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Installation Restoration Research Program

Summary and Evaluation for White Phosphorus Remediation: A Literature Review

by Yilda B. Rivera, Trudy Olin, R. Mark Bricka

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Prepared for Headquarters, U.S. Army Corps of Engineers

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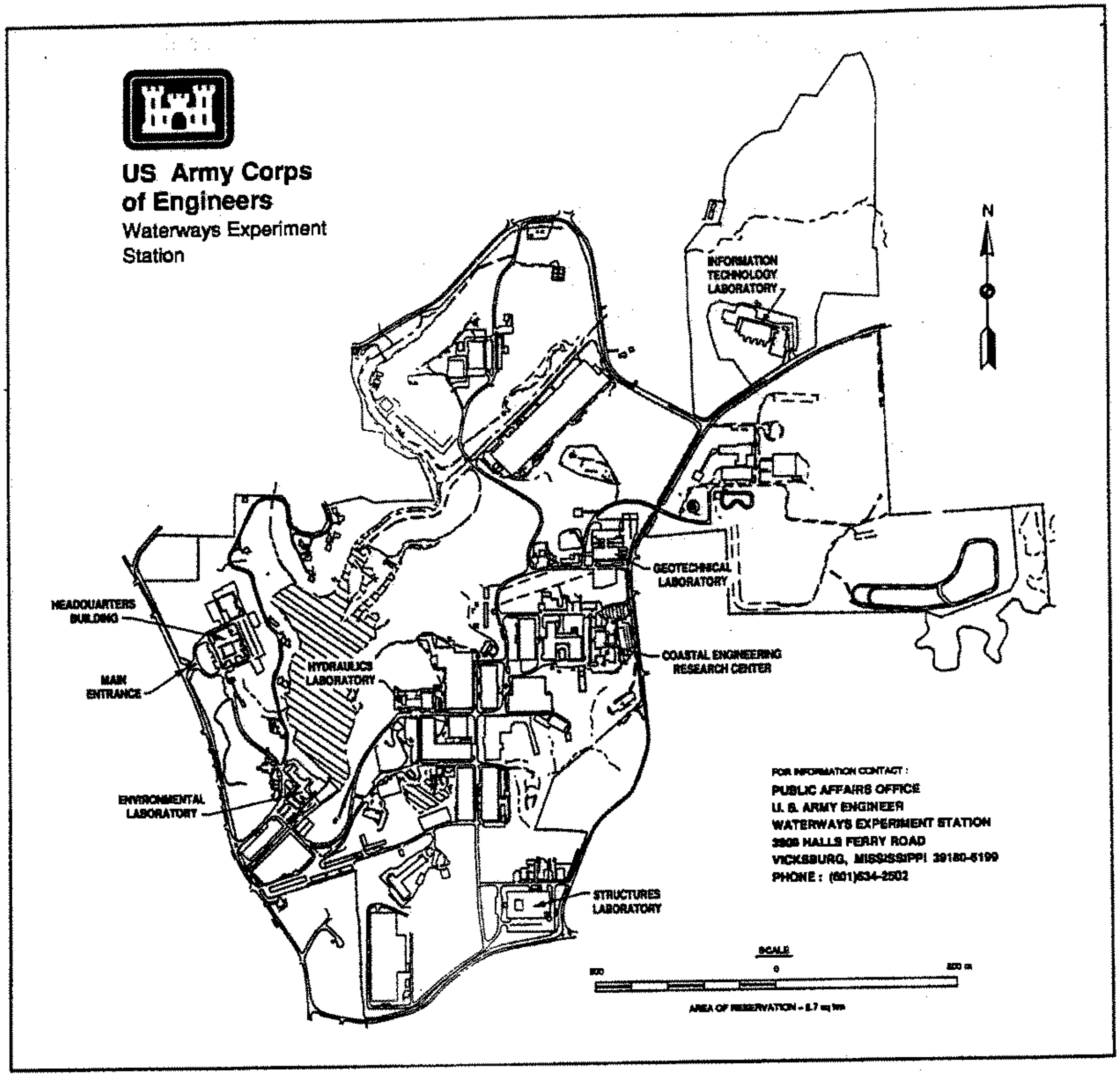

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Preface

The studies reported herein were conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The research was sponsored by the Department of Army Installation Restoration Research Program (IRRP). Dr. Clem Myer was the IRRP Coordinator at the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers. Dr. John Cullinane, WES, was the IRRP Program Manager.

This report was prepared by Mses. Yilda B. Rivera and Trudy Olin of the Environmental Resources Engineering Branch (EREB), EL, and Mr. R. Mark Bricka of the Environmental Restoration Branch (ERB), EL.

The work was conducted under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and Mr. Thomas R. Patin, Chief, EREB, and under the general supervision of Mr. Norman R. Francingues, Chief, EED, and Dr. John W. Keeley, Director, EL.

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
Fahrenheit degrees	5/9	Celsius degrees or kelvins[1]
feet	0.3048	meters
inches	2.54	centimeters
mile (U.S. statute)	1.609347	kilometers
pounds (mass)	0.4535924	kilograms
tons (2,000 pounds, mass)	907.1847	kilograms
yards	0.9144	meters

[1] To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9)(F - 32). To obtain kelvin (K) readings, use the following formula: K = (5/9)(F - 32) + 273.15.

1 Introduction

This report summarizes an extensive literature search that was conducted regarding the environmental fate of white phosphorus (WP) and applicable treatment technologies. The health risks associated with WP exposure, documented environmental effects, transformation processes, degradation products, and the potentially applicable treatment technologies will be identified and evaluated.

WP contamination has been identified in soil and water at military training and munitions production facilities and is the third highest ranked contaminant of concern of the U.S. Army (Feige and Strauss 1994). Until recently, long-term environmental contamination from the explosion of projectiles containing WP was considered unlikely due to the thermodynamic instability of WP in the presence of atmospheric oxygen. However, Berkowitz et al. (1981), in assessing the potential hazards associated with the use of phosphorus smoke munitions, reported that WP residues in aquatic systems can be extremely toxic. Berkowitz stated that the deposition or washout of any undegraded WP, especially in small water bodies, may create exposure risks to resident finfish, invertebrates, and waterfowl, even if resultant WP concentrations are in the low ppb range. All those concerns motivated the Interagency Testing Committee (ITC) to designate WP for priority testing under the Toxic Substances Control Act (TSCA) (BNA Chemical Regulation Daily, 1994). The ITC is a congressionally mandated committee comprised of representatives from more than a dozen Federal regulatory and research agencies. The ITC was established to make recommendations to the Environmental Protection Agency (EPA) regarding the chemical substances and mixtures to which the EPA would give priority consideration for the promulgation of rules. These rules are presented in 32 Code of Federal Regulations (CFR) part 184, subpart K.

The deposition of WP products into the environment from the incomplete combustion of smoke devices and from manufacturing practices has created concern regarding the fate of these agents in the environment. Therefore, the high toxicity of WP residues in wetland areas at military training facilities motivated the study and assessment of WP contamination.

