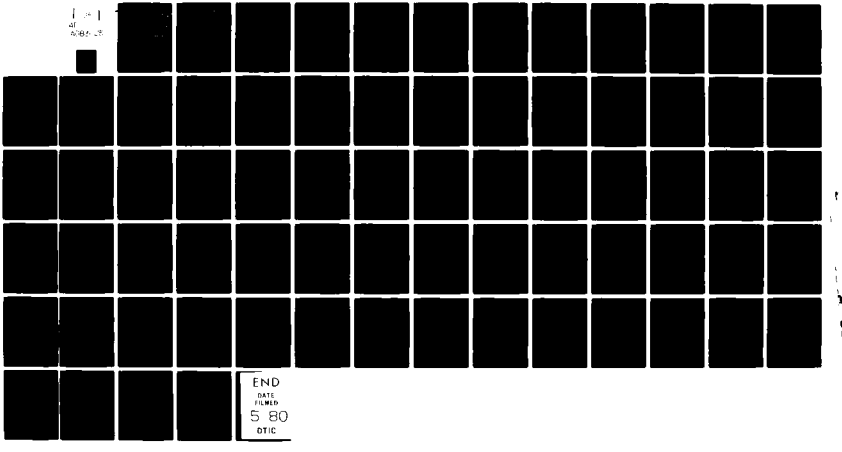

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A SUMMARY AND EVALUATION OF AQUATIC ENVIRONMENTAL DATA IN RELATION TO ESTABLISHING WATER QUALITY CRITERIA FOR MUNITIONS-UNIQUE COMPOUNDS

PART 3: WHITE PHOSPHORUS

FINAL REPORT

12

J.H. SULLIVAN, JR., H.D. PUTNAM, M.A. KEIRN,
B.C. PRUITT, JR., J.C. NICHOLS, AND J.T. McCLAVE

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The purpose of this report is to review the effects of white phosphorus (WP) on the aquatic environment and to recommend water quality criteria for the protection of aquatic organisms.

Chemical properties, analytical methods, manufacturing wastewater characteristics, and environmental fate of WP are reviewed and discussed.

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20. Abstract

Four freshwater algae were exposed to WP concentrations ranging from 7 to 670 µg/l. Two procaryotic species, Anabaena flos-aquae and Microcystis aeruginosa, showed a biostimulatory growth response. Conversely, two eucaryotic species, Navicula pelliculosa and Selenastrum capricornutum showed growth inhibition. N. pelliculosa was the more sensitive with significant effects apparent at 20 µg/l. Two marine species, Fucus distichus and Fucus vesticulosus, showed bioconcentration factors of 22X and 23X when exposed to 15 µg/l WP for 48 hours. These two marine algae did not show evidence of toxic effects, however.

Acute toxicity tests on eight species of freshwater invertebrates yielded 48-hour EC50 values ranging from 30 to >560 µg/l. Limited data on two marine species indicated they were no more sensitive than the freshwater forms ested.

Fish appear to be the most sensitive aquatic organisms to WP. Considering acute toxicity results for both freshwater and marine species, 96-hour LC50 values range from 2 to 154 µg/l. Many values were less than 10 µg/l. Longer term exposure showed LC50 of LT50 values less than 1 µg/l. Complete life-cycle tests using fathead minnows showed adverse effects at 0.4 µg/l, the lowest concentration tested. Projections based on linear regression techniques indicate a no-effect concentration of about 0.1 µg/l.

The fish data indicate a sensitivity to both time of exposure and concentration of WP. As time of exposure increases lower concentrations of WP produce adverse effects, suggesting that bioaccumulation is occurring. Measured bioaccumulation factors range from 12 to 58,000. Many values are in the 50 to 200 range. Atlantic cod had by far the highest bioaccumulation factor (several values >1000) possibly due to high tissue lipid levels characteristic of this species.

Three procedures were utilized in an attempt to determine a recommended water quality criteria for WP; 1) a new proposed procedure by EPA, 2) acute toxicity values multiplied by a general application factor, and 3) acute toxicity values multiplied by an experimentally derived application factor. The fact that a no-effect concentration was not determined in the chronic studies dictates that no criteria can be established using the new proposed EPA procedure. Further, without a known no-effect level an application factor cannot be experimentally determined. The lowest acute toxicity value multiplied by a "conservative" general application of 0.01 gives a value of 0.02 µg/l.

It is concluded that insufficient data exists to recommend final criteria for WP. However, available data indicate that a level equal to or less than 0.01 µg/l of WP should adequately protect aquatic organisms.

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A SUMMARY AND EVALUATION OF AQUATIC ENVIRONMENTAL DATA IN RELATION TO ESTABLISHING WATER QUALITY CRITERIA FOR MUNITIONS-UNIQUE COMPOUNDS

PART 3: WHITE PHOSPHORUS

FINAL REPORT

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I. Introduction

Since the early part of the 1970's the U.S. Army Medical Research and Development Command has been supporting research to determine the environmental hazards associated with waste discharges of its munitions industry. The objective of these studies has been to formulate the data base required for water quality criteria for munitions unique compounds by examining effects on mammalian and aquatic species and communities. The data base for the target compounds has been under periodic review to determine the necessary requirements for final water quality criteria. The development of water quality criteria is authorized by the Federal Water Pollution Control Act, as amended by the Clean Water Act of 1977 (Public Law 92-500).

The purpose of this report is to review the effects of white phosphorus (WP) on the aquatic environment and to recommend water quality criteria for the protection of aquatic organisms. White phosphorus is purchased by the Army from commercial sources, shipped to Pine Bluff Arsenal, Arkansas, and loaded on an intermittent basis as a component of incendiary and smoke generating weapons and warheads. It is shipped by rail in a molten state, transferred, and handled under a blanket of warm water.

White or yellow phosphorus constitutes the primary product in the refining of phosphate rock via the electric reduction process. In this process, elemental phosphorus vapor is condensed and collected under water. Water used in the storage and transfer of solid and liquid white phosphorus is known as "phossy water" and contains significant quantities of colloidal and larger sized WP particles along with dissolved elemental phosphorus. High concentrations of orthophosphate and other phosphorus oxides are present. Significant concentrations of fluoride, ammonia, silicates, and cyanide may also result from the commercial preparation.

White phosphorus is a substance of environmental concern since it is a potent poison (Burrows and Dacre 1974). It has been used in the past to make matches and pesticides, however usage has been virtually discontinued due to its extreme toxicity. In the aquatic environment phossy water has been shown to cause massive fish kills in marine environments (Jangaard 1972) and to create significant impacts on lacustrine systems (Pearson et al. 1976). Laboratory studies have shown that WP is highly toxic to fish. Incipient LC50s may be less than 1 µg/l WP and are significantly lower than acute 96-hour values. Such data indicate that the substance is a cumulative poison.

The existing data base includes studies of the chemical behavior of white phosphorus in water; invertebrate, algal, and fish bioassays; the effects of WP on tissue; the mechanism and extent of bioconcentration; as well as the response of a marine and a freshwater aquatic community to discharges of phossy water. The recommended acute and chronic safe levels for water were developed from this existing data base using the guidelines of the American Public Health Association (APHA) (1975), National Academy of Sciences (1973), and Environmental Protection Agency (EPA) (1976 and 1978) methodology. The latter documents contain the existing and proposed strategy necessary to provide application factors for predicting environmentally safe levels based on laboratory bioassays.

II. Chemical and Physical Properties

Phosphorus, atomic weight 30.974, can have valences of 0 (elemental phosphorus), +1, +3, +4, and +5. The most common form in nature is phosphate, PO_4^{-3}, where sp^3 hybrid orbitals of P^{+5} phosphorus are bonded to oxygen in a tetrahedryl configuration. Phosphorus as phosphate is essential to life as virtually all reactions in the living cell involve energy exchange via the bond energy of adenosine triphosphate. Biogeochemically, phosphorus, abundance 0.12 percent, is usually the macronutrient limiting to ecosystem production since it becomes bound in sediments as phosphate rock or apatites, $Ca(OH)_2 \cdot 3Ca(PO_4)_2$, $CaCl_2 \cdot 3Ca(PO_4)_2$, or $CaF_2 \cdot 3Ca(PO_4)_2$. The major commercial source of phosphorus is phosphate rock mined from marine sediment deposits (Halmann 1972).

Elemental phosphorus does not occur naturally in the biosphere and is manufactured by reducing phosphate rock with coke in an electric furnace to produce gaseous elemental phosphorus. This material is condensed and collected under water and forms the base for most refined commercial phosphorus and phosphate products. Existing in three allotropic forms -- white, red and black -- elemental phosphorus is comprised of atoms bonded in different arrangements. Commercially prepared elemental phosphorus made by the reduction of apatite is white phosphorus; white and red phosphorus are the commercially important forms. Since this material is extremely reactive and toxic, much of it is converted to the red form by heating at 240°C. Red phosphorus is much less reactive, relatively non-toxic, and therefore easier to handle. Yellow phosphorus is white phosphorus containing small amounts of the other allotropes (Corbridge 1966).

White phosphorus is a waxy white translucent solid which darkens with exposure to light. It is extremely reactive and ignites spontaneously in air to form phosphorus oxides. Complete combustion of elemental phosphorus results in the formation of phosphorus pentoxide. White phosphorus is a tetramer of phosphorus atoms with P-P bond lengths of 2.21 ± 0.02 angstroms and bond angles of 60°. Above 800°C, P_4 dissociates to form dimolecular P_2. The structure of white phosphorus is that of a regular tetrahedron with a phosphorus atom at each corner. The red allomer and the less common black form differ in molecular structure from white phosphorus. These allomers consist of long polymerized chains of phosphorus atoms and are much less reactive. The white or tetrahedral form of elemental phosphorus owes much of its reactivity to the fact that it maintains its discrete tetrahedral structure in the solid, liquid, and gaseous phases (Corbridge 1966). Bonding of the four phosphorus atoms in a tetrahedral configuration with bond angles of 60° involves extreme bond strain. Corbridge (1966) has suggested that these bonds are pd_2 hybrids. Solid white phosphorus exists as a cubic crystal made up of 56 tetrameric units at temperatures below the melting point, 44.1°C (Toy 1973). The auto-ignition temperature is 34°C. It is extremely soluble in carbon disulfide and non-polar organic solvents such as benzene and nearly insoluble in water but tends to form colloidal dispersions. The general chemical and physical properties of white phosphorus are summarized in Table 1.

Although white phosphorus has low solubility in water, its behavior in aqueous solutions is important since severe impact occurs in aquatic systems at elemental phosphorus concentrations well below the solubility

TABLE 1

GENERAL CHEMICAL AND PHYSICAL PROPERTIES OF WHITE PHOSPHORUS

CAS No.		7723-14-0
Empirical formula		P_4
Color		White, tinged yellow
Molecular structure		Tetrahedral
Form		Waxy translucent solid
Molecular weight		123.90
Crystal structure		Cubic crystals made up of 56 discrete tetramers at temperatures above -77°C. Hexagonal at lower temperatures.
Density		1.82
Hardness		0.5
Melting point		44.1°C
Boiling point		280°C
Auto-ignition temperature (air)		34°C
Specific heat		1.8 cal/g
Solubility:	H_2O	3 mg/l at 15°C
	Ethanol	2.5 g/l
	Ether	9.8 g/l
	Chloroform	25 g/l
	Benzene	28.6 g/l
	Carbon disulfide	1250 g/l

References: Corbridge 1966; Hawley 1977; Toy 1973; Van Waser 1958; Weast 1970; and Windholz et al. 1976.

limit. White phosphorus enters the aquatic environment as phossy water which contains dissolved and colloidal WP as well as larger suspended particles of the material. Phossy water is generated wherever white phosphorus is manufactured or stored under water. Table 2 shows typical concentrations of phosphorus forms in phossy water generated from the manufacture of white phosphorus and also from the loading of incendiary munitions. These data suggest that much of the WP in phossy water is dispersed or colloidal rather than dissolved. The resulting mixture of colloidal and dissolved WP reacts with dissolved oxygen and hydroxide ion to form various phosphorus oxides and acids as well as phosphine, PH_3 (Addison 1971; Lai and Rosenblatt 1977A; and Blumbergs et al. 1973). When elemental phosphorus is present in high concentration as a suspension it results in low to zero dissolved oxygen in water (Pearson et al. 1976, Blumbergs et al. 1973). Unreacted white phosphorus particles settle out and can be incorporated into aquatic sediments. The reactions of WP in water are the kinetics of oxidation of elemental phosphorus at low concentrations. Elemental phosphorus particles buried in anoxic sediments are stable for long periods of time (Ackman et al. 1971, Pearson et al. 1976). In the presence of dissolved oxygen however, WP concentrations decrease rapidly tc low levels (Campbell 1977, Lai and Rosenblatt 1977A). Very low concentrations persist for extended periods of time (see below). The problem of detection and analysis of the minute quantities of this highly labile material have lead to disparities in the results of various investigations. Thus data on the kinetics and decomposition products of white phosphorus in water are poorly defined. Reaction kinetics have been reported on both phossy water from WP manufacture or munitions loading (Bullock and Newlands 1969, Zitko et al. 1970, Campbell 1977, and Blumbergs et al. 1973) and on prepared solutions of WP in water (Lai and Rosenblatt 1977A, Addison 1971, Zitko et al. 1970).

Reported rates of oxidation for WP in water vary greatly and depend on pH, dissolved oxygen content, temperature, metal ions, and on the degree of dispersion of colloidal or suspended WP if the solubility is exceeded. Estimates of the half-life of WP in aerated water range from 0.85 hours at 30°C for a 1 ppm initial concentration in distilled water (Addison 1971) to ten days or greater (Zitko et al. 1970, Bullock and Newlands 1969, and Kimerle and Brautigam*) for suspensions at higher concentrations or for WP in the presence of iron. Disappearance rates for WP in terms of half-lives reported in the literature or calculated from other kinetic data are given in Table 3. One major factor controlling the rate of disappearance of WP apparently is whether it is suspended or dissolved. Lai and Rosenblatt (1977A) showed that soluble WP was removed about five times more rapidly than suspended WP from a mixture of 65 µg/l suspended WP and 140 µg/l soluble WP. At concentrations below the solubility limit, and in situations where a majority of the material is dissolved, WP initially decomposes in aerated water via a first order reaction (Lai and Rosenblatt 1977A, Bullock and Newlands 1969) to concentrations below 0.01 ppm. Decomposition to equilibrium levels of 0.04 to 0.10 ppb proceeds slowly thereafter. Lai and Rosenblatt (1977A) reported these equilibrium concentrations remaining from a 205 µg/l suspension after 20 to 25 days in aerated water. The work of Zitko et al. (1970) also suggests that the disappearance of WP, initially, follows first order kinetics. Preliminary results from Monsanto, Inc. (Kimerle and Brautigam 1978), however, suggest that WP at low concentrations decomposes to below 0.01 ppb rapidly. The latter authors did not observe a

* Personal communication. Kimerle, R.A. and G. Brautigam. Monsanto, Inc. 1978.

TABLE 2

TYPICAL PHOSPHORUS COMPOSITION OF "PHOSSY WATER"

Source	Total Phosphorus ppm as P	P_4 ppm as P_4	Orthophosphate ppm as P	PO_x ppm
ERCO Typical Wastewater[a] (Idler 1969)	18	13	NR[b]	NR
ERCO Ponds, 1970-71 (Addison et al. 1971)	NR	0.0012-0.265	NR	NR
Pine Bluff Arsenal Wastewater (Blumbergs et al. 1973)	450	14-37	243	208 as P
Pine Bluff Arsenal Wastewater (Pearson et al. 1976)				
23 April - 30 Dec. 1971	68.03	6.30	39.37	105.53[c]
3 Jan. - 17 Oct. 1972	53.07	12.61	29.45	72.93[c]

[a]ERCO (Electric Reduction Company of Canada)
Wastewater also contained 245 ppm F^-, 5 ppm NH_3 and 1 ppm CN.

[b]Not reported.

[c]Chemical species not reported.