This report is divided into eight chapters:

a. Introduction. Provides the purpose and scope of this report and brief information that motivated the study on WP. The organization of the report is presented.

b. Background. Presents a background on WP chemistry, uses, modes of dissemination, and documented environmental effects. A summary on environmental regulations on WP is also presented.

c. Analytical methods. Describes and compares two main methods for WP analysis.

d. Safety concerns. Provides some general information on safety aspects of WP, effects of absorption, medical surveillance program, and brief information on personal protective equipment and methods to use when handling WP.

e. Environmental fate. Presents several WP transformation processes, WP breakdown products, and phosphorus deposition in soils.

f. WP studies at military installations. Describes two basic studies: distribution of WP residues conducted by Cold Regions Research and Engineering Laboratory (CRREL) and several studies on WP wetland storage installation assessment conducted by the U.S. Army Engineer Waterways Experiment Station (WES) where the risk of WP contamination at 21 military installations is evaluated.

g. Treatment technologies. Presents and discusses several technologies currently being studied for the treatment of WP-contaminated soils.

h. Conclusions and recommendations. Presents a concise summary and the major conclusions on the literature review on WP contamination.

2 Background

Chemistry of White Phosphorus

WP is a transparent waxy solid. It darkens upon exposure to light and is highly reactive, igniting spontaneously in air at temperatures above 30 °C. WP should be stored and transported submerged in water to ensure its stability.

WP is the most reactive of the three allotropes of elemental phosphorus (white, red, and black). Its molecular structure is that of a regular tetrahedron with a phosphorus atom at each apex. The molecular formula is P_4 and the molecular weight is 124. WP has two forms: α- and β-. When α- white phosphorus is cooled below -76.9 °C at atmospheric pressure, the hexagonal modification (β-WP) is formed. This material has the same general appearance and characteristics as the α-form (Wasti, Abaidoo, and Villaume 1978). The heat of transformation of the α- and β-form is equal to -3.8 ± 0.2 Kcal/mole P_4 at -76.9 °C. β-WP is the common form of the element produced commercially and used in WP munitions. Impurities present in WP such as arsenic and hydrocarbons can change its color varying it from white to yellow; therefore, it is also referred to as yellow phosphorus. Arsenic and other nonhydrocarbon impurities found in a representative sample of WP are shown in Table 1.

WP is insoluble in water; only slightly soluble in alcohol (C_2H_6O), ether, and benzene (C_6H_6); and very soluble in carbon disulfide (CS_2), phosphorus chloride (PCl_3), phosphorus oxychloride ($POCl_3$), liquid sulfur dioxide (SO_2), and liquid ammonia (NH_3). It combusts spontaneously in air, burning to the pentoxide (P_4O_{10}). WP is very toxic and poisonous, approximately 50 mg constituting a fatal dose. Characteristics of α- WP are summarized in Table 2.

WP is commercially prepared by roasting phosphate ores with silica (SiO_2) and coke in an electric furnace. The silica reacts with the ore to form phosphorus pentoxide (P_4O_{10}), which is then reduced to WP by the coke. An overall approximation of the reaction is shown:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4\uparrow + 10CO\uparrow$$

Table 1
Representative Metal Concentration of Inorganic Contaminants in a WP Particle

Metal	Concentration, µg/g
Boron	715
Cadmium	0.88
Magnesium	3.60
Zinc	0.66
Silicon	377
Copper	1.22
Nickel	0.96
Manganese	0.58
Calcium	18.3
Molybdenum	0.09
Cobalt	0.57
Aluminum	20.0
Vanadium	4.20
Chromium	0.49
Iron	94.0
Lead	1.26
Barium	0.45
Sodium	9.50
Arsenic	84.0

Note: Table adapted from Yon, Wentsel, and Bane (1983).

The arrows (↑) in the equation show that WP (P_4 in the equation) and carbon monoxide (CO) are emitted as gases or vapors. The gaseous WP is cooled and condensed underwater to obtain high-purity (99.9-percent) WP.

Uses of WP

WP is used extensively in smoke-producing munitions and incendiary devices. Smoke munitions and incendiary devices are used by the U.S. Army

Table 2
Characteristics of WP

Parameter	Characteristics
Appearance	Colorless, white, or yellow waxy solid
Autoignition temperature	30 °C (moist air); higher in dry air
Boiling point	280.5 °C
CAS #	7729-14-0
Critical pressure	82.2 atm
Critical temperature	695 °C
Crystal structure	Cubic (56 molecules of P_4 per unit cell)
Density	1.828 g/cm^3
Heat capacity	22.18 cal/mole/degree (25 °C; 22.73 cal/mole/degree (44.1 °C)
Heat of combustion	710.2 ∓ 1.0 kcal/moleP_4
Heat of fusion	600 ∓ 3 cal/moleP_4 at 317.26 °K
Heat of sublimation	13.4 kcal/moleP_4
Index of refraction	1.8244 (D line, 29.2 °C)
Melting point	44.1 °C
Molecular formula	P_4
Molecular weight	123.90
Octanol/water partition coefficient	1,200
Solubility 25 °C (unless otherwise indicated)	
Absolute alcohol	2.5 g/ℓ
Benzene	28.6 g/ℓ
Carbon disulfide	1,250 g/ℓ
Chloroform	25 g/ℓ
Ether	9.6 g/ℓ
Water	4.1 mg/ℓ; 3 mg/ℓ at 15 °C
Olive oil	12.5 g/ℓ
Specific gravity	1.82 (solid, 20 °C); 1.745 (liquid, 44.5 °C)
Sublimation temperature	0.026 mm (20 °C); 0.122 mm (40 °C)
Vapor pressure	1 mm Hg at 76.6 °C; 0.026 mm Hg at 20 °C

Note: Gordon, Hartley, and Roberts (1992); Simmers, et al. (1993a-u); Yon, Wentsel, and Bene (1983).

in training to simulate, as closely as possible, the conditions likely to be encountered under combat situations. Its use as a screening smoke, deployed by means of bursting devices such as shells and grenades, is one source of its entry into the environment.

There are five basic systems for disseminating phosphorus smoke. They are artillery, tank guns, mortars, grenades, and aerial smoke systems (Yon, Wentsel, and Bane 1983). Artillery smoke munitions are available for 105-mm and 155-min howitzers (Figure 1). These weapon systems can provide obscuration. The prime function of the obscuration is to obstruct the visual spectrum and conceal the movement of friendly troops on the battlefield. Tank guns have munitions available for producing smoke for spotting and marking targets and signaling or dispensing obscuring smoke on small areas. WP-filled munitions are available for 75-mm, 90-mm, and 105-mm tank guns. The 60-mm, 81-mm, and 4.2-in.[1] mortars can deliver WP munitions for high-volume smoke operations (Figures 2 and 3). Smoke grenades are used for signaling and for screening small areas. They are used by the individual soldier, at distances of 30 to 35 m. Grenades are also launched by rifles and grenade launchers installed on tanks. Aerial smoke munitions consist of bombs, bomblets, and rockets. Some rockets are used in helicopter air delivery systems to produce smoke screens and to mark targets.