TABLE 3

DISAPPEARANCE RATE OF WHITE PHOSPHORUS FROM AERATED WATER

Reference	Source and Concentration of P_4 (ppm)	Water Source	Temperature °C	Half-Life (Hours)
Addison (1971)	1.0 ppm[a]	Distilled	30	0.85
Bullock and Newlands (1969)	1-50 ppm[a]	Sea water	30	80
		Sea water	0	240
		Freshwater	30	50
		Freshwater	0	150
Zitko et al. (1970)	0.060 contaminated mud	(Not defined for individual results)	12-13	20
	0.030-0.200 ERCO Phossy Water			7.5
	0.007-0.030[a]			2
	(not given) artificially contaminated mud			240-336
Blumbergs et al. (1973)	0.80 Pine Bluff Arsenal Phossy water	Freshwater	Not given. Room temp. Assumed	Initial 0.12 2nd 16
Campbell (1977)	0.226 Pine Bluff Arsenal Phossy water	Freshwater	27-34	0.67
Lai and Rosenblatt (1977A)	0.205[a]	Distilled & Fresh	22 and 40	3.5-6.0
Kimerle and Brautigam[b]	Not given specifically[a] ≈0.100 to 0.001	Ultrapure	20-25	43
		Ultrapure + 1 ppm Cu		2.4
		Ultrapure + 1 to 10 ppm Fe^{+3}		>700

[a]Artificially generated in laboratory using molten P_4.
[b]Unpublished preliminary data.

plateau in decomposition rate.

The disappearance rate from more concentrated WP suspensions apparently is controlled by diffusion (Bullock and Newlands 1969, Burrows and Dacre 1974) and the protection of WP from oxygen. Zitko et al. (1970), for example, showed more rapid reduction rates for WP concentrations from artificial suspensions of WP than from suspensions of contaminated sediment. Presumably the suspended sediment contained larger particulates and other competing oxygen-demanding materials.

Saline water may influence reaction rate. Bullock and Newlands (1969) reported rates 1.5 times faster in fresh than in salt water. These authors suggest that salts coagulate the colloidal particles and make them less accessible to oxygen.

Lai and Rosenblatt (1977A) showed that in solutions with concentrations well below the solubility maximum, dissolved oxygen exerts a marked effect on disappearance rate of WP. These authors ran a careful study of the kinetics of white phosphorus transformation products in water using thin layer chromatography and autoradiography and concluded that slow decomposition to equilibrium values followed initial first order kinetics. Lai and Rosenblatt (1977A) also showed the decomposition rate of WP was about 10 times slower under an argon-purged solution (dissolved oxygen, ≈ ±1.5 ppm) when compared to an air-purged solution (dissolved oxygen = 5.9-8.9 ppm). These authors postulated that material remaining after the initial rapid decrease may be a phosphorus species which behaves analytically but not kinetically like WP.

Bullock and Newlands (1969) suggest that oxidation kinetics for WP in water may parallel the kinetics of vapor phase reactions where minimum and maximum threshold concentrations exist between which WP reaction rates with oxygen are nearly independent of WP concentration. Above and below the threshold concentrations reaction rates are much lower.

Another possible protection mechanism for WP suspensions could be the formation of an oxide coat which is somewhat resistant to further oxidation. Blumbergs et al. (1973) studied the treatability of phossy water (Pine Bluff Arsenal effluent) and reported that the PO_x fraction was not easily converted to PO_4^{-3} by aeration and that complete conversion only occurred in the presence of a palladium/carbon catalyst.

Preliminary data from Monsanto, Inc.,* suggest that metal ions may have a marked influence on the stability of WP suspended or dissolved in water or in sediments. Their results (Table 3) show that solutions of WP are very rapidly degraded in the presence of copper ions at 1 ppm, but that similar concentrations of iron extend the half-life of WP by an order of magnitude. Such data suggest that some metals catalyze the oxidation while others may form complexes which lower the oxidation rate. In aquatic sediments, iron is prevalent and may combine with WP at the surface of particles to provide a passive ferrophosphorus coating that is resistant to oxidation. Such a phenomenon may also act to render the surface of suspended, colloidal WP particles passive.

*Personal communication. Kimerle, R.A. and G. Brautigam, Monsanto Inc., 1978.

The effects of pH and temperature on reaction rates are much less significant than the effects of WP phase (dissolved or suspended) and dissolved oxygen concentrations. Higher pH increased reaction rate in Lai and Rosenblatt's (1977A) study, as did increased temperature. These authors postulated that additional OH^- ions present at high pH favored direct reaction of WP to form hypophosphorous acid, H_3PO_2, or phosphine, PH_3.

Oxidizing agents other than oxygen (Cl_2 and O_3) are capable of removing WP from water (Campbell 1977, Blumbergs et al. 1973). Oxidation by these compounds could form the basis of wastewater treatment to meet water quality criteria or effluent standards for white phosphorus. Blumbergs et al. (1973) stated that federal regulations limited discharge of WP to the Arkansas River to 0.01 ppm. Aeration alone did not reduce WP to less than 0.01 ppm, but Blumbergs et al. (1973) reported that chlorination of the aerated effluent could reduce WP concentrations below this value. Campbell (1977) studied oxidation of suspensions of WP at Pine Bluff Arsenal phossy water and reported 90 percent reduction of WP concentrations in 2 hours by aeration (226 ppb WP was reduced to 21 ppb). Ozone, however, was capable of reducing 250-350 ppb WP to less than 5 ppb (the reported detection limit) within this same time period. Neither of these studies addressed the treatability of higher concentrations of phossy water. Pine Bluff's effluent typically has contained up to two orders of magnitude higher concentrations (Table 2 and Pearson et al. 1976).

The transformation products resulting from the decomposition of white phosphorus in water have been studied by Addison (1971), and Lai and Rosenblatt (1977A) with somewhat conflicting results. When white phosphorus is burned in air, complete combustion results in the formation of phosphorus pentoxide. This material reacts violently with water to form linear and cyclic polyphosphates (Van Waser 1958, Lai and Rosenblatt 1977A). In aqueous solution, WP may oxidize in a single step, or react stepwise to form several phosphorus oxides which are ultimately converted to phosphate as phosphoric acid. Possible intermediate compounds between WP and PO_4^{-3} are as follows:

Hypophosphite	Trimetaphosphate
Hydrophosphite	Tetrametaphosphate
Phosphite	Hexametaphosphate
Pyrophosphate	Phosphine
Tripolyphosphate	

Addison (1971) postulated that at low concentrations (1 ppm) elemental phosphorus is oxidized to phosphate in a single step since no intermediates are isolated by gas chromatography of trimethylsilyl derivatives or by thin layer chromatography. More recent work by Lai and Rosenblatt (1977A) has identified several intermediate oxidation products and defined a breakdown pathway to PO_4^{-3}. In this study, the oxidation products of 205 µg/l ^{32}P white phosphorus in aerated distilled water were separated by thin later chromatography, identified by parallel migration of various phosphorus standards, and located by autoradiography. This work suggested that oxidation of WP in water follows a stepwise path and that P_2O_5 is not a primary oxidation product. The principal products identified were H_3PO_2 (hypophosphorous acid), H_3PO_3 (phosphorous acid), and H_3PO_4 (orthophosphoric acid). Figure 1 shows the

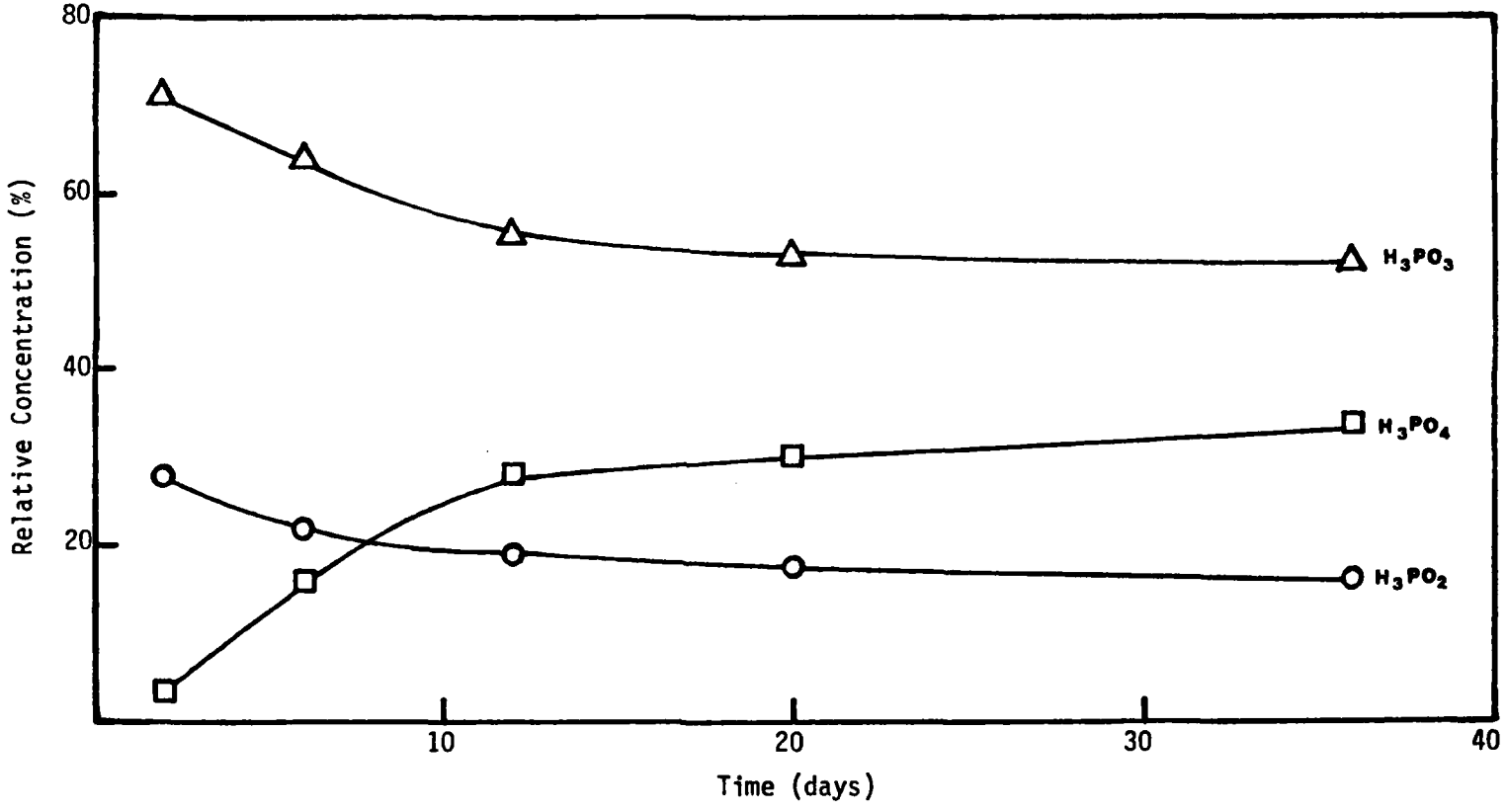


FIGURE 1. DISTRIBUTION OF OXIDATION PRODUCTS OF WHITE PHOSPHORUS.
SOURCE: LAI AND ROSENBLATT (1977A)

temporal changes in the abundance of these three species as the reaction progressed. Apparently a rapid reaction occurs to form the lower oxidation-state oxides of WP which hydrolize to form oxyacids, but complete oxidation to H_3PO_4 is slow. This agrees with the previously cited work of Blumbergs et al. (1973).

Elemental phosphorus can also react to form phosphine PH_3 especially at high pH (Addison 1971, Lai and Rosenblatt 1977A) by the following reaction:

$$P_4 + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3$$

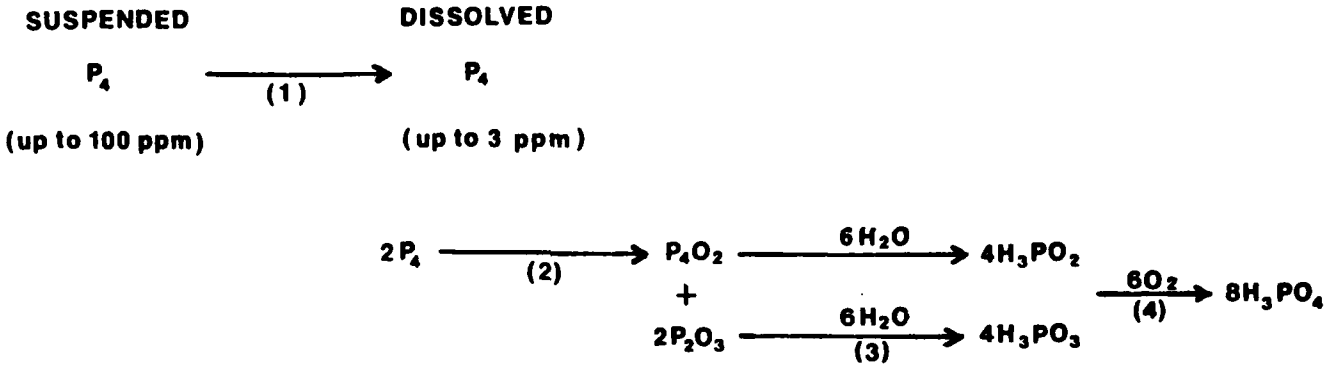
According to Lai and Rosenblatt (1977A) this amounts to 6 to 9 percent of the total reacted WP. These percentages were based on experiments using distilled water, pH 6.1 and river water at pH 7.5. Presumably PH_3 would either be lost to the atmosphere or quickly reacted to higher oxidation states. The amount of PH_3 in phossy water was therefore considered to be extremely small.

In summary the chemical behavior of white phosphorus can be diagramed as shown in Figure 2. The rate-determining step in aquatic systems is usually a diffusion-controlled dissolution of suspended WP to soluble WP. The soluble phosphorus decomposes quickly via first order kinetics to H_3PO_2 and H_3PO_3. Slower reactions transform the P^{+1} and P^{+3} acids into P^{+5} as H_3PO_4.

IIA. Analytical Chemistry for Environmental Monitoring

Classically, white phosphorus has usually been quantified by a three-step procedure: extraction with an organic solvent or steam distillation to separate WP from water soluble phosphorus compounds; oxidation of the extracted WP to PO_4^{-3} using Cl_2, Br_2, I_2, HNO_3 and $KMnO_4$ or other oxidizing agents; followed by colorimetric determination of PO_4^{-3} (Halmann 1972). Under ideal conditions the detection limit by this procedure is 0.01 mg/l (10 µg WP/l). While this technique is adequate for many applications, it is unsuitable for the quantification of WP in the water and sediments of aquatic ecosystems or in biological tissue where organic phosphorus compounds, such as phospholipids may also be extracted and cause positive interferences. Also, bioassay and field data suggest that acute and chronic effects on aquatic biota are significant at concentrations well below 10 µg/l.

In response to the fish kill in Placentia Bay (Jangaard 1972), Addison and Ackman developed a rapid gas chromatographic technique for low level WP detection (Ackman and Addison 1969; Addison and Ackman 1970; and Addison 1971). Analysis of white phosphorus by their technique also requires extraction of the organic soluble phosphorus species from the aqueous phase, usually with benzene or isooctane. This extract is then analyzed by gas-liquid chromatography on a nonpolar column at 100°C followed with detection by means of either a flame photometric detector (FPD) at 526 nm or a modified flame ionization detector (MFID). The choice of analytical conditions isolates a WP peak and eliminates most of the interferences from other phosphorus compounds or hydrocarbons. Detection limits for the gas chromatographic determination of WP are ultimately about 10^{-12} µg WP when a flame photometric detector is used. There is some disagreement among results, however, as to the concentration factor possible using solvent extraction. If the assumption is made that a tenfold concentration



Relative Reaction Rates

(1) Diffusion-controlled pathway. Rate is dependent on particle size, agitation, and other factors.
(2) First order kinetics; k (base e) ≈ 0.1 - 0.7/hour (Table 3) for disappearance of P_4 in distilled water.
(3) Very rapid hydrolysis to oxyacids.
(4) Slow oxidation to phosphate.

FIGURE 2. SUMMARY OF THE MAJOR DEGRADATION PATHWAY FOR WHITE PHOSPHORUS IN WATER.

during extraction is the practical maximum, the detection limit is 0.1 to 0.2 µg/l WP in water. The flame photometric gas chromatographic technique has been used on almost all of the reported environmental analyses of water, sediment, and biological tissue, and for monitoring challenge concentrations in laboratory bioassays.

Gas chromatographic analysis of WP provides a rapid, specific procedure to quantify this material. Bullock and Newlands (1969) considered that a sample can be chromatographed every 5 minutes compared to a time factor of 90 minutes per sample for the classical procedure. The analysis time required for neutron activation was not given. Table 4 summarizes the analytical procedures for WP analysis in the reported ecological and toxicological studies. With the exception of Zitko et al. (1970), all of these studies used techniques similar to those of Addison and Ackman (1969). Some disagreement exists as to the potential detection limits reported by Addison and Ackman (Ackman and Addison 1969; Addison and Ackman 1970), Bentley et al. (1978), Kimerle and Brautigam*, and some of the work of Lai and Rosenblatt (1977B). Lai and Rosenblatt studied the efficiency of extraction versus the water/solvent ratio and found that a 10:1 ratio would extract 95 percent of the WP while a 20:1 ratio would extract only 67 percent of the WP. Bentley et al. (1978) reported greater than 90 percent recovery at a water/solvent ratio of 200:1 for extractions of six solutions ranging in concentration from 0.5 to 7.7 µg/l WP. Bentley et al. (1978) reported a measured 0.005 µg/l concentration in one bioassay experiment. These authors reported their lowest detection limit as 0.0038 µg/l.** Addison and Ackman's procedures called for a 1:1 or 2:1 ratio of water/solvent to obtain 0.1 to 0.2 µg/l WP detection limits. Addison and Ackman reported, however, that a concentration factor of 25 to 50 times could be obtained by evaporation of extracts (Addison and Ackman 1970). Lai and Rosenblatt (1977B) reported that significant losses occurred when benzene extracts were concentrated. Concentration by 50 percent reportedly resulted in a 20 percent WP loss, 90 percent concentration resulted in 50 percent or more WP loss from the extract. Kimerle and Brautigam* consider that the limit of detection by gas-liquid chromatography is 0.01 - 0.05 µg/l. These authors studied the behavior of low concentrations of WP (0.01 - 1.0 µg/l) and found that 100:1 to 200:1 extraction ratios (water/benzene) can quantitatively remove low WP concentrations from water. Their experience also suggests that a ten-fold concentration of the extract under a nitrogen atmosphere is feasible (35 - 50 percent loss is experienced) if suitable controls are run to determine loss rate. They use flame photometric detection and generally employed 1:1 to 10:1 water:solvent ratios followed by concentration of the extract where required. Under "clean room" conditions, this procedure will provide ±20 percent reproducibility at concentrations as low as 0.010 µg/l WP in laboratory-prepared solutions. These investigators indicate that in environmental monitoring, routine analyses have a detection limit of 0.05 µg/l WP for water samples and a 7.5 to 10 µg/kg WP for tissue and sediment samples.

The kinetic data in the previous section showed that concentrations of WP in the presence of oxygen are extremely unstable. However, extracted material is indefinitely stable in organic extracts (Bentley et al. 1978; Addison 1971; and Lai and Rosenblatt 1977B). Environmental and tissue samples are therefore stabilized by immediate extraction (Pearson et al.

*Personal communication. Kimerle, R.A. and G. Brautigam, Monsanto, Inc. 1978.

**Personal communication. Bentley, R.E. 1978.

TABLE 4

SUMMARY OF ANALYTICAL METHODOLOGY USED FOR DETERMINATION OF P_4 IN ENVIRONMENTAL SAMPLES AND AQUATIC TOXICOLOGY STUDIES

Authors	Purpose		Detection Limit or Lowest Conc. Measured (ppb)
	Environmental Monitoring		
Long Harbour Placentia Bay Monitoring			
Ackman et al. 1970	Accumulation in tissue	GLC/FPD[a]	1
Ackman et al. 1971	Sediment concentration	GLC/FPD	2
Addison et al. 1971	H_2O concentration	GLC/FPD	0.1
Addison et al. 1972	H_2O, effluent & sediment concentration	GLC/FPD	0.1 (H_2O) 2 (sediment)
Yellow Lake - Pine Bluff Arsenal Input			
Pearson et al. 1976	H_2O, sediment and fish tissue concentration	GLC/FPD	0.02
Monsanto - Environmental Monitoring			
Kimerle & Brautigam[b]	Toxicology, kinetics, environmental monitor	GLC/FPD	0.01-0.05
	Toxicological Studies		
Pearson et al. 1978	Acute fish bioassay	GLC/FPD	0.5
Bentley et al. 1977	Bioassay and bioaccumulation	GLC/MFID	0.005 (H_2O) 7.5 (tissue)
Maddock & Taylor 1976	Acute fish bioassay; bioaccumulation	GLC/FPD	0.25
Dyer et al. 1970	Bioassay, tissue	GLC/FPD	0.1
Dyer et al. 1972	Accumulation		
Fletcher 1971	Bioaccumulation, tissue analysis	GLC/FPD	1
Fletcher 1973	Acute bioassay	GLC/FPD	0.1
Fletcher 1974	Bioaccumulation	GLC/FPD	1
Fletcher et al. 1970, 1971	Bioassay monitoring & tissue analysis	GLC/FPD	0.5
Fletcher & Hoyle 1972	Bioassay monitoring & tissue analysis	GLC/FPD	0.5
Zitko et al. 1970	Bioassay, bioaccumulation	Extraction, colorimetric	≈10

[a] GLC = Gas liquid chromatography
FPD = Flame photometric detector
MFID = Modified flame ionization detector

[b] Personal communication. Kimerle, R.A. and G. Brautigam, Monsanto, Inc. 1978.

1976; Ackman et al. 1971; Addison et al. 1970; Addison et al. 1971). Sediment samples and biological tissue concentration are also stable when frozen (Ackman et al. 1971; Dyer et al. 1972). However, white phosphorus concentrations decrease rapidly in living tissue (Maddock and Taylor 1976; Fletcher 1974).

Recent work by Lai and Rosenblatt (1977B) has shown that thermal neutron activation analysis can quantitate WP to ±10 percent at 0.01 µg/l WP in water and can detect as little as 0.001 µg/l. This procedure involves extraction of WP from a water sample using benzene; oxidation of the extracted phosphorus to phosphate; then activation by thermal neutron bombardment. The resulting $^{32}PO_4^{-3}$ can be quantitated by standard radiochemical procedures. The 0.001 µg/l detection limit is set by background phosphorus contamination of reagents. This blank requires application of appreciable correction factors at $^{32}PO_4^{-3}$ levels below 0.010 µg/l. These authors did not make a complete study of the possible interferences from organic phosphorus species or phosphine. Therefore, while the neutron activation technique is extremely sensitive, extraction using the organic solvent may result in positive interferences which would limit its usefulness in detecting low level WP concentrations in the environment. This technique would also require easy access to nuclear facilities to activate specimens.

Burrows and Dacre (1974) have reviewed techniques for measuring phosphine and oxyacids of phosphorus, P^{+1} and P^{+3}. These procedures are also discussed by Lai and Rosenblatt (1977A). Toxicity studies and/or kinetic data suggest that these transformation products of WP are not of critical environmental concern. The oxyacids can be quantitated either as trimethylsilyl derivatives or by thin layer chromatography (Addison 1971; Lai and Rosenblatt 1977A). Phosphine can be quantitated at the 0.01 µg/l concentration level by gas chromatographic analysis (Addison 1971, and Burrows and Dacre 1974).

In summary, the analysis of white phosphorus in environmental samples consists of immediate extraction of the sample with benzene, most commonly, or other organic solvents, such as hexane or isooctane, followed by gas chromatography on a nonpolar column. A flame photometric detector at 526 nm or an alkali salt-modified flame ionization detector are capable of detecting 10^{-12}g of WP. This results in detection limits of 0.10 to 0.20 ppb. Use of high water:solvent ratios or extract concentration can extend the detection limit to 0.05 µg/l under ideal conditions. In samples which do not contain biological material or phosphine, thermal neutron activation analysis can extend detection below the 0.01 µg/l level, possibly to as low as 0.001 µg/l WP.

III. Toxicological Aspects

The earliest study of the toxic effects of white phosphorus to aquatic organisms was reported by Isom (1960). Subsequent published work concerning the toxicity of this material to aquatic life has been performed either by, or under the auspices of two organizations; the Fisheries Research Board of Canada, and the U.S. Army Medical Research and Development Command (USAMRDC).

The majority of the aquatic toxicity tests of WP using marine algae, invertebrates, and fish, as well as bioassays using euryhaline fish have been performed by researchers affiliated with the Fisheries Research Board of Canada. This work was done in response to massive fish kills occurring in Placentia Bay, Newfoundland, beginning in 1969. The work implicated WP in the effluent discharged by the Electric Reduction Company of Canada, Ltd. (ERCO) as the cause of this crisis and demonstrated the extremely toxic nature of this constituent to marine life (Idler 1969, Chamut et al. 1972). Subsequent work with one marine fish has been performed by researchers with the ICI Brixham Laboratory, UK (Maddock and Taylor 1976).

Virtually all of the recently published work investigating the toxicity of WP to freshwater aquatic organisms has been sponsored by the U.S. Army (Bentley et al. 1978 and Pearson et al. 1978). The primary purpose of the work was the establishment of a data base from which quality criteria consistent with the protection of aquatic life could be formulated.

Algae

Freshwater Algae. Bentley et al. (1978) investigated the toxicity of white phosphorus to four species of freshwater algae. Two of the species were eucaryotes: Navicula pelliculosa, a diatom; and Selenastrum capricornutum, a Chlorophyte. The other two species, Anabaena flos-aquae and Microcystis aeruginosa, were members of the procaryotic Myxophyceae. Chlorophyll a concentrations and either cell numbers or optical density relative to control cultures were used as measures of growth response in cultures exposed to nominal WP concentrations ranging from 7 to 670 µg/l. Exposure to WP for 96 hours under static test conditions resulted in a concentration-related inhibitory response by the two eucaryotes. The two procaryotic species showed a biostimulatory growth response as a function of increasing concentration up to 670 µg/l. The pattern of growth response for each species is summarized in Table 5.

Bentley et al. (1978) considered that the algae tested did not exhibit a consistent growth-response to WP and therefore did not report an acute toxic level (EC50 and LC50). The data suggest that the mode of effect of WP on procaryotic cells differs from the effect on more highly organized eucaryotic cells. The apparent EC50 for Navicula pelliculosa, the most sensitive species lies between nominal concentrations of 60 and 80 µg/l. The acute response levels suggest that freshwater algae are less sensitive to WP than fish. An analysis of variance on the 96-hour cell number data of Bentley et al. (1978) and subsequent testing of mean response by Dunnett's test (Steel and Torrie 1960) showed that the no-effect level for Navicula was between nominal concentrations of 7 and 20 µg/l ($P < 0.05$).

Marine Algae. Fletcher (1971) reported bioconcentration factors of 22X and 23X for two marine species Fucus distichus and Fucus vesiculosus, exposed to measured WP concentrations of 15 ± 9.0 µg/l* for 48 hours under

*Mean ± one standard error of the mean.

TABLE 5
RESPONSE OF FOUR FRESHWATER ALGAL
SPECIES TO ELEMENTAL PHOSPHORUS

Algal Species Tested	Response[a] to Increasing P_4 Concentration at:		
	24 Hours	48 Hours	96 Hours: EC50
Eucaryotes:			
Navicula pelliculosa	inhibition	inhibition	inhibition:60-80 µg/l
Selenastrum capricornutum	stimulation	inhibition	inhibition:>200 µg/l
Procaryotes:			
Microcystis aeruginosa	stimulation	stimulation	stimulation:>100 µg/l
Anabaena flos-aquae	stimulation	stimulation	stimulation:>100 µg/l

[a] Measured as either cell numbers or optical density or chlorophyll a concentration relative to controls receiving no P_4.

flow-through conditions. Seven days after transfer to WP-free seawater, no detectable levels of elemental phosphorus (<0.002 µg/g) were found in the tissue of either species. This author did not, however, report any toxic effects to the algae during or after exposure.

Aquatic Invertebrates

Freshwater Species. Acute toxicity studies conducted by Bentley et al. (1978) and Pearson et al. (1978) demonstrated that WP is toxic to invertebrates. In the former study, three species of macroinvertebrates and one zooplankton species were tested under static test conditions in acute toxicity tests of 48 hours duration. These organisms were: the amphipod (Gammarus fasciatus), the isopod (Asellus militaris), the midge (Chironomus tentans), and the cladoceran (Daphnia Magna). Pearson et al. (1978) conducted preliminary 48-hour and 96-hour statis bioassays of WP using four other macroinvertebrates: two midges, (Chaoborus punctipennis) and a Glyptotendipes species, a glass shrimp, (Palaemonetes kadiakensis), and an Oligochaete (Branchiura sowerbyi). The organisms included in these two studies are representative of the broad spectrum of invertebrate forms found in freshwater ecosystems. In addition to the static tests, flow-through tests were conducted by Bentley et al. (1978) in order to define incipient EC50 values for Daphnia and for Chironomus larvae.

The results of the static and flow-through acute bioassays of WP effects on invertebrates are summarized in Tables 6 and 7. White phosphorus concentrations represent measured values for Pearson et al. (1978) - nominal for Bentley et al. (1978). As a group invertebrates appeared to be less sensitive than fish to the acute effects of WP. The relative effect of WP on the invertebrates, however, differed by an order of magnitude or more among the species tested. One organism, Asellus militaris was unaffected by over 500 µg/l of WP. The most sensitive organism, Daphnia magna, had a 48-hour EC50 of 30 µg/l. This concentration is in the same range as 48-hour static LC50s the freshwater fish tested by Bentley et al. (1978). In spite of the low static acute EC50, the flow-through 48-hour acute value for D. magna was greater than 50 µg/l. The incipient EC50 for this organism (11 µg/l) was higher than the incipient LC50 for the bluegill and catfish when tested under flow-through conditions.

Chronic studies, conducted by Bentley et al. (1978) over two generations, indicated that up to 6.9 µg/l of WP produced no effects in Daphnia magna. The maximum allowable toxicant concentration (MATC)* for this organism was found to lie between 6.9 and 8.7 µg/l of elemental phosphorus.

The chronic effects of WP were also studied by Bentley et al. (1978), using the midge Chironomus tentans. Poor survival and reproduction among control and challenged organisms in this study prevented the completion of a life cycle study. Midge larvae were significantly stressed ($P \leq 0.05$) within an 8-day exposure period to 0.14 µg/l but were unaffected after 28 days exposure to 0.67 µg/l. The poor survival among control organisms suggests that the experimental system was adding a stress factor beyond that of the challenge chemical. Use of the Chironomus tentans data from this experiment as a basis for criteria formulation would therefore be questionable.

*Maximum Acceptable Toxicant Concentration (MATC): the highest concentration of toxicant that has no adverse effect on survival, growth or reproduction of a species based on the results of a life-cycle or partial life-cycle toxicity test. A life-cycle or partial life-cycle test cannot produce a value for the MATC; a test can only produce limits within which the MATC must fall.

TABLE 6

ACUTE TOXICITY OF WHITE PHOSPHORUS TO FRESHWATER AND MARINE INVERTEBRATES UNDER STATIC TEST

Organism	Acute Toxic Concentration ($\mu g\ P_4/l$)[a]		Comments[b]	Reference
	48-Hour EC50	Other		
I. Freshwater Invertebrates				
Cladoceran *Daphnia magna*	30(25-37)	24-hr EC50, 34(28-41)		Bentley *et al.* (1978)
Oligochaete *Branchiura sowerbyi*	38(12-120)		Preliminary bioassay Measured concentration	Pearson *et al.* (1978)
Glass Shrimp (Mysid) *Palaemonetes kadiakensis*	59.6(30.9-88.4)	96-hr EC50, 32(19.7-51.6)	Measured concentration	Pearson *et al.* (1978)
Amphipod *Gammarus fasciatus*	250(130-310)	24-hr EC50, >420<560		Bentley *et al.* (1978)
Isopod *Asellus militaris*	>560	24-hr EC50, >560		Bentley *et al.* (1978)
Phantom Midge *Chaoborus punctipennis*	38(12-120)		Preliminary bioassay Measured concentration	Pearson *et al.* (1978)
Midge *Chironomus tentans*	140(110-190)	24-hr EC50, 260(210-330)		Bentley *et al.* (1978)
Midge *Glyptotendipes* sp.	38(12-120)		Preliminary bioassay Measured concentration	Pearson *et al.* (1978)
II. Marine Invertebrates				
Amphipod *Gammarus oceanicus*		24-hr EC50, >3000<4000	Preliminary bioassay, Incipient EC50	Zitko *et al.* (1970)
American Lobster *Homarus americanus*		168-hr EC50, >20 <40	Incipient EC50, P_4 released from contaminated sediments, Measured concentration	Zitko *et al.* (1970)

[a] EC50 based on immobilization of the organism. Numbers in parentheses represent 95 percent fiducial limits or confidence interval.