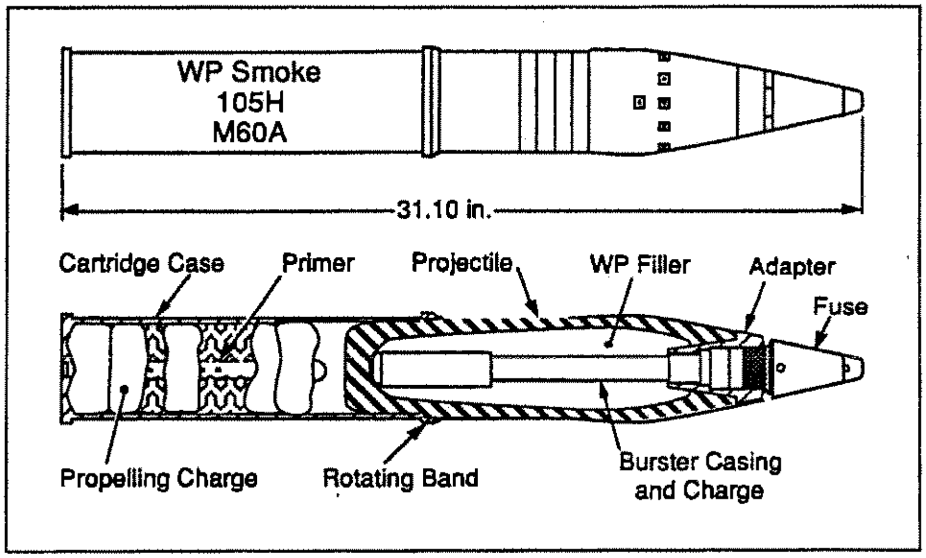

Figure 1. Diagram of a smoke-producing WP round (Racine et al. 1992)

At one time, WP was used in matches and fireworks and as a rat poison, but these uses were discontinued due to the high toxicity of WP (Gordon, Hartley, and Roberts 1992). It is still used in analytical chemistry, in the

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[1] A table of factors for converting non-SI units of measurement to SI units is presented on page vii.

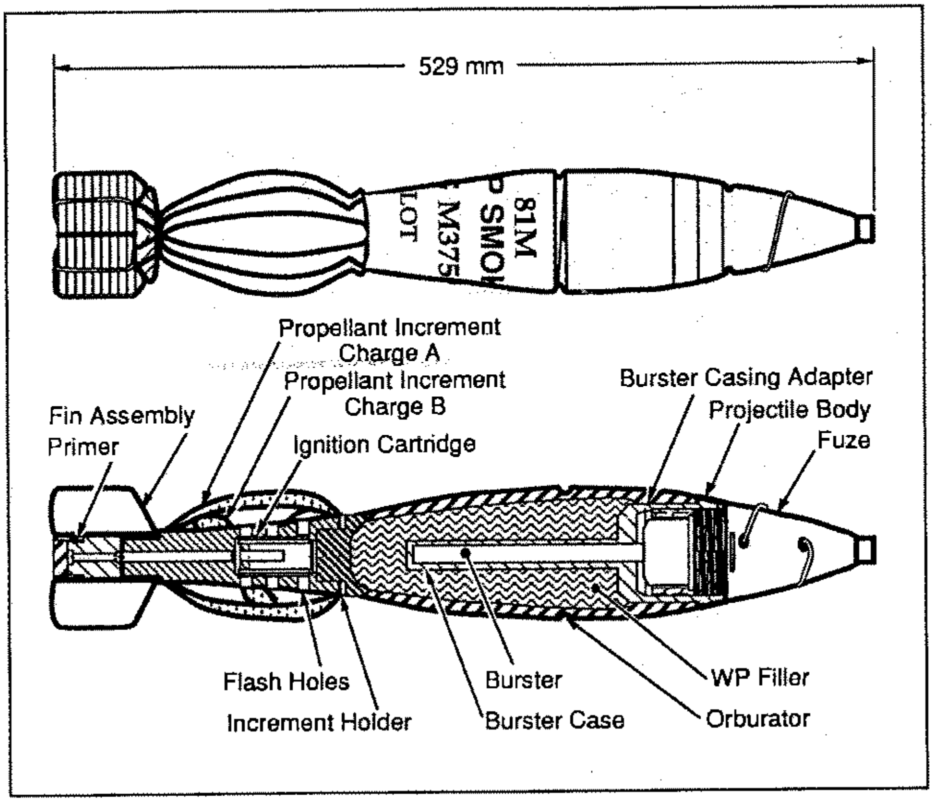

Figure 2. WP smoke round for 81-mm mortar (Walsh and Collins 1993)

manufacture of phosphoric acid and other phosphorus compounds, phosphor bronzes, metallic phosphides, as an additive to semiconductors, and in electroluminescent coatings.

Mode of Dissemination

When WP-filled munitions are deployed, WP reacts spontaneously with air. As long as oxygen is in contact with WP, the reaction will proceed to completion, and all the WP will combust. WP forms a dense cloud of white smoke consisting primarily of phosphorus oxides that react with water vapor to form various phosphoric acids (Chapter 5, Environmental Fate). When WP munitions are deployed, the phosphorus breaks up into minute particles which are dispersed over a large area. If the WP is immersed in water, it will immediately cease burning until it is again exposed to oxygen (Figure 4). Once in the water, the particles settle into the sediment where they remain stored. The stored particles are available to be consumed by the aquatic organisms and the waterfowls. WP is very toxic to waterfowl and may be magnified up to the food chain.

Figure 3. An 81-mm mortar (Walsh and Collins 1993)

The water generated from WP manufacture, production processes, and transport operations (phossy water) is another significant source of WP introduction to the environment. The term phossy water refers to water that has come into direct contact with the solid or liquid phosphorus. This water contains significant amounts of colloidal and larger WP particles as well as lesser amounts of dissolved phosphorus.

Environmental Effects of WP

Significant levels of WP have been observed in the environment. The knowledge of the environmental effect of WP on aquatic species is derived from studies initiated in the late 1960s in response to a massive fish kill caused by wastewater discharged from a factory manufacturing elemental phosphorus in Placentia Bay, Newfoundland (Idler 1969; Burrows and Dacre 1973). Sullivan et al. (1979) reported WP content in the effluent from the Electric Reduction Company of Canada to be 13 ppm. Discharge rates of 567 and 739 kg/day (1,250 and 1,630 lb/day) were reported for the WP and total phosphorus, respectively. Sediment monitoring showed that concentrations ranging from 83 to 1,940 ppm of WP were present around the plant outfall by May 1969. Two months later, tidal action had spread contaminated sediment to give concentrations of 0-18 ppm in soft muds inshore of the outfall and up to 1 mile away from the discharge. One core sample taken at this distance showed a concentration of 95-ppm WP. Concentrations in the bottom sediment, where the particulate WP settles as sludge, were measured at 5,000 ppm near the effluent pipe and 1 ppm at a distance 2.4 km from the pipe (Gordon, Hartley, and Roberts 1992).