[b] Unless otherwise noted, all reported values based on nominal concentrations.

TABLE 7

ACUTE TOXICITY OF WHITE PHOSPHORUS TO FRESHWATER AND MARINE INVERTEBRATES UNDER FLOW-THROUGH TEST CONDITIONS

Organism	Acute Toxic Concentration (µg P_4/l)[a]		Comments[b]	Reference
	48-Hour EC50	Other		
I. Freshwater Invertebrates				
Cladoceran *Daphnia magna*	>50	24-hr EC50, >50 192-hr EC50, 11(5-24)	Nominal concentration Nominal conc., Incipient EC50	Bentley *et al.* (1978)
Midge *Chironomus tentans*	111(31-399)	24-hr EC50, >240 120-hr EC50, 20(4-99)	Nominal concentration Nominal conc., Incipient EC50	Bentley *et al.* (1978)
II. Marine Invertebrates				
American lobster *Homarus americanus*		LT50 = 620(563-682) hrs at 23.0 (±6.0) µg P_4/l		Fletcher (1971)
Amphipod *Gammarus oceanicus*	24-hr EC50, ca 6500		Nominal conc., Incipient EC50	Zitko *et al.* (1970)

[a] EC50 based on immobilization of the organism. Numbers in parentheses represent 95 percent fiducial limits or confidence interval.

[b] Unless otherwise noted, all reported values based on measured concentrations.

Marine Species. Limited bioassay results (Fletcher 1971; Zitko et al. 1970) for two marine invertebrates; the amphipod Gammarus oceanicus, and the American lobster Homarus americanus are also included in Tables 6 and 7.

Incipient lethal levels for the marine Gammarus species were about 1000 times the level for a freshwater form of the same genus. Gammarus oceanicus, moreover, can recover from short-term exposure to fairly high concentrations of WP:

WP Concentration	Exposure Time	% Recovery
8 mg/l	3 hours	100
17 mg/l	1 hour	90
40 mg/l	1 hour	20

Apparently toxicity to lobsters is irreversible (Zitko et al. 1970). These investigators studied the toxicity of WP released from the contaminated sediment of Long Harbour, Newfoundland and estimated an incipient LC50 which was between 20 and 40 µg/l. Both Zitko et al. (1970) and Fletcher (1971) reported that the response in lobsters was a function of the product of exposure time and concentration. Sublethal exposure of the lobster to WP did not affect molting.

These limited studies suggest that marine invertebrates are no more sensitive to the acute effects of WP than freshwater forms. The LT50 for the lobster of 620 hours reported by Fletcher (1971) for 23 µg/l WP under flowing water conditions is consistent with the results of Zitko et al. (1970). Marine invertebrates do not appear to be as sensitive to WP toxicity as both freshwater and marine fish.

Fish

Freshwater Species. Based on the work of Bentley et al (1978) and limited data from Pearson et al. (1978) fish appear to be the most sensitive group of freshwater aquatic organisms to white phosphorus. Bentley et al. (1978) conducted static and flow-through acute bioassays of WP using bluegill, Lepomis macrochirus, and channel catfish, Ictalurus punctatus, as test organisms. Static acute tests were also conducted using rainbow trout, Salmo gairdneri, and fathead minnow Pimephales promelas. Pearson et al. (1978) studied the acute effects of WP on the bluegill and on the mosquito fish, Gambusia affinis, under static conditions. Chronic studies of the effects of WP were carried out by Bentley et al. (1978) in embryo-larvae (egg-fry) tests using catfish and fathead minnow as test organisms. A complete life cycle test was performed on the fathead minnow by Bentley et al. (1978). All static and flow-through acute bioassays reported by Bentley et al. (1978) were based on nominal WP concentrations, as was the fathead minnow egg-fry study. Concentrations of WP in chronic bioassays for the fathead minnow represented measured concentrations. Pearson et al. (1978) also based their bioassay results on measured WP concentrations.

Tables 8 and 9 summarize the acute toxic responses found under static and flow-through conditions. The bluegill, used to test the effects of changes in temperature, pH, and water hardness, was the most sensitive organism to the acute effects of WP having a minimum static 96-hour LC50 of 2(1-4)* µg/l at 25°C, pH 7.0, and 35 mg/l total hardness. The flow-through 96-hour LC50 was 2.4(1.7-3.5)* µg/l for this organism. Low pH or high hardness decreased the sensitivity of the bluegill to WP. Pearson et al (1978) found the bluegill to be somewhat less sensitive than Bentley et al (1978) based on static test results. Pearson's work was done in dechlorinated tap water at a hardness of 50-60 mg/l $CaCO_3$; nearly twice the hardness of water used in the bulk of the work of Bentley et al. (1978). The duration of exposure greatly influenced the LC50 for the two fish tested under flow-through conditions. Incipient LC50s for bluegill and channel catfish were 5 and 17 times lower than 96-hour static LC50s respectively.

The acute toxicity to various life stages was examined under static test conditions by Bentley et al. (1978) using the fathead minnow as the test organism. Eggs were the most resistant life stage; susceptibility of this organism increased with age (Table 8). Sixty-day-old fry were the most sensitive age group tested in the experiment. The 96-hour LC50 of this age group was similar to that of adult fish.

White phosphorus is relatively unstable in water when oxygen is present and the dynamics of its decomposition are poorly understood (see Section II). In a test of WP stability under static test conditions, Bentley et al. (1978) found that initial concentrations were reduced by a factor of 2.5 to 5.9 times within a 96-hour period. One such test showed a reduction of over 40 times (41 µg/l → 1 µg/l). During chronic exposure conditions (flow-through tests) discussed below, the nominal concentration was 1.5 to 1.7 times the measured. Interpretation of bioassay data based on nominal concentration should consider these possible differences. For example, acute toxicity (96-hour LC50) for the bluegill would actually be in the range of 1-2 µg/l based on a measured/nominal ratio of 1.4 : 2.

The longer term (egg-fry and full life-cycle) tests carried out by Bentley et al. (1978) utilized measured challenge concentrations. The results of the long-term tests were evaluated by analysis of variance (ANOVA) followed by Dunnett's comparison of individual treatment means with control. Unfortunately, these analyses were made utilizing average values of the replicates within the various tests. In order to obtain the maximum amount of information from the data, the statistical analyses were repeated utilizing individual raw data values. In several cases, this showed that lower levels of WP were producing statistically significant effects than had been revealed previously. In addition to Dunnett's test, the Williams's (1972) procedure was applied to the data. This test is specifically designed to detect differences in situations where an increasing or decreasing response with challenge concentrations is expected.

*Parentheses indicate the 95 percent fiducial limits or 95 percent confidence interval.

TABLE 8

ACUTE TOXICITY OF WHITE PHOSPHORUS TO FRESHWATER, EURYHALINE, AND MARINE FISHES UNDER STATIC TEST CONDITIONS

Organism	Acute Toxic Concentration (µg P_4/l)[a]		Comments[b]	Reference
	96-Hour LC50	Other		
I. Freshwater Fish				
Bluegill *Lepomis macrochirus*	72(NR)[c]	48-HR LC50, 105(NR) 72-HR LC50, 53-73		Isom (1960)
		163-HR LC50, 25(NR) 24-HR LC50, 27(22-32) 48-HR LC50, 9(5-16)		Bentley, *et al.* (1978)
	6(4-9)			
	5(3-6)		T=15°C, pH=7.0, TH=35 mg/l $CaCO_3$	
	5(4-7)		T=20°C, pH=7.0, TH=35 mg/l $CaCO_3$	
	2(1-4)		T=25°C, pH=7.0, TH=35 mg/l $CaCO_3$	
	5(3-6)		T=20°C, pH=7.0, TH=35 mg/l $CaCO_3$	
	4(2-6)		T=20°C, pH=7.0, TH=100 mg/l $CaCO_3$	
	86(74-101)		T=20°C, pH=7.0, TH=250 mg/l $CaCO_3$	
	69(55-84)		T=20°C, pH=6.0, TH=35 mg/l $CaCO_3$	
	8(5-11)		T=20°C, pH=7.0, TH=35 mg/l $CaCO_3$	
	4(3-6)		T=20°C, pH=8.0, TH=35 mg/l $CaCO_3$	
	4(2-7)		Initial Age of P_4 Test Solution = 0 HRS	
	4(3-6)		Initial Age of P_4 Test Solution = 12 HRS	
	6(4-8)		Initial Age of P_4 Test Solution = 24 HRS	
	5(3-7)		Initial Age of P_4 Test Solution = 48 HRS	
	9(6-12)		Initial Age of P_4 Test Solution = 96 HRS	
	29.0(19.3-43.7)		Measured Conc.	Pearson, *et al.* (1978)
Fathead Minnow *Pimephales promelas*		24-HR LC50, 101(73-141) 48-HR LC50, 36(24-46)		Bentley, *et al.* (1978)
	20(16-25)			
		24-HR, LC50, >560	Eggs	
		48-HR, LC50, >560	Eggs	
	>560		Eggs	

TABLE 8 - Continued

	154(96-247)	24-HR, LC50, 154(96-247) 48-HR, LC50, 154(96-247)	1 HR, Post-Hatch, Fry 1 HR, Post-Hatch, Fry 1 HR, Post-Hatch, Fry	
	74(54-103)	24-HR, LC50, 93(53-165) 48-HR, LC50, 75(54-104)	7 Days, Post-Hatch, Fry 7 Days, Post-Hatch, Fry 7 Days, Post-Hatch, Fry	
	21(11-28)	24-HR, LC50, 26(18-38) 48-HR, LC50, 25(17-37)	30 Days, Post-Hatch, Fry 30 Days, Post-Hatch, Fry 30 Days, Post-Hatch, Fry	
	18(15-22)	24-HR, LC50, 27(22-32) 48-HR, LC50, 21(17-25)	60 Days, Post-Hatch, Fry 60 Days, Post-Hatch, Fry 60 Days, Post-Hatch, Fry	
Channel Catfish Ictalurus punctatus		24-HR, LC50, 152(99-232) 48-HR, LC50, 87(69-109)		
Rainbow Trout Salmo gairdneri	22(15-32)	24-HR, LC50, 61(39-98) 48-HR, LC50, 28(16-48)		
Mosquito Fish Gambusia affinis	63.0(45.1-81.9)		Measured Conc.	Pearson et al. (1978)
II. Euryhaline Fish				
Atlantic Salmon Salmo salar		NR-HR, LC50, 18(NR)	Seawater Bioassay, Incipient LC50	Zitko, et al. (1970)
III. Marine Fish				
Atlantic Herring Clupea harengus	ca. 3.7	$LT50_{(HRS)} = 300(\mu g\ P_4/l)^{-0.87}$		

[a] Numbers in parentheses represent 95 percent fiducial limits.
[b] Unless otherwise noted, all reported values based on nominal concentrations.
[c] NR = Not reported.

TABLE 9

ACUTE TOXICITY OF WHITE PHOSPHORUS TO FRESHWATER, EURYHALINE AND MARINE FISHES UNDER FLOW-THROUGH TEST CONDITIONS

Organism	Acute Toxic Concentration (µg P_4/l)[a]		Comments[b]	Reference
	96-Hour LC50	Other		
I. Freshwater Fish				
Bluegill				
Lepomis macrochirus	2.4(1.7-3.5)	24-HR LC50, >3.2	Nominal Conc.	Bentley, *et al.* (1978)
		192-HR LC50, 0.6(0.4-1.1)	Nominal Conc.	
			Nominal Conc., Incipient LC50	
Channel Catfish				
Ictalurus punctatus	>19	24-HR LC50, >19		
		624-HR LC50, 4.2(3.3-5.4)	Incipient LC50	
II. Euryhaline Fish				
Brook Trout				
Salvelinus fortinalis	ca. 2.6	LT50(HRS) = 156C(µg P_4/l)$^{-0.503}$	Seawater Bioassay	Fletcher, *et al.* (1970)
		LT50(HRS) = 200 HRS @ 0.50 µg P_4/l		
Atlantic Salmon				
Salmo salar	ca. 2.3	LT50(HRS) = 153C(µg P_4/l)$^{-0.555}$	Seawater Bioassay	Fletcher and Hoyle (1972)
		LT50 = 195 HRS @ 0.79 µg P_4/l	Seawater Bioassay	
		LT50 = 50.2 HRS @ 22.8 µg P_4/l	Freshwater Bioassay	
III. Marine Fish				
Atlantic Cod				
Gadus morhua	ca. 2.5	LT50(HRS) = 159 C (µg P_4/l)$^{-0.559}$		Fletcher and Hoyle (1972)
		LT50 = 125 HRS @ 1.89 µg P_4/l		
		48-HR LC50, 14.4(NR)	Dissolved P_4	Maddock and Taylor (1976)
Atlantic Herring				
Clupea harengus		LT50 = 3.6 HRS @ 100 µg P_4/l		Fletcher, *et al.* (1972)
Smelt				
Osmerus mordax		NA	Results Presented Graphically	
Mummichog				
Fundulus heteroclitus		LT50 = 85.2 HRS @ 90.0 µg P_4/l	Preliminary Bioassay	Fletcher, *et al.* (1971)
		LT50 = 102 HRS @ 20.2 µg P_4/l		
Cunner				
Tautogalabrus adspersus		LT50 = 190 HRS @ 3.4 µg P_4 /l	Preliminary Bioassay	
		LT50 = 171.0 HRS @ 0.5 µg P_4/l	Preliminary Bioassay	
		LT50 = 19.0 HRS @ 22.8 µg P_4/l	Preliminary Bioassay	
		LT50 = 23.0 HRS @ 74.0 µg P_4/l	Preliminary Bioassay	
		LT50 = 14.0 HRS @ 100.0 µg P_4/l	Preliminary Bioassay	

[a] Numbers in parentheses represent 95 percent fiducial limits.
[b] Unless otherwise noted, all reported values based on measured concentrations.

The 30-day egg-fry exposure of channel catfish to WP (Bentley et al. 1978) resulted in a significant ($P < 0.05$) reduction in percent survival and fish length at a concentration of 6.8 µg/l. No significant effects were found at 5 µg/l.

The fathead minnow was more sensitive to long-term exposure than the catfish. Table 10 summarizes the lowest significant ($P < 0.05$) response concentrations for certain critical tests for the fathead minnow. In the egg-fry study, length of the young fish was significantly reduced compared to controls at the lowest WP concentration tested (0.6 µg/l). Eggs spawned by fish exposed to the lowest WP concentration (0.4 µg/l) showed poor hatchability (less than 16 percent produced viable fry). In addition, several other adverse effects, including decreased length and weight, were observed at 0.4 µg/l during the full life-cycle test.

Since effects were observed at the lowest concentrations tested the MATC was not defined by either partial or complete life-cycle data for the fathead minnow. Therefore, regression techniques (Snedecor and Cochran 1967) were applied to the fish length and weight data from the life-cycle test to estimate a no-effect level. A linear model relating the dependent variable, or measured effect, y, to the WP challenge concentration, x, was fitted to the data (see Figures 3 and 4). Then, the concentration, x_c, at which the upper 95 percent confidence limit on the predicted effect (α = 0.05, single-tailed consideration) was equal to the predicted effect at a WP challenge concentration of zero was determined. This value, x_c, can be considered as an estimate of the no-effect level, since, according to the regression model the predicted mean effect at all concentrations exceeding this value will be significantly different from that predicted in the control. Finally, a confidence band was placed about x_c (Finney 1952). The results of this analysis are summarized in Table 11. Appropriate caution should be exercised in interpreting these results since 1) the underlying model assumption is that there is a response at all concentrations and 2) the correlation coefficients ($0.54 < r < 0.81$) indicate only a moderately good fit of the data to the linear model.