The incident of the massive fish kill in Placentia Bay resulted in an avalanche of studies on the toxicological aspects of WP. Virtually all of the recently published work investigating the toxicity of WP to freshwater aquatic

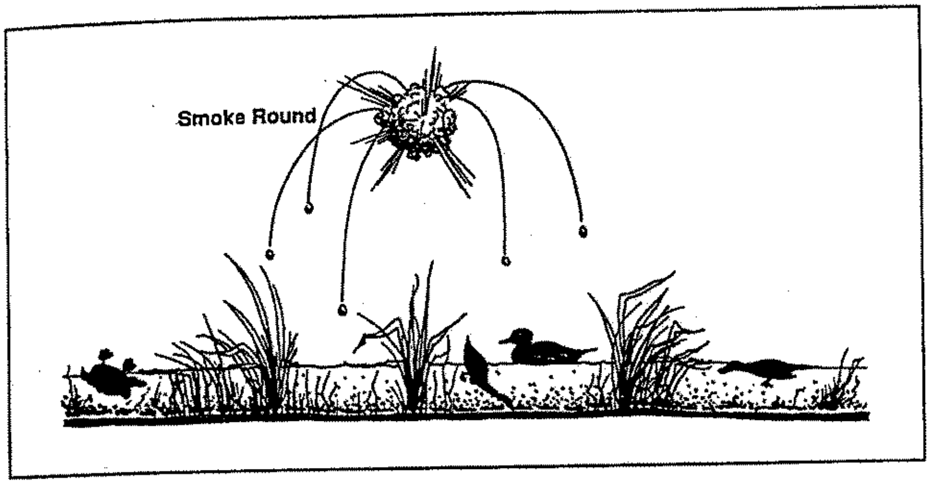

Figure 4. Proposed method by which WP from a smoke round exploding above the surface of shallow pond might be deposited and buried in ERF sediments (Racine et al. 1992)

organisms has been sponsored by the U.S. Army (Pearson et al. 1975). Toxicological studies on WP indicate that the substance is highly toxic to fish. The incipient lethal level in water is probably less than 1 ppb for most fish (Burrows and Dacre 1973). Phosphorus poisoning appears to be cumulative and irreversible. Furthermore, WP can be passed on to humans since a considerable portion, 25 percent or more, remains in the muscle of the fish after processing, storage, and cooking (Dyer et al. 1972 as cited in Burrows and Dacre 1973). WP is so toxic to some fish that it is difficult to set maximum safe levels.

The effect of wastewaters contaminated with WP on the biota of a shallow lake at Pine Bluff Arsenal (PBA), Arkansas, was investigated by Pearson et al. (1975). The wastewaters were discharged from a WP munitions-filling facility at PBA. Species abundance and distribution of benthic macroinvertebrates were adversely affected by the concentration of WP in the water and sediments of a shallow lake that received wastewater from the munitions filling operation (Pearson et al. 1975). Possible detrimental effects on human health, the legal ramifications of this discharge, and the uncertainty about its environmental fate led to the closure of the lake to all recreation.

The death of thousands of migrating waterfowl at Eagle River Flats (ERF), Alaska, has been documented (Racine et al. 1993b; Racine et al. 1993c; Walsh et al. 1993; and "EPA plans remediation handbook for explosives, radioactive waste-report on defense plant wastes" 1993). ERF is a 1,000-ha estuarine salt marsh at Fort Richardson. The annual dieoff of an estimated 1,000-2,000 migrating dabbling ducks and 10-50 swans in ERF was attributed to the ingestion of WP particles deposited in the sediments resulting from artillery and infantry training with smoke munitions (Racine et al. 1992). This marsh has been used for the past 40 years as an artillery impact range by the U.S. Army. The distribution and highest concentrations of WP were localized in two of the six feeding pond areas, covering about 15 ha. These two areas appear to represent the major sources of waterfowl poisoning in ERF (Racine et al. 1993a,b,c). In 1991, following the waterfowl mortality at ERF, the Assistant Secretary of the Army suspended the firing of WP munitions in wetland areas (Racine et al. 1994).

Salt marshes are among the most important coastal wetlands. They are dynamic, complex, and highly productive, supporting fisheries and waterfowl. The anoxic conditions of the bottom sediments preserve the highly reactive WP. Factors that determine the persistence of these particles include sediment porosity, moisture content, and temperature. Careful study of dying birds at ERF indicated that WP residues were present in their fat, gizzard contents and other digestive tissues, liver, and skin and breast muscle ("EPA plans remediation handbook for explosives, radioactive waste-report on defense plant wastes" 1993). WP was also found in the sediments where they were feeding. Other munitions-derived chemicals were also found, but not at levels high enough to cause death. However, there is controversy over the determination of WP as the contaminant directly responsible for the waterfowl mortality.

Environmental Regulations

WP is governed by several regulatory agencies. Worker's health, environmental aspects, and transportation are each regulated by a different agency within the Government. The agencies and regulations presented in this section are as follows:

a. National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA).

b. Environmental Protection Agency (EPA).

c. Department of Transportation (DOT).

NIOSH/OSHA

In 1978, NIOSH, along with OSHA, established a Permissible Exposure Limit for WP of 0.1 mg/m^3 8-hr, time-weighted average threshold limit value (TWA-TLV)—40-hr work week (Lide 1994). However, this level may not provide to exposed workers sufficient protection from undesirable effects (Gordon, Hartley, and Roberts 1992).

EPA

In 1977, EPA had suggested a permissible ambient goal of 1.4-$\mu g/\ell$ WP based on health effects (Sittig 1985). In 1979, Sullivan et al. (1979) recommended a 0.01-$\mu g/\ell$ WP as an environmentally safe concentration for marine and estuarine waters, based on an evaluation of available aquatic environmental data. An ambient water quality criterion for WP in water of 0.04 $\mu g/\ell$ is recommended for the protection of freshwater aquatic life (Gordon, Hartley, and Roberts 1992).

Resource Conservation and Recovery Act (RCRA). RCRA of 1976, Public Law (PL) 94-580, is the statutory basis for Federal regulation of solid and hazardous waste. The U.S. EPA has promulgated regulations implementing RCRA (40 CFR-Code of Federal Regulations- 260-264; 265-267) that identify and provide management requirements for the disposal of solid and hazardous wastes and promote resource conservation and recovery. WP is classified and regulated as characteristic hazardous material under RCRA because of its ignitability.

Toxic Substance Control Act (TSCA). The TSCA of 1976 (PL 94-469) addresses the commercial manufacture, use, and distribution of chemical substances. The use of smoke munitions by the Army for testing and training was not affected by the TSCA because the present smoke materials were developed before the TSCA became effective and were inventoried on the initial TSCA Inventory list (45 FR-Federal Regulation- 505444, 29 July 80; as cited in Yon, Wentsel, and Bane 1983). The Inventory list is a compilation of each chemical substance that is manufactured or processed in the U.S.

Although the use of WP munitions by the Army was not affected by TSCA, the concerns about the WP poisoning of waterfowl and contamination of waterways motivated the ITC to designate, in 1994, WP for priority testing under the TSCA. The ITC is a congressionally mandated committee, as established by TSCA §2603 §4(e)(2)(A), comprised of representatives from more than a dozen Federal regulatory and research agencies. According to TSCA §2603 §4(e), this committee is established to make recommendations to the EPA regarding the chemical substances and mixtures to which the EPA should give priority consideration for the promulgation of a rule. These recommendations are in form of a list. Within 12 months after the ITC designates a chemical for testing, the EPA must begin the rule-making process for the industry-funded studies or state why the tests are not necessary.

Federal Water Pollution Control Act (FWPCA). The policy and procedures for control of discharges of oil and hazardous substances into the environment are detailed in the FWPCA, PL 95-576, and in the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), PL 96-510 (Yon, Wentsel, and Bane 1983). EPA has promulgated regulations under the FWPCA that identify and establish reporting requirements for approximately 270 hazardous substances. These reporting requirements are based on harmful quantities as defined by the regulation.

According to Yon, Wentsel, and Bane (1983), each Army installation with the capability for a release of a reportable quantity of oil or hazardous substance to the environment is required, pursuant to the Army Regulation (AR) 200-1, to prepare and to maintain and implement a Spill Prevention and Countermeasure Control (SPCC) Plan and an Installation Spill Contingency Plan (ISCP). The reportable quantity for any hazardous substance is 1 lb (0.454 kg), unless otherwise specified in section 311 of the FWPCA. WP is the most stringently regulated compound with limits of 1 lb (0.454 kg) (Table 3).

Table 3
Reportable Quantity of WP Under Clean Water Act

Compound	Reportable Quantity per 24-hr Period
White phosphorus	1 lb (0.454 kg)
Phosphoric acid	5,000 lb (2,270 kg)

Note: Yon, Wentsel, and Bane 1983.

DOT

The DOT formulates the regulations for safe transportation of hazardous materials, poisonous substances, explosives, and other dangerous articles including phosphorus. The modes of transportation covered by the regulation are surface, air, and water carriers. In accordance with CFR 49, parts 171-190 and 297, the DOT regulates the safe transportation of hazardous materials, such as phosphorus, and explosive particles, by surface and air carriers (Yon, Wentsel, and Bane 1983). All commercial water carriers transporting hazardous materials are governed by DOT regulations as specified in CFR 46, parts 146-149 (Yon, Wentsel, and Bane 1983). WP is listed as a hazardous material by DOT (Table 4).

Table 4
WP as a Department of Transportation Hazardous Material

Name	Hazard Class	Id. No.	Required Labels
White phosphorus - dry	Flammable solid	UN1381	Flammable solid and poison
White phosphorus - in water	Flammable solid	UN1381	Flammable solid and poison

Note: Table adapted from Yon, Wentsel, and Bane 1983.

3 Analytical Methods

Introduction

WP has 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 chorine (Cl_2), bromine (Br_2), iodine (I_2), nitric acid (HNO_3), and potassium permanganate ($KMnO_4$) or other oxidizing agents; followed by colorimetric determination of PO_4^{-3} (Sullivan et al. 1979). The detection limit of WP was 0.01 mg/ℓ (10 μg/ℓ). However, bioassays and field data suggested that acute and chronic effects on aquatic biota are significant at concentrations well below 10 μg/ℓ (Sullivan et al. 1979).

While Gas-Liquid Chromatography (GLC) and Neutron Activation Technique (NAT) were developed for low-level WP detection, GLC is more widely used than NAT. Both are described in the following paragraphs.

Gas-Liquid Chromatography

Addison and Ackman (1970) developed a GLC procedure for low-level WP detection. The method was designed to detect WP in sediments contaminated with colloidal WP from a production plant in Long Harbour, Placentia Bay, Newfoundland. Benzene extracts of mud, water, and biological samples are injected into a GLC equipped with a flame photometric detector (FPD). The correct choice of analytical conditions isolates a WP peak and eliminates most of the interferences from other phosphorus compounds or hydrocarbons. The GLC-FPD technique has been used in the majority of the reviewed literature on water, sediment, and biological tissue analyses. Addison and Ackman (1970) report that sediment and water samples can be extracted with toluene and analyzed by gas chromatography/mass spectrometry. The mass spectrometer was used as a detector because it is programmable to scan for the WP molecule. This eliminates the misidentification of phosphorus due to coeluting peaks or any interference in the matrix.

Taylor and Walsh (1992) optimized GLC analytical methods for determining WP in contaminated sediments. Their results show that the GLC method has a better than 80-percent recovery rate for WP. Fluidizing the sediments by adding half to equal amounts of water to saturated soil, volume by volume basis, greatly increases WP recovery. After collection, samples were found to remain stable for 9 to 10 months if refrigerated at 4 °C and kept from drying out by capping them tightly to prevent desiccation. The extracts in contact with the soil are stable for several weeks if not shaken.

A variety of solvents are used to extract WP from a soil matrix. A list of solvents used for WP extraction and their disadvantages are shown in Table 5. Some of these solvents are very toxic, and difficulty is encountered when working with them, transporting them, and disposing of them. Taylor and Walsh (1992) report that isooctane, a nonpolar solvent, is the least toxic of the solvents. Taylor and Walsh (1992) discussed some inconveniences of using each of the solvents.

Table 5
Solvents for WP

Solvent Type	WP Solubility, g/ℓ	Matrix Extracted for WP	Disadvantages
Benzene	29	Sediment Water Tissue Air	Human carcinogen and teratogen
Isooctane	N/A[1]	Sediment Tissue	
Hexene	N/A	Sediment Water	
Toluene	N/A	Sediment	Aromatic, not compatible with flame photometric detector
Acetone	N/A	Sediment	Does not readily dissolve WP
Methanol	N/A	N/A	Does not readily dissolve WP
Carbon Disulfide	1,250	N/A	Strong disagreeable odor, not compatible with flame photometric detector
Ether	9.8	N/A	Highly flammable, anaesthetic
Chloroform	25	N/A	Anaesthetic
Ethanol	25	N/A	

Note: Table adapted from Taylor and Walsh (1992).
[1] Not available.

GLC can also be modified as required by the mode of contamination and the characteristics of the samples. Further studies conducted by Walsh and Taylor (1993) optimized the method for detection of very low (less than 1-μg/kg) WP concentrations. They used a portable capillary-column gas chromatograph to analyze sediments from ERF. The ERF sediments did not mix with the nonpolar isooctane despite vigorous agitation. This poor mixing was attributed to the small particle sizes typical of the ERF sediments. Hydrometer analyses of these sediments showed that the silt and clay fractions were greater than 97 percent in contrast with the one used by Addison and Ackman, which consisted mainly of mixed gravel, sand, silt, and clay (Walsh and Taylor 1993). Up to 60 samples per 8-hr work day can be processed and analyzed with GLC.