Euryhaline Species. White phosphorus is acutely toxic to euryhaline fish at concentrations in the same range as for freshwater forms. Two fish species have been tested; the Atlantic salmon, Salmo salar, and the brook trout Salvelinus fortinalis. Results of flow-through toxicity tests for these organisms are presented in Table 9. Table 8 presents an incipient LC50 for Salmo salar under static test conditions in sea water. In general the investigators (Fletcher et al. (1970) and Fletcher and Hoyle (1972) reported toxicity results in the form of regression equations. Ninety-six-hour LC50 values were estimated from these relationships. No-effect levels for these two species were below the lowest concentrations tested:

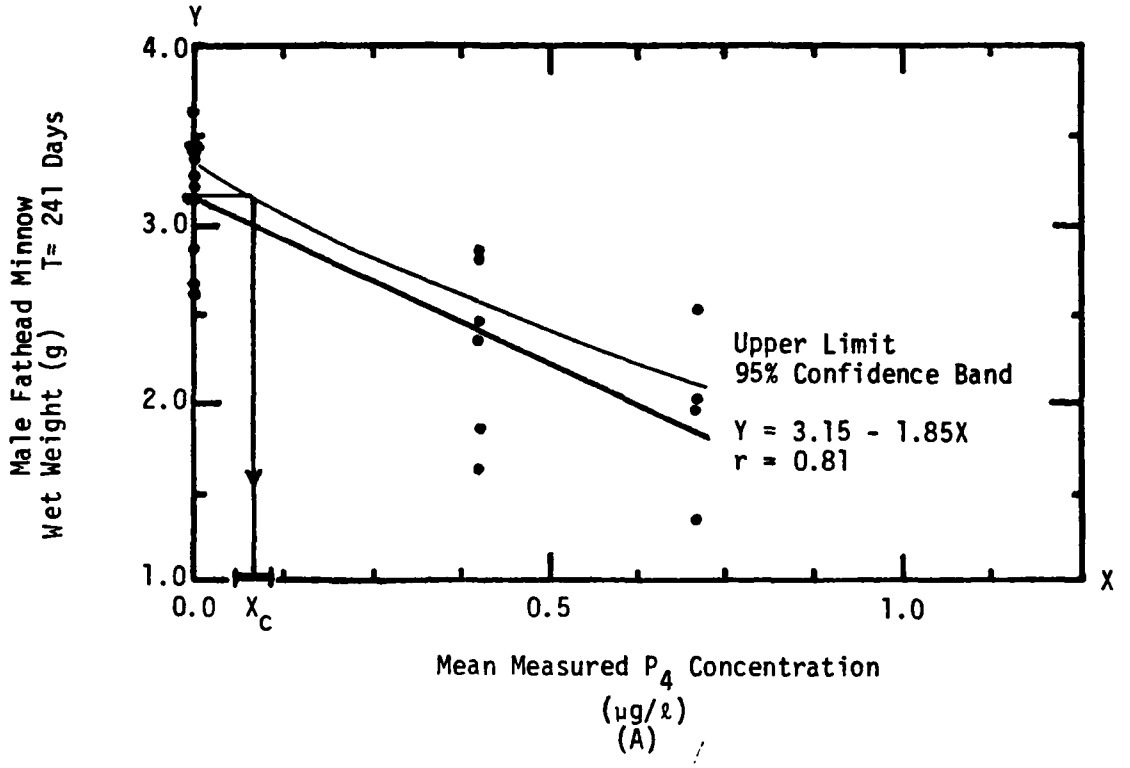
Species	Lowest WP Conc. Tested	LT50 (hours)	Reference
Salmo salar	0.79 µg/l	195	Fletcher and Hoyle (1972)
	Control	>720	
Salvelinus fortinalis	0.5 µg/l	121	Fletcher et al. (1970)
	Control	200 (151-264)	

TABLE 10

LONG-TERM TEST RESULTS FOR FATHEAD MINNOW (PIMPEHALES PROMELAS)

Test Description	Variable	Lowest Significant ($P < 0.05$) Response Concentration($\mu g\ P_4/l$): Dunnett	Williams
Egg-Fry 30-Day Test	30-day length	0.6[a]	0.6[a]
Full Life-Cycle Test	60-day length	0.4[a]	0.4[a]
	150-day % survival	1.5	1.5
	241-day % survival	1.5	1.5
	241-day length male	0.71	0.71
	241-day length female	0.71	0.71
	241-day weight male	0.4[a]	0.4[a]
	241-day weight female	0.71	0.4[a]

[a]Lowest challenge concentration



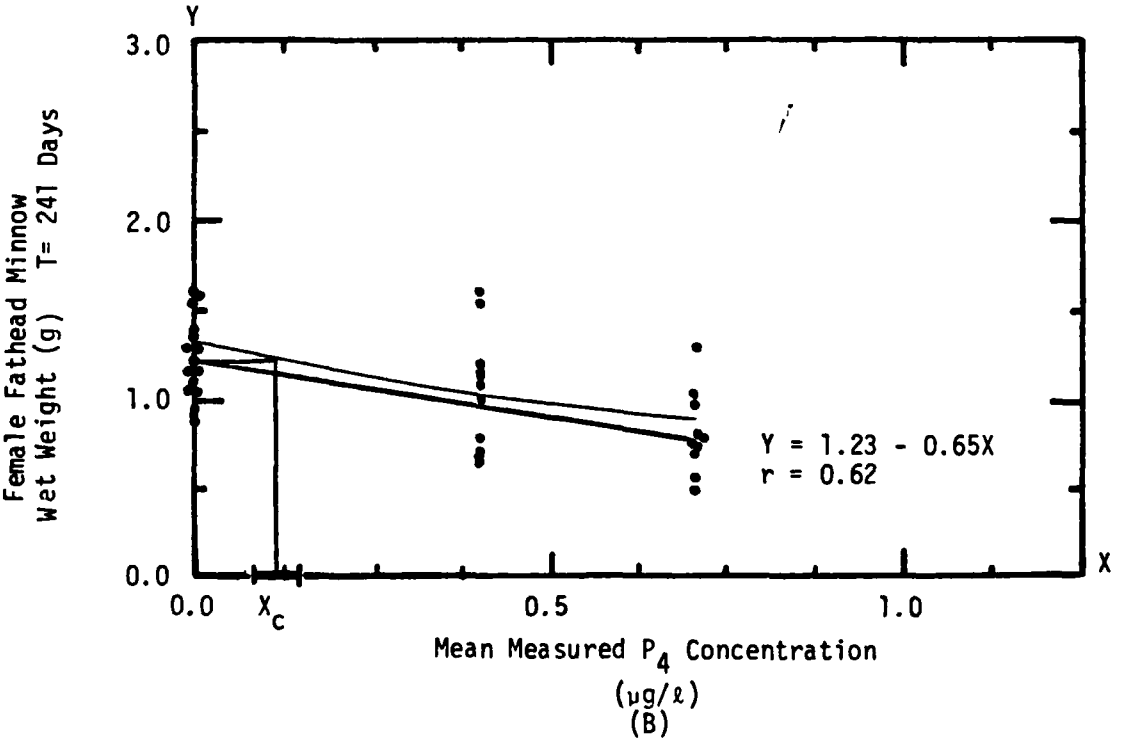


FIGURE 3. EFFECT OF WHITE PHOSPHORUS ON THE WET WEIGHT OF (A) MALE AND (B) FEMALE FIRST GENERATION FATHEAD MINNOWS EXPOSED CONTINUOUSLY FOR 241 DAYS.

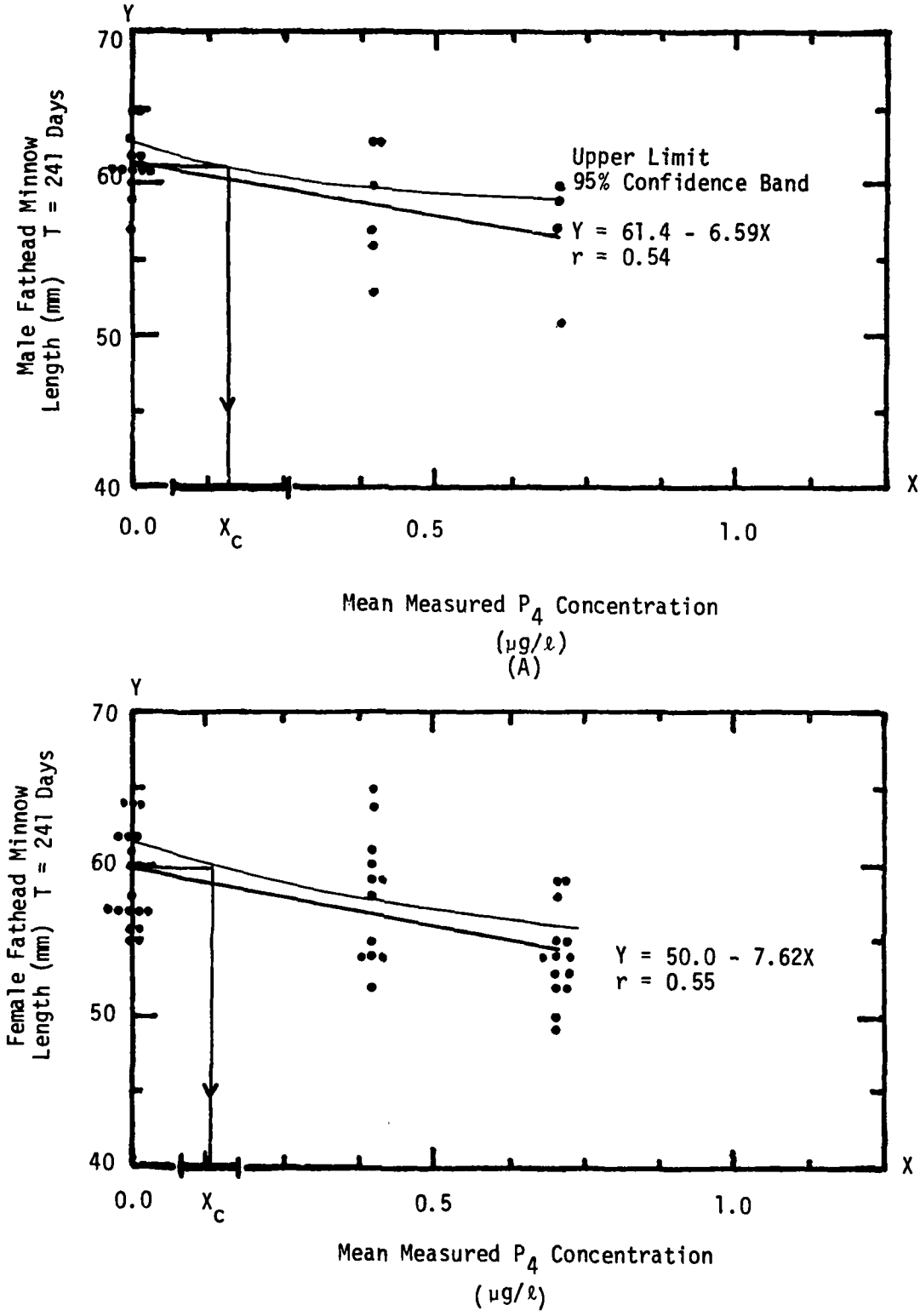


FIGURE 4. EFFECT OF WHITE PHOSPHORUS ON THE LENGTH OF (A) MALE AND (B) FEMALE FIRST GENERATION FATHEAD MINNOWS EXPOSED CONTINUOUSLY FOR 241 DAYS.

TABLE 11

EFFECT OF WHITE PHOSPHORUS ON THE GROWTH OF FIRST GENERATION FATHEAD MINNOWS 241 DAYS POST-HATCH EXPOSED CONTINUOUSLY TO MEAN MEASURED P_4 CONCENTRATIONS RANGING FROM 0.0 TO 0.71 µg P_4/l

Subgroup	Effect Parameter Y	Units	Total No. Exposed Fish	Regression Equation	r	X_c Upper Limit of 95 Percent Confidence Interval About the Intercept (µg P_4/ ℓ)	90 Percent Confidence Interval About X_c (ug P_4/ℓ)
Males	Length	mm	23	Y=61.4 - 6.59 X	0.54	0.17	0.07-0.26
Females	Length	mm	47	Y=50.0 - 7.62 X	0.55	0.13	0.08-0.18
Males	Wet weight	g	23	Y=3.15 - 1.85 X	0.81	0.08	0.06-0.11
Females	Wet weight	g	47	Y=1.23 - 0.65 X	0.62	0.11	0.08-0.15

Both of these investigators concluded that toxic effects to these species were dose-related (a function of time and concentration) rather than related strictly to concentration.

Marine Species. Similar test results for the acute effects of WP on marine fish, the cod, Gadus morhua; the herring, Culpea harengus; the smelt, Osmerus mordax; the mummichog, Fundulus heteroclitus; and the cunner, Tautogalabrus adspersus are reported in Tables 8 and 9.

Acute LC50 values estimated from the regression equations for the cod indicate that this species is approximately as sensitive as the bluegill, the most sensitive freshwater species (Fletcher and Hoyle 1972). The herring is similarly sensitive to WP as determined by static acute bioassay tests (Zitko et al. 1970). These two species, Gadus morhua and Culpea harengus appeared to be the most sensitive marine organisms tested. No-effect levels were not defined for marine fish since the lowest concentrations tested (as low as 1.89 µg/l) caused mortalities.

Bioaccumulation

The ability of white phosphorus to accumulate in the tissues of aquatic organisms has been the subject of extensive investigation, particularly with regard to uptake by marine life. Acute lethal doses are strongly time-dependent. The delayed but inevitable death of organisms exposed for short periods at high concentrations or exposed for long periods at very low concentrations suggests a possible bioaccumulatory mechanism. Tables 12, 13, and 14 summarize invertebrate and fish tissue accumulation factors for both marine and freshwater organisms.

The only data for plant and invertebrate WP uptake comes from flowing water studies done by Fletcher (1971). In this work, tanks containing two marine algal species (see Section III) and the invertebrates listed in Table 12 were exposed to 15 µg/l WP. The organisms survived the exposure but concentrated WP up to 42 times the water concentration. The bioconcentration factor appeared to be related directly to relative lipid content since the periwinkle has the highest overall lipid content of the mollusks. In the starfish and the lobster, the distribution of tissue concentrations of WP was also directly dependent on tissue lipid content. Organisms quickly lost their accumulated WP content after transfer to clean water. After 7 days depuration, no detectable tissue WP (less than 0.002 µg/kg) was found in marine algae, shellfish, or lobsters. No periodic sampling of the lobsters or other invertebrates was carried out to determine when tissue concentration reached equilibrium. The lobster data suggests that for the lipid-rich ovary and hepatopancreas equilibrium was not achieved in the 2-day study.

The relative bioaccumulation factors in the various organs of freshwater, euryhaline, and marine fish are shown in Tables 13 and 14. The liver (especially liver oil in cod) is the organ which accumulates the largest amount of WP. In this organ, concentration factors ranged from less than 12 to 58,000. The extremely high values for the cod exposed to 1 µg/l WP (Dyer et al. 1970) may have been an artifact of the manner in which the fish were

TABLE 12

BIOCONCENTRATION OF WHITE PHOSPHORUS IN MARINE MACROINVERTEBRATES[a]

Organism[b]	Exposure Conditions P_4 Concentration (µg/l)[c]	Exposure Conditions Duration (Days)	Tissue	Tissue Bioconcentration Factor
Blue mussel				
Mytilus edulis (10)	15±9	2	Whole organism[d]	10
Clam				
Mya arenaria (5)	15±9	2	Whole organism[d]	23
Periwinkle				
Littorina littorea (10)	15±9	2	Whole organism[d]	42
Quahog				
Arctica islandica (5)	15±9	2	Whole organism[d]	17
Starfish				
Asterias vulgaris (1)	15±9	2	Whole organism	27
Asterias vulgaris (5)	15±9	2	Pyloric caeca	131
			Body wall	12
			Periovisceral fluid	<1
American lobster				
Homarus americanus (5)	15±9	2	Hepatopancreas	1270
Homarus americanus (5)	23±7	Until Death (~25 days)	Hepatopancreas	1970
Homarus americanus (5)	15±9	2	Ovary	267
Homarus americanus (5)	23±7	Until Death (~25 days)	Ovary	412
Homarus americanus (5)	15±9	2	Tail muscle	34
Homarus americanus (5)	23±7	Until Death (~25 days)	Tail muscle	31
Homarus americanus (5)	15±9	2	Chela muscle	26
Homarus americanus (5)	23±7	Until Death (~25 days)	Chela muscle	23
Homarus americanus (5)	15±9	2	Gill	18
Homarus americanus (5)	23±7	Until Death (~25 days)	Gill	9
Homarus americanus (5)	15±9	2	Hemolymph	5
Homarus americanus (5)	15±9	Until Death (~25 days)	Hemolymph	4

[a] Reference: Fletcher (1971).