Neutron Activation Technique

The NAT method is fully described in Lai (1979a). NAT is a rapid and highly sensitive method for the determination of phosphorus in environmental waters. The method is capable of detecting 0.01-μg/ℓ WP with an accuracy of 10 percent and a precision of 12 percent. NAT is free from interferences of other organic and inorganic phosphorus compounds. The cost per analysis is low compared with that of other techniques (Lai 1979a). The technique involves initial extraction with benzene at a water:benzene ratio of 10 or less. The benzene extract is then oxidized with 8 M nitric acid (10:1) for 2 hr by agitation, with a WP recovery of ≥99 percent as PO_4^{-3}. The nitric acid solution is reduced to less than 0.5 ml in an evaporation chamber at low temperature, and activation analysis proceeds. The solution is transferred to polyethylene tubing and irradiated in the National Bureau of Standards reactor for 1 hr at a neutron flux of 5×10^{13} *n*/cm^2-sec. The radioactive phosphorus is separated by precipitation as yellow ammonium phosphomolybdate after the addition of nitric acid, a phosphorus carrier, and molybdic acid reagent in the presence of heat and stirring. The precipitate is purified by washing with nitric acid and dissolved in ammonium hydroxide, followed by further precipitation as $MgNH_4PO_4 \cdot 6H_2O$ by the addition of a magnesia mixture and ammonium hydroxide. This mixture is further washed with ammonium hydroxide 5 percent and 95-percent alcohol. This is followed by filtration.

The reported detection limit for WP using NAT is 0.001 μg/ℓ. Interference by other inorganic and organic phosphorus species is considered essentially insignificant. While the NAT is extremely sensitive under experimental conditions, extraction using benzene may result in positive interferences which would limit its usefulness in detecting low-level WP concentrations in the environment. One of the disadvantages of NAT is that only a few laboratories have a nuclear reactor available for neutron activation analysis. Lai (1979a) reports that a set of eight samples can be processed in 2 work days.

4 Safety Concerns

General Information

WP may spontaneously ignite if exposed to air. At ambient ordinary temperatures and pressures, WP is practically insoluble and nonreactive with water. Thus, it is safely stored and transported submerged in water. However, at elevated temperatures and pressures, WP reacts with water (steam) to produce phosphine (PH_3), phosphorus acid (H_3PO_3), phosphorus pentoxide (P_4O_{10}), and hydrogen (H_2). It should be handled with forceps, as contact with the skin may cause severe burns. It is dangerous when exposed to heat and is incompatible with all oxidizing agents, elemental sulfur, and strong caustics.

The list of chemicals presented in Table 6 are incompatible with WP. A reaction between WP and one of these materials could present an explosion hazard and may generate highly reactive and toxic products.

WP reacts with carbon dioxide at elevated temperatures to produce phosphorus pentoxide and carbon monoxide according to the reaction:

$$P_4 + 10CO_2 \rightarrow P_4O_{10} + 10CO$$

Therefore, CO_2 extinguishers should not be used to extinguish WP fires.

Adverse Effects of Absorption

Phosphorus routes of exposure include inhalation of vapor, fumes or mist, ingestion, and skin and eye contact. Animal experiments indicate that acute and systemic poisoning may follow skin burns.

High concentrations of the vapors evolved by burning WP are irritating to the respiratory tract, skin, and eyes (Sax 1984). If phosphorus is ingested, it can be absorbed through the gastrointestinal tract or the lungs. The absorption of toxic quantities of phosphorus has an acute effect on the liver and is

Table 6
Chemicals Incompatible With WP

Chemical	Molecular Formula	Reaction
Acids	--	Reacts violently
Alkali metal nitrides	--	Formation of highly flammable compound
Alkaline hydroxides	--	Formation of pyrotechnic compound on boiling
Ammonium nitrate	NH_4NO_3	Explosion on impact
Animal charcoal	Not available	Ignition reaction
Antimony pentachloride	$SbCl_5$	Ignites on contact
Antimony pentafluoride	SbF_5	Ignition reaction on contact
Barium bromate	$Ba(BrO_3)_2$	Explosive reaction by heat, percussion, or light friction
Barium chlorate	$Ba(ClO_2)_2$	Explosive reaction by heat, percussion, or light friction
Barium iodate	$Ba(IO_3)_2$	Explosive reaction by heat, percussion, or light friction
Beryllium	Be	Incandescent reaction in phosphorus vapors
Boron trifluoride	BF_3	Incandescent reaction
Boron triiodide	BI_3	Incandescent reaction
Bromates	--	Explosion reaction by heat, percussion, or light friction
Bromine (gas, vapor)	$BR_{2(g),(v)}$	Incandescent reaction
Bromine (liquid)	$Br_{2(1)}$	Explosive reaction
Bromine, carbon disulfide	Br_2, CS_2	Yields slimy by-product that explodes violently on heating
Bromine trifluoride	BrF_3	Incandescent reaction
Bromoazide	BrN_3	Explosive reaction
Calcium bromate	$Ca(BrO_3)_2$	Explosive reaction by heat, percussion, or light friction
Calcium chlorate	$Ca(ClO_2)_2$	Explosive reaction by heat, percussion, or light friction
Calcium hydroxide (hot)	$Ca(OH)_2$	Evolves phosphine, which may ignite in air
Calcium iodate	$Ca(IO_3)_2$	Explosive reaction by heat, percussion, or light friction

(Sheet 1 of 6)

Table 6 (Continued)

Chemical	Molecular Formula	Reaction
Caustic alkalies (boiling)	--	Evolves phosphine, which may ignite in air
Carbon + air	--	Ignition at room temperature
Cerium	Ce	Violent reaction on heating to 400 - 500 °C
Cesium	Cs	Vigorous reaction below 250 °C
Cesium acetylene carbide	$CsHC_2$	Incandescent reaction on heating
Cesium nitride	Cs_3N	Vigorous reaction
Chlorates (moist)	--	Explosive reaction on contact
Chlorine (gas)	$Cl_{2(g)}$	Ignition reaction
Chlorine (liquid)	$Cl_{2(1)}$	Explosive reaction
Chlorine dioxide	ClO_2	Ignition and possible explosion
Chlorine monoxide	ClO	Explosive reaction
Chlorine trifluoride	ClF_3	Ignition reaction
Chlorine trioxide	ClO_3	Explosive reaction
Chlorine + heptane	$Cl_2 + C_7H_{16}$	Possible explosive reaction
Chlorosulfonic acid	$HClSO_3$	Explosive reaction @ 25-30 °C
Chlorosulfuric acid	$HClSO_3$	Explosion hazard
Chromic anhydride	CrO_3	Explosive reaction
Chromic acid	H_2CrO_4	Explosive reaction
Chromium trioxide (molten)	CrO_3	Explosive reaction
Chromyl chloride	$Cr(OCl_2)$	Explosive reaction with moist phosphorus
Copper	Cu	Incandescent reaction on heating
Cyanogen iodide	CIN	Incandescent reaction with molten phosphorus
Dinitrogen pentaoxide	N_2O_5	Ignition on heating
Dinitrogen tetroxide	N_2O_4	Violent combustion
Fluorine (gas)	$F_{2(g)}$	Ignites on contact

(Sheet 2 of 6)

Table 6 (Continued)

Chemical	Molecular Formula	Reaction
Halogens or interhalogens	--	Ignition or incandescent reaction
Halogen azides	--	Explosive reaction
Heptasilver nitrate octaoxide	Ag_7NO_{11}	Explosion on impact
Hexalithium disilicide	Li_6Si_2	Incandescent reaction
Hydrogen peroxide	H_2O_2	Violent reaction when heating in air
Hypochlorites	--	Explosion hazard
Iodates	--	Explosive reaction with heating, percussion, or light friction
Iodine	I_2	Ignites on contact
Iodine, carbon disulfide	I_2, CS_2	Vigorous reaction
Iodine monochloride	ICl	Violent reaction
Iodine monobromide (molten)	IBr	Violent reaction
Iodine pentafluoride	IF_5	Explosive reaction
Iron	Fe	Incandescent reaction on heating
Lanthanum	La	Violent reaction on heating to 400-500 °C
Lead oxides	--	Explosion on grinding
Lead peroxide	PbO_2	Explosive reaction
Lithium	Li	Violent reaction on heating
Lithium carbide	Li_2C_2	Combustion on heating
Lithium silicide	Li_6C_2	Incandescent reaction
Magnesium bromate	$Mg(BrO_3)_2$	Explosive reaction by heat, percussion, or light friction
Magnesium chlorate	$Mg(ClO_2)_2$	Explosive reaction by heat, percussion, or light friction
Magnesium iodate	$Mg(IO_3)_2$	Explosive reaction by heat, percussion, or light friction
Magnesium perchlorate	$Mg(ClO_4)_2$	Explosive reaction on mixing
Manganese	Mn	Incandescent reaction in phosphorus vapor

(Sheet 3 of 6)

Table 6 (Continued)

Chemical	Molecular Formula	Reaction
Metal acetylides	--	Incandescent with warm phosphorus
Mercuric oxide	HgO	Explosion on percussion
Mercurous nitrate	$HgNO_3$	Explosion on percussion
Neodymium	Nd	Violent reaction on heating
Nickel	Ni	Incandescent reaction on heating
Nitrates	--	Possible explosion
Nitrogen acid vapor	$HNO_{3(v)}$	Ignition reaction
Nitrogen bromine	NBr	Violent explosion on contact
Nitrogen chloride	NCl	Explosive reaction
Nitrogen dioxide	NO_2	Ignition reaction on heating
Nitrogen oxide	N_2O	Ignition reaction on heating
Nitrogen tribromide	NBr_3	Explosive reaction
Nitrogen tribromide hexaammoniate	$NBr_3 \cdot H_{18}\,N6$	Explosive reaction
Nitrogen trichloride	NCl_3	Explosive reaction
Nitrosyl fluoride	NOF	Incandescent reaction
Nitryl fluoride	NO_2F	Explosion hazard
Oil of turpentine	Not available	Incompatible
Osmium	Os	Incandescent reaction in phosphorus vapor
Oxidizing materials	--	Explosive reaction
Oxygen	O_2	Vigorous reaction
Performic acid	Not available	Explosive reaction
Peroxyformic acid	H_2CO_3	Explosive reaction
Platinum	Pt	Incandescent reaction on heating
Praseodymium	Pr	Violent reaction on heating
Potassium	K	Explosive reaction
Potassium bromate	$K(BrO_3)$	Explosive reaction by heat, percussion, or light friction

(Sheet 4 of 6)

Table 6 (Continued)

Chemical	Molecular Formula	Reaction
Potassium chlorate	$KClO_2$	Explosive reaction by heat, percussion, or light friction, evolves spontaneously flammable phosphine on boiling
Potassium hydroxide	KOH	Explosive reaction
Potassium iodate	KIO_3	Explosive reaction by heat, percussion, or light friction
Potassium iodate, water	KIO_3, H_2O	Violent reaction and possible explosion
Potassium nitride	K_3N	Formation of highly flammable compound on heating
Potassium permanganate	$KMnO_4$	Explosion on grinding
Potassium peroxide	K_2O_2	Ignition and possible explosion
Rubidium	Rb	Vigorous reaction
Rubidium acetylene carbide	$RbHC_2$	Incandescent reaction on heating
Seleninyl chloride	$SeOCl_2$	Possible explosion
Selenium monochloride	Se_2Cl_2	Explosion on mixing
Selenium oxychloride	$SeOCl_2$	Possible explosion
Selenium oxyfluoride	$SeOF_2$	Spontaneous ignition reaction
Selenium tetrafluoride	SeF_4	Violent reaction
Silver nitrate	$AgNO_3$	Explosive reaction by heat, percussion, or light friction
Silver oxide	Ag_2O	Ignition on impact
Sodium	Na	Explosive reaction
Sodium bromate	$NaBrO_3$	Explosive reaction by heat, percussion, or light friction
Sodium carbida	Na_2C_2	Ignition reaction in phosphorus vapor
Sodium chlorate	$NaClO_2$	Explosive reaction by heat, percussion, or light friction
Sodium hydroxide	NaOH	Evolves spontaneously flammable phosphine on boiling
Sodium iodate	$NaIO_3$	Explosive reaction by heat, percussion, or light friction
Sodium peroxide	Na_2O_2	Explosive reaction

(Sheet 5 of 6)

Table 6 (Concluded)

Chemical	Molecular Formula	Reaction
Sulfur	S	Ignition and explosion on warming
Sulfuric acid (boiling, concentrated)	H_2SO_4	Ignition
Sulfur trioxide (liquid)	$SO_{3(l)}$	Immediate ignition on contact
Sulfur trioxide (vapor)	$SO_{3(V)}$	Ignition reaction, which may be delayed
Thorium	Th	Incandescent reaction on heating
Vanadium oxytrichloride	$VOCl_3$	Possible explosion
Zinc bromate	$Zn(BrO_3)_2$	Explosive reaction by heat, percussion, or light friction
Zinc chlorate	$Zn(ClO_2)_2$	Explosive reaction by heat, percussion, or light friction
Zinc iodate	$Zn(IO_3)_2$	Explosive reaction by heat, percussion, or light friction
Zirconium (in vacuum)	Zr	Incandescent reaction on heating

(Sheet 6 of 6)

accompanied by vomiting and marked weakness. The most common symptom of long, continued absorption of small amounts of phosphorus is necrosis of the mandible or jaw bone, known as "phossy-jaw." Phossy-jaw can result from exposure as limited as 10 months, but commonly results from continuous low-level absorption over several years.