[b] The number in parentheses is the number of organisms tested.

[c] Mean and standard deviation.

[d] No shells were tested.

TABLE 13

BIOCONCENTRATION OF WHITE PHOSPHORUS IN FISH

Organism	Exposure Conditions P_4 Concentration (µg/l)	Exposure Conditions Duration (Days)	Tissue Bioconcentration Factor Muscle	Liver	Other Viscera	Remarks	Source
I. Freshwater Fish							
Bluegill *Lepomis macrochirus*	46	0.67(16 Hours)	--	44	--	Analysis of pooled tissue from 16 fish	Pearson *et al.* 1976
Freshwater drum *Aplodinotus grunniens*	NR[a]	NR	--	69	--	Environmental field samples, Pine Bluff Arsenal, Arkansas	Pearson *et al.* 1976
Fathead minnow *Pimephales promelas*	2.2±0.31 (Mean + 95% C.I.)	1-7	<45-155	--	<82-200[b]	--	Bentley *et al.* 1978
Channel catfish *Ictalurus punctatus*	NR	NR	--	44	--	Environmental field samples, Pine Bluff Arsenal, Arkansas	Pearson *et al.* 1976
"	1.8±0.23 (Mean ± 95% C.I.)	1-47	50-106 (239)	<12-67	44-106	The single value of 239 resulted from replicates of 78 and 394.	Bentley *et al.* 1978
"	0.18±0.02 (Mean ± 95% C.I.)	1-47	31-94	Not Detected	<27-100	Tissue concentrations were generally barely detectable.	Bentley *et al.* 1978
II. Euryhaline Fish							
Atlantic salmon *Salmo salar*	22.8-763	Until Death[c] (LT50 = 3.1 to 2.1 Days)	24-48	26-91	257-658 (Pyloric caeca)	Freshwater-maintained (15 fish)	Fletcher 1974
"	1900	Until Death (LT50 = 0.1 Day)	12	27	29 (Pyloric caeca) 56 (Brain) 16[d] (Blood)	Seawater-maintained (95 fish)	"
"	0.79-1900	Until Death (LT50 = 0.1 to 8.1 Days)	20	41	28[e]	Seawater-maintained (95 fish)	"

TABLE 13 - Continued

III. Marine Fish						
Atlantic cod *Gadus morhua*	1	0.67(16 hours)	172[f] (Red) 71 (White)	58000 (Oil) 20000 (Whole Liver)	--	P_4 feedstock too dilute. P_4 conc. in control tanks without fish reached 20-30 µg/l.	Dyer *et al.* 1970
"	21-83	0.67(16 hours)	54-83 (Red) 9-26 (White)	2750-7350 (Oil) 883-2000 (Whole Liver)	--	P_4 feedstock concentration increased to allow P_4 buildup in exposure tanks	"
"	630	(1/2 hour)	1 (White)	68 (Oil) 30 (Whole Liver)	--	--	"
"	1.89-5780	Until Death[c] (*LT50 = 0.06 - 5.2*)	44 (*whole fish, 103*)	2460	67[g]	Calculated from regression equation of tissue P_4 concentration on water concentration r^2 = 0.794 to 0.956 for the various organs tested.	Fletcher 1974
"	4.4-29 (10.8)[i]	Until Death[c] (LT50 = 0.7 - 7.3)	10-34[h]	115-281[h] (2314)[i]	--	Dissolved P_4 with no colloidal material present.	Maddock and Taylor 1976

[a] NR = Not reported.

[b] Includes liver tissue also for this species.

[c] No individual data given. Median lethal time (LT50) reported.

[d] Blood analysis: Bioconcentration factor; 40X in erythocytes, 5X in plasma.

[e] Average bioconcentration factor for pyloric caeca, esophagus, intestine, gill, and kidney tissues. See Table 14.

[f] Values reported by Dyer *et al.* 1970 differ slightly from this table. Results in the citation appear to be slightly in error based on the reported data and have been recalculated above.

[g] Average bioconcentration factor for pyloric caeca, spleen, testes, ovary, esophagus, intestine, and gill tissues. See Table 14.

[h] Calculated from tissue concentration data. Apparently the results in Table 2 of Maddock and Taylor 1976 have been given the wrong units, i.e. they should be µg/kg rather than µg/g for tissue concentrations. The former units would allow the data to agree with the authors' stated range of bioconcentration factors.

[i] One concentration, 10.8 µg/l, resulted in a liver bioconcentration factor calculated as 2314. All other liver tissue bioconcentration factors ranged from 115-281 in the reported studies.

TABLE 14

BIOCONCENTRATION OF WP IN TISSUES OF ATLANTIC COD AND SALMON EXPOSED UNTIL DEATH

Tissue	Cod *Gadus morhua*		Salmon *Salmo salar*	
	Number of Fish	Bioconcentration Factor	Number of fish	Bioconcentration Factor
Whole Fish	40	103	--	--
Liver	74	2460	96	53
Bile	66	279	--	--
Pyloric caeca	69	118	86	41
Spleen	69	97	--	--
Ovary	36	72	--	--
Testes	32	72	--	--
Esophagus	68	49	86	26
Muscle	74	44	86	20
Intestine	69	43	86	25
Skin	69	25	86	19
Gill	69	16	96	20
Kidney	--	--	86	14

Reference: Fletcher (1974). Cod were exposed to 1.89 to 5780 µg/l until death (see Table 12). Salmon were exposed to 0.79 to 1900 µg/l until death (see Table 12).

exposed rather than a true concentration factor. The cod, however, had by far the highest liver bioconcentration factor, probably due to the exceptionally high content of lipids in the liver of this species. Bioconcentration in the organs of fish apparently relates to their relative lipid content.

Accumulated WP in fish tissue disappears rapidly from living fish after transfer from water containing WP. After the transfer of fathead minnow and channel catfish exposed to WP for 77 and 47 days, respectively, no detectable concentrations were found after 2 days depuration (Bentley et al. 1978).

Fletcher (1974) documented the rapid uptake and removal rates for WP in salmon and cod tissues. In the salmon, Salmo salar, the half-life of WP in the liver of fish exposed to 1.6 mg/l for 40 minutes was estimated at 0.90 to 1.02 hours and 2.71 to 5.54 hours in intestinal contents. WP is metabolized somewhat slower in the cod (Gadus morhua). In this fish, Fletcher (1974) estimated a half-life for WP ranging from 4 to 13 hours in the liver and 4.7 and 6.2 hours in muscle and blood, respectively, under exposure conditions similar to the above. Relatively constant WP concentrations appeared to be reached in cod tissues after 12 to 24 hours exposure to 8 µg/l WP (Fletcher 1974).

WP rapidly becomes concentrated to levels 20 to 100 times above ambient in the tissues of aquatic organisms, or up to several thousand times in cod liver tissue. However, this effect does not represent a bioaccumulation in the sense that pesticide residues permanently lodge in tissue. WP remains mobile, consequently its concentration rapidly decreases after transfer of a contaminated organism to clean water.

Mechanisms of Toxicity

White phosphorus is one of the most highly toxic inorganic substances known. The literature on human health effects and mammalian toxicology has recently been reviewed by Craig et al. (1978). These authors attribute WP's toxic effect biochemically to its potent reducing power.

The great susceptibility of eucaryotic as opposed to procaryotic cells probably results from two factors. First, WP is lipid soluble (see Section II) and would be expected to localize in cytoplasmic membrane systems or in lipid storage organelles. Secondly, the proper functioning of an eucaryotic cell, whether it is a microorganism like a diatom, or a cell in the liver of a vertebrate, is highly dependent on the spatial organization and compartmentalization of biochemical reactions by the phospholipid membranes of the endoplasmic reticulum. Procaryotic cells contain a much simpler intracellular organization and no internal membranes (DeRobertis et al. 1970). This factor could render them less sensitive to the disruptive effects of WP.

The affinity of WP for lipids could allow it to concentrate in the endoplasmic reticulum of a eucaryotic cell where it would directly affect membrane-bound enzymatic reactions. Cameron and Patrick (1966) state that acute poisoning by WP is similar to the effects of other hepatotoxins because it interferes with protein synthesis on the granular endoplasmic

reticulum. Li et al. (1969) made similar conclusions based on studies of the effects of WP on cultured cells. Although the WP concentrations required to produce effects were higher than those producing effects in aquatic organisms, definite alterations of the fine structure of the cells occurred as a response to white phosphorus. Cell replication ceased but viability of the culture was not affected to a great extent. Cellular morphology was altered due to a breakdown of the nuclear membrane, resulting in the formation of multinucleate cells. Staining tests suggested that WP broke down ribonuclear protein or stopped its synthesis. Cytoplasmic organization was also disrupted. The data suggested that WP strongly affects intracellular organization and membrane-bound protein synthesis, but only slightly affects respiration.

The affinity of WP for lipids may partially account for Navicula pelliculosa being the most sensitive of the algae tested. It is eucaryotic and therefore would be expected to be more susceptible to cellular disruption from WP than the cyanophytes. Additionally, the principal storage products of diatoms are lipids (Duke and Reiman 1977). The high lipid content in this microorganism would probably allow a higher intracellular WP build-up than would the starch storage products characteristic of Selenastrum. Concentration of WP in the oil droplets of Navicula could provide a significantly higher concentration intracellularly than would occur with Selenastrum.

In higher aquatic organism, WP enters via the gills (or the intestinal tract) circulates in the blood and damages all tissue which it contacts (Jangaard 1972). The relative tissue concentrations found in histological studies probably do not relate to WP effects as much as protection of the compound from reaction by means of adsorption in stored lipid. Damage to the organism appears generally to be related to exposure time times concentration. The rapid cleaning of WP concentrations after an organism is removed from WP exposure probably relates to rapid oxidation of the compound in the body of the organism. This results in further tissue damage even after the organism escapes from the exposure site.

The gross effects of acute and chronic WP toxicity to fish generally relate to hemolysis (green intestines, jaundiced livers, and/or reddening of the skin); however, the primary effect may be due to other factors. The specific symptoms of WP toxicity vary among fish species. In acute poisoning of mammals, rapid death is due to the effects of shock and from the damage to the cardiovascular system (Craig et al. 1978). Death occurring within a few days but due to lower doses usually can be attributed to renal or liver failure and from damage to the digestive tract. The mode of toxicity for aquatic organisms may be analogous to the mode in mammals; however, no definitive studies have been performed.

In the lobster clotting of the hemolymph occurs prior to death and may hasten the process through asphyxiation. The primary effects probably result from damage to other organs since the clotting occurs only after the organism has exhibited extreme symptoms of stress (Zitko et al. 1970; Fletcher et al. 1971).

IV. Environmental Fate and Effects

Freshwater

Field studies of the environmental fate and effects of white phosphorus in freshwater ecosystems are limited to studies of Yellow Lake at Pine Bluff Arsenal (PBA), Arkansas, by the U.S. Army Material Development and Readiness Command and at Columbia, Tennessee, by Monsanto, Inc. Rosenblatt et al. (1973) and Pearson et al. (1976) reported on the situation at Pine Bluff Arsenal. Kimerle and Brautigam* have communicated some preliminary results of biomonitoring of WP manufacturing wastewater at Monsanto, Inc., Columbia, Tennessee plant.

At PBA, phossy water from storage and loading operations is discharged to a small settling pond. A ditch carries pond overflow some 50 meters into White Phosphorus Creek at a point approximately one mile upstream of Yellow Lake. The lake covers an area of about 170 acres and has an average depth of about 4 feet during dry weather. The lake was formed as an oxbow in the floodplain of the Arkansas River and is inundated during periods of high river flow. In addition to phossy water discharge, the lake receives some stormwater runoff. In the past some DDT from an old eroding landfill site could enter the lake via stormwater flow. DDT can no longer enter the lake (Pearson 1978) from the old landfill site, however.

Rosenblatt et al. (1973) cited data on in-lake water quality of Yellow Lake. White Phosphorus Creek reportedly contained WP concentrations of 1 to 3 mg/l and was devoid of life other than bluegreen algae and bacteria. From December 1971 to October 1972 measurements in Yellow Lake indicated that concentrations of about 0.14 mg/l WP occurred in the water column. From July 1971 to June 1972 concentrations in the lake ranged from 0 to 2.6 mg/l with a mean of 0.22 mg/l. Sediment concentrations were reported ranging from 0.1 to 3 mg/l (presumably this should be mg/kg). Rosenblatt et al. (1973) reported that the lake "teems with fish and water fowl". However, it was also stated that extensive fish kills were evident after heavy rains but that the exact cause of the kills was not known.

Pearson et al. (1976) reported average WP concentrations in Yellow Lake of 0.24 mg/l in 1973 and 2.46 mg/l in 1974 with an overall range for the two years of 0 to 4.0 mg/l. However, in January 1975 two sets of samples from 18 stations in the lake showed a maximum of 0.04 mg/l WP with most values around 0.0002 mg/l (0.2 µg/l). No reason for this sharp drop in concentration was noted. Likewise sediment concentrations in October 1974 and January 1975 showed a maximum of 0.04 mg/kg. Most sediment concentrations however were less than 0.001 mg/kg. These concentrations are well below the 0.1 to 3 ppm figures reported by Rosenblatt et al. (1973). The highest water and sediment concentration of WP occurred in a small arm of the lake which is connected to the lake proper via a short, narrow channel. White Phosphorus Creek flows into this backwater. The lake outlet is located in this same small arm, therefore water from the creek mixes with the lake proper to only a limited extent. Prior to November, 1974, however, the spillway was located in the main part of the lake.

*Personal communication. Kimerle, R.A. and G. Brautigam, Monsanto, Inc. 1978.

Biological assessments of the effects of WP in Yellow Lake were primarily limited to the macroinvertebrates. In March, July, and October, 1974, and January, 1975, Pearson et al. (1976) sampled the macrobenthos of the natural substrates of this ecosystem. Limited fish sampling was done during the October study in order to measure tissue concentrations of WP in that trophic level.

The bottom of Yellow Lake consists mainly of silt and clay covered by 2 to 13 cm of flocculant material. This presents a restrictive environment for benthic organisms. The dominant organisms in this compartment were midge larvae and Oligochaetes. The lake proper was dominated by midge larvae while the backwater was heavily dominated by the Oligochaete Limnodrilus hoffmeisteri. This organism occurred in such large numbers in the restricted backwater that it composed nearly 50 percent of the collection for the entire lake during the March and October samplings, yet it was present in very small numbers in the lake proper and was never the dominant taxon there. In the lake proper, the midges; Coelotanypus concinnus, Procladius culciformis, Chaoborus punctipennis, Tanypus stelatus, Chironomus plumosus and Palpomyia tibialis and the Oligochaete, Branchiura sowerbyi were dominant. Each of these organisms made up about 10 to 30 percent of the population. In the backwater the flocculant sediment layer was slightly shallower (2-2.5 cm) than the lake proper and the bottom fauna was nearly a monoculture of Limnodrilus during March and October. In July Chaoborus punctipennis was also present in large numbers in the backwater.

Diversity indices (Shannon-Weaver) in the lake proper generally ranged from 1.5 to 2.5 but were lower at some stations during October. In contrast, the diversity in the backwater was much lower, especially at the station nearest the mouth of White Phosphorus Creek. The range of diversity index at this station was 0.09 to 0.83. Overall, the backwater mean diversity was 0.95 with a maximum of 1.70. The station farthest from the mouth of White Phosphorus Creek had higher diversities than the rest of the backwater.

These data suggest that White Phosphorus Creek has an adverse impact on the adjacent benthic community except for Limnodrilus. This organism may be resistant to WP. The population attributes for the macrobenthos in the lake proper were typical of such an environment and displayed no apparent WP related effects. Concentrations of WP in the water column, however, were generally slightly above the MATC for Chironomus tentans (0.067 to 0.14 µg/l) as were the sediment concentrations in some parts of the main lake. Water and sediment WP concentrations in the impact backwater were several times those in the lake proper; especially at the two stations closest to the mouth of the creek. The sediment concentrations ranged from 2 to 43.3 µg/kg (wet weight) and water concentrations from 1.2 to 40.4 µg/l. These concentrations were generally above the MATC for Daphnia magna and Chironomus tentans and approached the incipient LC50s for these organisms (see Table 7). The concentrations at the station nearest the creek were above the 24- and 48-hour EC50s for some of the invertebrates tested (Tables 6 and 7). This suggests that WP concentrations above the MATC limits for invertebrates may adversely affect macroinvertebrate communities in the aquatic ecosystem. None of the other physical or chemical parameters reported suggests an explanation for the observed differences in community structure between the backwater and the main lake.

Pearson et al. (1976) performed regression analyses on diversity index and abundance of the organism Limnodrilus hoffmeisteri for the months March, October, and January versus the mean WP sediment concentration for October and January. On the basis of these analyses Pearson et al. (1976) concluded that a critical threshold concentration of WP for macroinvertebrates in sediments was 0.25 to 4.0 µg/l (presumably this should be µg/kg). However, the validity of the statistical methods utilized in the analysis appears to be questionable. At sediment concentrations of WP below 10 µg/l (sic), the correlation between concentration and population attribute breaks down. Only the two stations nearest the mouth of the creek appear to show a distinct effect when presented graphically. Based on the data in this report, the no-effect level for WP in sediments probably lies below 2 µg/kg (wet weight), the minimum sediment concentrations found at the two stations which showed adverse impact. Below 0.6 µg/kg other environmental effects seem to mask the effect of WP.

Pearson et al. (1976) also reported WP concentrations in fish livers before and after a 62 mm rain in October 1974. Fourteen fish from Yellow Lake were taken before the rain and eight after (see Table 13). Mean concentrations in channel catfish livers before and after were 3.13 and 138.75 µg/kg, respectively. In the freshwater drum, liver concentrations of 4.5 and 308.85 µg/kg were measured. Some dead fish were noted after the rain and livers from two of these showed WP concentrations of 2034 and 7620 µg/kg (see Table 13). No measurements of WP concentrations in the lake before and after the rain were made. These results suggest strongly, however, that storm events increase WP concentrations in the lake by either increasing the input from White Phosphorus Creek or by resuspension of WP rich lake sediments or by both mechanisms.

At the Columbia, Tennessee, facility of Monsanto, Inc., bioconcentration of WP by fish used as biomonitors was a factor of 30 or less.* Concentrations of WP in the tissues of these fish were less than 5 µg/kg. Fish reportedly survive in waste ponds at Monsanto, but no water quality data were given regarding WP levels in these systems.

In summary, WP in freshwater environments appears to be distributed between the sediments and the water column. Fish responded to changes in WP concentrations in the water within a matter of hours and concentrated the material some 30-50 times in their livers. Dead fish were observed with liver concentrations from 2000-8000 µg/kg. Fish surviving "spikes" of WP apparently eliminate the material from their tissues to a level in equilibrium with the prevailing WP concentration. In aquatic sediments the presence of up to 0.6 µg/kg on a wet weight basis did not produce an observable effect on a benthic community dominated by midge larvae. Sediment concentrations above 2 µg/kg (range 2 to 43.3 µg/kg) on a wet weight basis, drastically altered benthic community structure.

Marine

The Fisheries Research Board of Canada began a data-gathering program to determine the cause of massive fish kills which occurred in Placentia Bay, Newfoundland, immediately after an elemental phosphorus manufacturing plant

*Personal communication. Kimerle, R.A. and G. Brautigam, Monsanto, Inc. 1978.

was put into operation on Long Harbour by Electric Reduction Company of Canada (ERCO) in 1969. Laboratory bioassay results and environmental data implicated white phosphorus as the primary agent responsible for the observed damage. Section III of this report reviews the laboratory results.

The environmental data consist of documentation of WP tissue levels in dead fish from kills; tissue WP levels in live fish from the area; areal and temporal extent of water and sediment concentrations; and data on changes in the distribution of benthic organisms in the area of the plant discharge. The majority of this information has been compiled by Jangaard (1972). Unfortunately, no chemical monitoring occurred concurrently with the fish-kill observations such that the concentration or dose/response effects could be determined. Secondly, some marine fish, which were the organisms most seriously affected, may have traveled out of the plume between the time of exposure and appearance of symptoms or death. Therefore, the areal extent of environmental impact could not be precisely defined.

Immediately after the beginning of operations in December, 1968, fish mortalities occurred at distances up to 1-1/2 miles from ERCO's plant in Long Harbour, Newfoundland. The plant was shut down for repairs and reopened in January, 1969. The plant processed phosphorus until May 2, 1969, when it was closed to install pollution abatement facilities. From January to May, however, large quantities of suspended solids, WP (average concentration 13 ppm or 1270 pounds/day), fluoride, cyanide, and ammonia were discharged. Fish kills occurred throughout Placentia Bay and had extended into adjacent St. Mary's Bay by April 1969. Significant fish kills occurred over an area roughly 20 by 50 miles. Environmental monitoring efforts began in May, 1969. Fish tissue sampling extended until April, 1970. Water and sediment monitoring was carried on until spring of 1971.

In order to prevent continued contamination of the environment with WP, ERCO built a pond series with a capacity of 3.8×10^6 cubic feet and began to recycle all process water which had come into contact with elemental phosphorus. Prior to this modification, plant discharge had resulted in siltation over an area 2000 x 300 feet around the plant outfall up to sediment depths of 18 inches. This discharged material, containing up to one percent WP content (Ackman et al. 1970), apparently created a layer of low to zero dissolved oxygen in the bottom waters. Following the fish kills, ERCO removed most of the silt by dredging. At the end of this clean-up (August 1971), an area approximately 400 feet square still contained contaminated sediment with concentrations ranging from 0.1 to 1100 µg/kg WP.

The distribution of WP in water and sediment of Long Harbour was monitored by the Fisheries Research Board of Canada (Ackman et al. 1971; Addison et al. 1971; and Addison et al. 1972) to document possible fresh discharges and/or resuspension of WP deposits. Concentrations of WP were measured in thousands of samples of effluent, sediment, and water during this period. Elemental phosphorus concentrations were generally less than 3 µg/l in Long Harbour in 1969 and were limited to trace amounts (approximately 0.1 to 0.5 µg/l) at most stations. Only samples taken directly over the silt deposit contained higher concentrations. These ranged up to 500 µg/l during the period 1969-1970.

Detectable WP in the water column was limited to Long Harbour. During 1970 and 1971, seawater concentrations were generally far below 1 µg/l in Long Harbour.

Sediment monitoring showed that concentrations ranging from 83 to 1940 mg/kg of WP were present in the silted area in May, 1969, immediately after cessation of operations. No WP-contaminated sediment was found in the outer part of Long Harbour in May. By July, 1969, tidal action had spread contaminated sediment to give concentrations of 0-18 mg/kg in soft muds inshore of the outfall and up to one mile away from the discharge. One core sample taken at this distance showed a concentration of 95 mg/kg. Sampling of stations where all of the sediment was not mechanically removed showed that WP concentrations did not decrease significantly over an 18-month period. The persistence of detectable but low (less than or equal to 1 µg/l) concentrations of WP in the water column over contaminated deposits suggests that WP was maintained in the water column due to sediment resuspension in the absence of discharge of WP.

Ackman et al. 1970 and Hodder et al. 1972 have documented the effects of the effluent on fish populations. These data showed that extensive mortalities occurred over the entire upper area of Placentia Bay. Fish census data reported by Hodder et al. suggested that 5/6 of the herring (Culpea harengus) population was destroyed in the area during 1969; Ackman et al. (1970) reported an 80-90 percent loss. The documentation of fish kills suggests that the fish were moving counter-clockwise up the bay, contacted the plume and died either on the spot or many miles distant (Ackman et al. 1970). No WP concentrations were monitored in conjunction with fish mortality or migration, however.

The results of cod (Gadus morhua) and herring (C. harengus) tissue analysis showed that fish which contained concentrations above 500 µg/kg in muscle died rapidly while fish with concentrations of 50 to 100 µg/kg were able to move several miles before death.

Ackman et al. (1970) sampled fish muscle tissue in dead and live fish taken before and after dredging operations in Long Harbour. The dredging resulted in concentrations of 0.5 to 1.0 µg/l in the harbor near the dredge. Elemental phosphorus was undetectable in 44 percent of the fish caught before dredging while a total of 78 percent contained less than 10 ppb in their flesh. After dredging, all fish taken contained detectable WP in their tissues. The distribution of tissue concentrations in live and dead fish is shown below:

	Percent in Each Concentration Range				
WP Concentration in flesh (ppb)	0-9	10-91	20-29	30-39	Over 40
Live Fish	55	26	11	3	5
Dead Fish	33	22	11	-	33

These data suggest that significant effects on marine fish populations occur at seawater concentrations of WP less than 1 µg/l.

Marine invertebrates were apparently less sensitive to WP toxicity than fish. Peer (1972) studied the distribution of invertebrates in Long Harbour in May, 1969, and found that deaths were confined to the inner harbor. Live mussels, Modiolus modiolus, were found within 300 feet of the effluent pipe while scallops (Pecten sp.) occurred within 1000 feet of the discharge. Amphipod populations were extremely reduced in the inner harbor, however, and Echinarachinus parma (sand dollar) mortality was significantly increased. Black (1973) studied the effects of the pollution episode on the mussel, Mytilus edulis, and the periwinkle Littorina littorea. Mussel populations apparently were unaffected. Littorina populations may have been destroyed by the discharge since no organisms predating the discharge could be found. Sediment WP concentrations in the area studied in these two investigations ranged from 0.07 to 1400 µg/kg. Comparison of the above data relating to invertebrate distributions in the harbour with the sediment WP concentrations reviewed earlier in this section suggests that environmental effects on marine invertebrates occur at concentrations above about 50 µg/kg of WP in sediment.

The WP monitoring data taken during this study suggest that in the marine environment concentrations greater than 1 µg/l in water do not persist for appreciable periods of time. Sediment concentrations, however, are stable and resuspension may provide a source to maintain 0.5 to 1.0 µg/l in overlying water. Such concentrations apparently affect fish populations and allow bioaccumulation of up to 10 to 40 times in flesh of the herring. Sediment concentrations above 70 µg/kg and water concentrations of 3 µg/l are associated with impacts on the invertebrate community in the form of selected mortalities. No concentration or dose-effect relationship can be defined for the acute effects of the 1969 fish kills or Littorina disappearance.

V. Criteria Development

In developing water quality criteria, all available data were considered. However, the laboratory bioassay results were the only data where WP concentrations could be related directly to biologic effects. Three approaches, outlined below, were compared in order to arrive at suitable criteria:

1. The proposed EPA procedure as outlined in the Federal Register (EPA 1978).
2. Traditional approaches (APHA 1975; National Academy of Sciences 1973; EPA 1976) which develop criteria based on application factors and acute toxicity values (EC or LC50s) for sensitive species.
   a. The lowest LC or EC50 value found multiplied by a conservative application factor. This factor is chosen by experience in order to provide a conversion to chronic effects based on the nature of the toxicant.
   b. The lowest LC or EC50 value found multiplied by the lowest experimentally derived application factor.

Proposed EPA Procedure. The recently proposed EPA procedure provides a very detailed protocol for evaluating a bioassay data base to determine water quality criteria. Precise procedures have been described for converting data to a common basis and for deriving criteria from the converted data. This procedure may or may not be adopted in its present form. To facilitate the reader's understanding of this procedure, the same paragraph notation will be utilized herein as that used in the "Guidelines" section of the EPA procedure.

IA. Final Freshwater Fish Acute Value

A. Data base (see Tables 8 and 9).
B. Adjust nominal concentrations by a factor 0.77 to simulate results based on measured concentrations (see Table 15)
C. Adjust for reported test results from 24-, 48-, and 72-hour tests by factors of 0.66, 0.81 and 0.92, respectively (see Table 15)
D. Adjust values from static tests by a factor of 0.71 to simulate results from flow-through tests (see Table 15)
E. For each species the geometric mean of the LC50 values (corrected when necessary) is shown in Table 16.
F. The geometric mean of all species geometric means is 17.7 µg/l.
G. The final freshwater fish acute value is the lower of the following values:
   1. The geometric mean from item F, above, divided by 3.9, i.e. 4.5 µg/l.
   2. The lowest LC50 value (corrected when necessary) based on measured concentrations from a flow-through test (i.e. 1.1 µg/l)

   Therefore, the final freshwater fish acute value for white phosphorus is 1.1 µg/l.

IB. Final Saltwater Fish Acute Value

A. Data base (see Tables 8 and 9)
B. Adjust nominal concentrations by a factor of 0.77 to simulate results based on measured concentrations (see Table 18)
C. Adjust for reported test results from 24-, 48-, and 72-hour tests by factors of 0.66, 0.81 and 0.92, respectively (see Table 18)
D. Adjust values from static tests by a factor of 0.71 to simulate results from flow-through tests (see Table 18)
E. For each species the geometric mean of the LC50 values (corrected when necessary) is shown in Table 17.
F. The geometric mean of all species geometric means is 4.2 µg/l.
G. The final saltwater fish acute value is the lower of the following values:
   1. The geometric mean from item F, above, divided by 3.7, i.e., 1.1 µg/l.
   2. The lowest LC50 value (corrected when necessary) based on measured concentrations from a flow-through test, i.e., 1.8 µg/l.

   Therefore, the final saltwater fish acute value for white phosphorus is 1.1 µg/l.

TABLE 15

DATA BASE FOR FRESHWATER FISH ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Species	Test Type of Reported LC50	Reported LC50 (µg/ℓ)	Overall Correction Factor	Corrected LC50 (µg/ℓ)	Reference
Bluegill	Nom.[a], 96-hr., Static	72	0.547	39.4	Isom (1960)
		6		3.28	Bentley et al. (1978)
		5		2.73	
		5		2.73	
		2		1.09	
		5		2.73	
		4		2.19	
		86		47.0	
		69		37.7	
		8		4.37	
		4		2.19	
		4		2.19	
		4		2.19	
		6		3.28	
		9		4.92	
	Meas.[b], 96-hr., Static	29.0	0.71	20.6	Pearson et al. (1978)
	Nom., 96-hr., Flow-thru	2.4	0.77	1.85	Bentley et al. (1978)
Fathead Minnow	Nom., 96-hr., Static	20	0.547	10.1	Bentley et al. (1978)
		>560		-	
		154		84.2	
		74		40.5	
		21		11.5	
		18		9.84	
Channel Catfish	Nom., 96-hr., Static	73	0.547	39.9	Bentley et al. (1978)
	Meas., 96-hr., Flow-thru	>19	1.0	-	
Mosquito fish	Meas., 96-hr., Static	63.0	0.71	44.7	Pearson et al. (1978)
Brook Trout	Nom., 96-hr., Static	22	0.547	12.0	Bentley et al. (1978)
Atlantic Salmon	Nom., ~48-hr., Flow-thru	22.8	0.624	14.2	Zitko et al. (1970)

[a]Nominal.

[b]Measured.

TABLE 16

COMBINED DATA BASE FOR FRESHWATER FISH ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Fish Species	No. of Values	Geometric Mean of All LC50 Values by Species, µg/l
Bluegill	17	4.75
Fathead Minnow	5	21.1
Channel Catfish	1	39.9
Mosquito fish	1	44.7
Brook Trout	1	12.0
Atlantic Salmon	1	14.2

TABLE 17

COMBINED DATA BASE FOR SALTWATER FISH ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Fish Species	No. of Values	Geometric Mean of All LC50 Values by Species, µg/l
Atlantic Herring	1	2.02
Brook Trout	1	2.00
Atlantic Salmon	1	1.77
Atlantic Cod	2	4.75
Cunner	1	37.6

TABLE 18

DATA BASE FOR SALTWATER FISH ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Species	Test Type of Reported LC50	Reported LC50 (µg/ℓ)	Overall Correction Factor	Corrected LC50 (µg/ℓ)	Reference
Atlantic Herring	Nom.[a], 96-hr., Static	~3.7	0.547	2.02	Zitko et al. (1970)
Brook Trout	Nom., 96-hr., Flow-thru	~2.6	0.77	2.00	Fletcher et al. (1976)
Atlantic Salmon	Nom., 96-hr., Flow-thru	~2.3	0.77	1.77	Fletcher & Hoyle (1972)
Atlantic Cod	Nom., 96-hr., Flow-thru	~2.5	0.77	1.93	Fletcher & Hoyle (1972)
	Meas.[b], 48-hr., Flow-thru	14.4	0.81	11.7	Maddock & Taylor (1976)
Cunner	Nom., ~24-hr., Flow-thru	74.0	0.508	37.6	Fletcher et al. (1971)

[a]Nominal.
[b]Measured.

IIA. Final Freshwater Fish Chronic Value

A. Chronic values are calculated as the geometric mean of the MATC limits for life-cycle or partial life-cycle tests, one-half of the geometric mean of the MATC limits derived from embryo-larval tests (see Table 19).
B. Acceptable chronic values are available for one species as a result of embryo-larval tests, however, no acceptable chronic value is available for another species employed as test organism in both life-cycle and embryo-larval tests.
C. The final freshwater fish chronic value is the lowest of the following values:
   1. The lowest individual chronic value, which is indeterminate, but is less than 0.40 µg/l.
   2a. For each species the geometric means of chronic values from item A above is determined (see Table 19).
   2b. The geometric mean of the geometric means of all species cannot be determined, but is less than 2.9 µg/l.
   3. This item requires matched pairs of MATC limits and 96-hour LC50 values based on flow-through tests performed with measured concentrations. Since the 96-hour LC50 from flow-through toxicity test results for the species for which acceptable chronic values are available is indeterminate (see Table 9), no such matched pairs exist.

Therefore, since the lowest value from item C above is indeterminate, i.e. <0.40 µg/l, no final freshwater fish chronic value for white phosphorus can be derived.

IIB. Final Saltwater Fish Chronic Value

A. See item IIA.A above.
B. No acceptable chronic values are available for saltwater fish, therefore, no final saltwater fish chronic value can be derived.

IIIA. Final Freshwater Invertebrate Acute Value

A. Data base (see Tables 6 and 7).
B. If EC50 values are available from one test for more than one of the following time periods, 24-, 48-, 72- and 96-hours, use only the one for the longest duration (see Table 20).
C. Adjust nominal concentrations by a factor of 0.77 to simulate results based on measured concentrations (see Table 20).
D. EPA protocol contains no Item III-D. However, W. A. Brungs, Technical Assistant Director, EPA Environmental Research Laboratory, Duluth, Minn., has indicated a correction factor of 0.43 should be applied to convert 48-hour EC50 values to 96-hour EC50 values (see Table 20).*
E. Adjust values from static tests by a factor of 1.1 to simulate results from flow-through tests (see Table 20).
F. For each species, the geometric mean of the LC50 values (corrected when necessary) is shown in Table 21.
G. The geometric mean of all species geometric mean is 25.4 µg/l.

*Personal communication. Brungs, W.A., EPA Environmental Research Laboratories, Duluth, Minn. 1978.

TABLE 19

DATA BASE FOR FRESHWATER FISH CHRONIC VALUE
WHITE PHOSPHORUS

Life-Cycle Tests - Concentrations in µg/l

Fish Species	Response Parameter	MATC Limits	Geometric Mean
Fathead Minnow	2nd generation hatchability of eggs from exposed parents	0-0.40[a]	<0.40[a]

Embryo-Larval Test

Fish Species	Response Parameter	MATC Limits	Geometric Mean	1/2 Geometric Mean
Fathead Minnow	Length	0-1.5[a]	<1.5[a]	<1.5[a]
Channel Catfish	Survival & Length	5.0-6.8	5.83	2.92

Summary of Chronic Value Data

Fish Species	Geometric Mean
Fathead Minnow	<0.40[a]
Channel Catfish	2.92

[a]Lowest challenge concentration.

TABLE 20

DATA BASE FOR FRESHWATER INVERTEBRATE ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Species	Test Type of Reported LC50	Reported LC50 (µg/ℓ)	Overall Correction Factor	Corrected LC50 (µg/ℓ)	Reference
Daphnia magna	Nom.[a], 48-hr., Static	30	0.364	10.9	Bentley et al. (1978)
	Nom., 48-hr., Flow-thru	>50	0.331	-	
Branchiura sowerbyi	Nom., 48-hr., Static	38	0.364	13.8	
Palaemonetes kadiakensis	Meas.[b], 96-hr., Static	32	1.1	35.2	Pearson et al. (1978)
Gammarus fasciatus	Nom., 48-hr., Static	250	0.364	91.1	Bentley et al. (1978)
Asellus militaris	Nom., 48-hr., Static	>560	0.364	-	
Chaoborus punctipennis	Meas., 48-hr., Static	38	0.437	18.0	Pearson et al. (1978)
Chironomus tentans	Nom., 48-hr., Static	140	0.364	51.0	Bentley et al. (1978)
	Nom., 48-hr., Flow-thru	111	0.331	36.8	
Glyptotendipes sp.	Meas., 48-hr., Static	38	0.437	18.0	Pearson et al. (1978)

[a]Nominal.
[b]Measured.

TABLE 21

COMBINED DATA BASE FOR FRESHWATER INVERTEBRATES ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Invertebrate Species	Number of Values	Geometric Mean of All LC50 Values by Species, µg/l
Water Flea	1	10.9
Tubificid	1	13.8
Glass Shrimp	1	35.2
Scud	1	91.1
Phantom Midge	1	18.0
Midge (*Glyptotendipes* sp.)	1	18.0
Midge (*Chironomus tentans*)	2	43.3

H. The final freshwater invertebrate acute value is the lower of the following values:
   1. The geometric mean from Item G, above, divided by 21, i.e., 1.2 µg/l.
   2. The lowest LC50 value (corrected when necessary) based on measured concentrations from a flow-through test, i.e., 10.9 µg/l.

   Therefore, the final freshwater invertebrate acute value for white phosphorus is 1.2 µg/l.

IIIB. Final Saltwater Invertebrate Acute Value

A. Data base (see Tables 6 and 7)
B. EC50 values are only available for test durations of 24 hours.
C. Adjust nominal concentrations by a factor of 0.77 to simulate results based on measured concentrations (see Table 22)
D. EPA protocol contains no Item III-D. However, W. A. Brungs, Technical Assistant Director, EPA Environmental Research Laboratory, Duluth, Minn., has indicated that a correction of 0.43 should be applied to convert 48-hour EC50 values to 96-hour EC50 values (see Table 22)*.
E. Adjust values from static tests by a factor of 1.1 to simulate results from flow-through tests (see Table 22)
F. For each species, the geometric mean of the LC50 values (corrected when necessary) is shown in Table 23.
G. The geometric mean of all species geometric mean is 1,650 µg/l.
H. The final saltwater invertebrate acute value is the lower of the following values:
   1. The geometric mean from G, above, divided by 49 (i.e., 34 µg/l) or
   2. The lowest EC50 value based on measured concentrations from a flow-through test.

   Therefore, the final saltwater invertebrate acute value for white phosphorus is 34 µg/l.

IVA. Final Freshwater Invertebrate Chronic Value

A. Chronic values are calculated as the geometric mean of the MATC from life-cycle or partial life-cycle tests (see Table 24)
B. Acceptable chronic values are available for one species of freshwater invertebrate.
C. The final freshwater invertebrate chronic value is the lower of the following values:
   1. The lowest chronic value, i.e., (7.7 µg/l).
   2. The geometric mean of the geometric means for all species divided by 5.1 (i.e., 7.7/5.1) equals 1.5 µg/l.

   Therefore, the final freshwater invertebrate chronic value for white phosphorus is 1.5 µg/l.

IVB. Final Saltwater Invertebrate Chronic Value

A. Chronic values are calculated as the geometric mean of the MATC from life-cycle or partial life-cycle tests.

*Personal communication. Brungs, W.A., EPA Environmental Research Laboratories, Duluth, Minn. 1978.

TABLE 22

DATA BASE FOR SALTWATER INVERTEBRATE ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Species	Test Type of Reported LC50	Reported LC50 (µg/ℓ)	Overall Correction Factor	Corrected LC50 (µg/ℓ)	Reference
Gammarus oceanicus	Nominal, 24-hr., Flow-thru	~6500	0.331	2150	Zitko et al. (1970)
	Nominal, 24-hr., Static	~3500	0.364	1270	

TABLE 23

COMBINED DATA BASE FOR SALTWATER INVERTEBRATES ACUTE VALUE
WHITE PHOSPHORUS - 96-HOUR LC50s

Invertebrate Species	Number of Values	Geometric Mean of All LC50 Values by Species, µg/l
Beach Flea	2	1,650

TABLE 24

DATA BASE FOR FRESHWATER INVERTEBRATE CHRONIC VALUE

Life-Cycle Tests - Concentrations in µg/ℓ

Invertebrate Species	Response Parameter	MATC Limits	Geometric Mean
Daphnia magna	1st generation adult 21-day survival; number of offspring from exposed parents; 2nd generation 42-day survival	6.9-8.7	7.7

Summary of Chronic Value Data

Invertebrate Species	Geometric Mean
Daphnia magna	7.7

B. No acceptable saltwater chronic value is available, therefore no final saltwater invertebrate chronic value can be derived.

VA. Final Freshwater Plant Value

A. Tests were conducted on four species of algae.
B. The lowest available plant toxicity value is the 96-hour no-effect level based on growth inhibition of Navicula pelliculosa, i.e. >7 <20 µg/l geometric mean equals 12 µg/l. Therefore the freshwater plant value for white phosphorus is 12 µg/l.

VB. Final Saltwater Plant Value

A. Not applicable.
B. No values are available for saltwater plants, therefore no final saltwater plant value can be derived.

VIA. Freshwater Residue Limited Toxicant Concentration (RLTC)

A. The lowest published lethal dose (i.e., LDLo) appearing in the Registry of Toxic Effects of Chemical Substances, 1977, is the oral LDLo for humans, i.e., 1400 µg/kg.
B. Sufficient data are available to establish the RLTC (see Table 25)
C. The arithmetic average bioconcentration factor (BCF) of all freshwater fish species arithmetic averages is 73.
D. Not applicable.
E. The freshwater RLTC for white phosphorus is the lowest maximum permissible tissue concentration from Item A above divided by the measured bioconcentration factor from Item C above, i.e., 1400/73 = 19 µg/l.

VIB. Saltwater Residue Limited Toxicant Concentration

Insufficient data are available for this analysis.

VII. Other Data

Other data will be considered in other criteria setting procedures which follow.

VIIIA. Final Freshwater Values

A. The "final freshwater acute value" is the lower of the final freshwater fish acute value and the final freshwater invertebrate acute value (i.e. 1.1 µg/l)
B. The "final freshwater chronic value" is the lowest of the following values:
   1. The final freshwater fish chronic value (i.e., less than 0.40 µg/l).
   2. The final freshwater invertebrate chronic value (i.e., 1.5 µg/l).
   3. The final freshwater plant value (i.e., 12 µg/l), and

TABLE 25

DATA BASE FOR FRESHWATER RESIDUAL LIMITED TOXICANT CONCENTRATIONS (RLTC)

Fish Species	BCF (For Exposure Duration Greater Than 27 Days)				Reference
	Tissue	Reported Range	Average	Species Average	
Fathead Minnow	Muscle	127 - <160	127	127	Bentley et al. (1977)
Channel Catfish	Muscle	24.6 - 100	64	64	
Atlantic Salmon	Muscle	24 - 28	27	27	Fletcher (1974)

4. The freshwater RLTC (i.e., 19 µg/l).
Therefore, since the lowest freshwater chronic value is indeterminate, i.e., less than 0.40 µg/l, no "final freshwater chronic value" for white phosphorus can be derived.

VIIIB. Final Saltwater Values

A. The "final saltwater acute value" is the lower of the final saltwater fish acute value and the final saltwater invertebrate acute value, i.e., 39 µg/l.
B. Insufficient data are available to establish a "final saltwater chronic value" for white phosphorus under this guideline.

IXA. Final Freshwater Values

A. An acceptable "final freshwater chronic value" is available only for invertebrates, i.e. 1.5 µg/l.
B. The maximum freshwater white phosphorus concentration should never exceed the final acute value, i.e., 1.1 µg/l.
The 24-hour average white phosphorus concentration should never exceed the lower of the following values:
1. The final freshwater acute value from Item VIIIA.A. above times 0.44, i.e., (1.1)(0.44) = 0.48 µg/l.
2. The final freshwater chronic value from Item VIIIA.B. above, i.e. an indeterminate value but less than 0.40 µg/l.
Therefore, the freshwater 24-hour average concentration criterion for white phosphorus cannot be developed by this guideline.

IXB. Final Saltwater Values

A. Insufficient data are available to establish a criterion for white phosphorus under this guideline.

General Application Factor. A procedure for deriving environmentally safe concentrations that is frequently utilized when only acute toxicity data are available is the use of an application factor. This factor is applied to the lowest acute toxicity value. The ability of white phosphorus to persist in aquatic systems, particularly in sediments, as well as its cumulative toxicity would indicate that the commonly accepted, conservative application factor of 0.01 is appropriate for white phosphorus (National Academy of Sciences 1973; EPA 1976). Applying this factor to the lowest acutely toxic result, 2 µg/l for the bluegill, gives a safe concentration of 0.02 µg/l.

Experimentally Derived Application Factor. A third procedure for deriving environmentally safe concentrations is similar to the previously discussed procedure except that the application factor is experimentally derived. Where both acute and chronic data are available for a species, the experimental application factor is the ratio of the highest challenge concentration resulting in no significant adverse effect (i.e. the lower of the MATC limits) to the lowest acute EC50 or LC50 value for that species. If data for more than one species exists, the minimum application factor is utilized. This factor, multiplied by the lowest acute EC50 or LC50 value for any species, determines an environmentally safe concentration.

The experimental application factors are shown in Table 26. The lowest application factor based on conclusive partial or complete life-cycle toxicity tests was 0.07. The life-cycle tests for fathead minnows showed effects at 0.4 µg/l, the lowest concentration tested. This concentration gives an application factor of <0.02. Using regression techniques vs. the life-cycle tests gives a lowest no-effect level of 0.08 µg/l. This concentration results in the minimum application factor of 0.004.

Utilizing the lowest estimated application factor of 0.004 and the lowest acute, 96-hour LC50 for bluegill (2 µg/l) a value of 0.008 µg/l is obtained as a maximum safe concentration of WP.

Final Criteria Formulation. The lack of a demonstrated no-effect level in the aquatic toxicity testing done to date requires that any determination of an environmentally safe concentration be based on less reliable extrapolation techniques. Because of this, it is concluded that insufficient information exists to recommend final criteria for white phosphorus. However, the available data indicate that an environmentally safe concentration should be equal to or less than 0.01 µg/l as WP.

TABLE 26

EXPERIMENTALLY DERIVED APPLICATION FACTORS - WHITE PHOSPHORUS

Species	Lowest Reported Acute Value		Chronic Value		Application Factor
	Test Type of Reported EC50/LC50	EC50/LC50 (µg/l)	Response Parameters	MATC Limits (µg/l)	
Channel Catfish	Nominal, 96-HR LC50, Static	73	Egg/Fry 30-Day Test; Survival & Length	5.0-6.8	0.07
Fathead Minnow	Nominal, 96-HR LC50, Static	18	Full Life-Cycle Test; 2nd Generation Hatchability of Eggs From Exposed Parents	<0.40	<0.02
			Full Life-Cycle Test; 1st Generation, 241 Days Post-Hatch, Male, Wet Weight - Male, Length	0.08-0.17	0.004
Daphnia	Nominal, 48-HR EC50, Static	30	Life-Cycle Test; 1st Generation - 21-Day Survival, Number Offspring from Exposed Parents, 2nd Generation - 42-Day Survival	6.9-8.7	0.23

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