Chronic poisoning can also result from long continued absorption, particularly through the lungs and through the gastrointestinal tract. This gives rise to a generalized form of weakness accompanied by anemia, loss of appetite, diarrhea, and pallor. WP can also cause changes in the long bones. Seriously affected bones may become brittle, leading to spontaneous fractures. WP is especially damaging to the eyes. Some symptoms that have been reported following inhalation are photophobia with myosis, dilation of pupils, retinal hemorrhage, congestion of the blood vessels, and rarely optic neuritis. It also has adverse effects on the teeth.

Medical Surveillance

A wide range of potential health effects exists from exposure to WP. It is necessary that workers exposed to WP be subjected to periodic medical screening tests. A complete medical examination surveillance program is recommended, beginning with an initial medical evaluation with history, physical and dental examination with X-rays of teeth, liver function tests, and a complete blood count. Gordon, Hartley, and Roberts (1992) recommend that examinations should be conducted on a semiannual basis. The medical screens should give special consideration to the skin, eyes, jaw, teeth, respiratory tract, and liver.

Scrupulous hygiene should be maintained to prevent the development of WP effects on the jaw. Any required dental work should be completed before workers are assigned to areas of possible WP exposure because carious teeth and poor dental hygiene may increase the risk of WP absorption (Sittig 1985). Workers experiencing any jaw injury, tooth extractions, or any abnormal dental conditions should be removed from areas of exposure and observed. Examinations with X-ray photography may show necrosis; however, in order to prevent full development of the separation of a dead bone fragment from a healthy bone, the disease should be diagnosed in earlier stages.

Personal Protective Methods

Because of the high reactivity of WP in air, the use of a glove box or other suitable enclosed area purged with nitrogen is recommended to handle this substance in a laboratory. A worker should wear appropriate clothing and eye protection to prevent any possibility of skin and eye contact when handling the substance outside a glove box. Employees should wash immediately when skin is exposed to WP. The clothing should be removed immediately if wetted or contaminated with the substance. Emergency showers and eyewash should be provided in the work place. The level of protection used will be determined by full consideration of the specific chemical contaminants present in the work area, the performance characteristics of available protective clothing, and site and/or task-specific requirements and limitations. Refer to The NIOSH Pocket Guide to Chemical Hazards (1990) for a list of recommendations for respirator selection to use when working with white phosphorus.

5 Environmental Fate

WP Transformation Processes

This section presents several WP transformation processes: oxidation, hydrolysis, and biotransformation. Among these, the predominant WP transformation processes are oxidation and hydrolysis.

Oxidation

Vapor phase. Oxidation is the most dominant chemical transformation of WP in munitions smokes. Spanggord et al. (1983) reported that the oxidation reaction in the vapor phase proceeds by a branching-chain mechanism and is diffusion limited. Berkowitz et al. (1981) reported that when phosphorus munitions are deployed in the atmosphere, WP particles settle to the ground and continue burning for 6-7 min. The gas-phase hydrolysis of WP has been reported to be catalyzed by metal ions and by H_3PO_4 (Van Wazer 1958)

Aqueous systems. WP in aqueous systems generally exists in three forms: dissolved WP, colloidal WP, and suspended WP. Studies on the natural degradation of WP in environmental waters indicate that both suspended and dissolved WP are highly reactive and are rapidly oxidized to lower states of phosphorus in aerated waters. The form of WP can significantly affect its persistence in the environment. Aqueous phase reaction of WP typically involves a rapid oxidation with dissolved oxygen (DO) to oxyacids of phosphorus.

Many factors can affect the oxidation kinetics of WP:

a. WP form: suspended or dissolved.

b. DO concentration.

c. Salt concentration.

d. Metal ion concentration.

e. pH.

f. Temperature.

Details of these are discussed in the following paragraphs.

While reaction of WP with DO is relatively quick, dissolved WP reacts faster than suspended WP, as expected. Lai and Rosenblatt (1977) report that in a solution containing 65 $\mu g/\ell$ of suspended WP and 140 $\mu g/\ell$ of dissolved WP, the oxidation of the dissolved WP was five times faster. At concentrations below the solubility limit of 3 mg/ℓ, WP is expected to exist predominantly in the dissolved phase.

WP in the dissolved phase is reported to oxidize in first order reaction kinetics to concentrations below 0.01 ppm. This reaction is highly dependent on the DO concentration, with higher DO concentrations greatly increasing the reaction kinetics (Lai and Rosenblatt 1977). Half-lives of dissolved WP range from 0.85 to 20 hr with distilled water (Sullivan et al. 1979). Sullivan also reported a half-life of 240 hr with seawater. Such a large half-life would suggest a mixture containing colloidal and suspended WP.

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

Metal ions have a strong influence on the oxidation rate. Solutions of WP are very rapidly degraded in the presence of copper ions at 1 ppm, and similar concentrations of iron extend the half-life by an order of magnitude (Sullivan et al. 1979). Such data suggest that some metals catalyze the oxidation while others form complexes that lower the oxidation rate. Sullivan et al. (1979) report that since the iron ion is prevalent in aquatic sediments, it may combine with WP at the surface of particles to provide a passive ferro-phosphorus coating that is resistant to oxidation. The interactions of metal ions with WP should be studied in greater detail due to the presence of metal ions in natural waters and in soils.

Results of studies (Lai 1979b) show that the degradation rate is independent of the WP concentration. Results of previous studies (Lai and Rosenblatt 1977) also suggest that the degradation rate is a function of the dissolved oxygen concentration, temperature effects, and pH of the solutions.

Lai (1979b) studied the effect of pH on the degradation of WP. The results showed little variation in the degradation rate between pH 2 and 6. Above pH 6, the degradation rate of WP is increased (Table 7). The increase of P_4 reactivity with increasing pH was attributed to the presence of higher concentration of hydroxide that reacts with WP according to the reactions:

Table 7
Effect of pH on WP Degradation[1,2]

pH	Final WP Concentration, μg/ℓ	WP Degraded, percent
2	6.8	84.5
4	7.7	82.5
6	7.5	83.0
8	1.8	95.9
10	0.74	98.3

Note: From Lai (1979b).

[1] The initial WP concentration for the study was 44 μg/ℓ.

[2] The elapsed time was 69 hr.

$$P_4 + 4OH^- + 4H_2O \rightarrow 4H_2PO_2^- + 2H_2$$

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

The temperature effect on WP degradation was also studied by Lai (1979b). The results showed that solutions at lower temperatures had much lower degradation rates in spite of higher dissolved oxygen contents, which normally enhanced degradation (Table 8).

Table 8
Effect of Temperature on WP Degradation[1,2]

Temperature, °C	Final WP Concentration, μg/ℓ	WP Degraded, percent	Half-live, hr
3	37.0	15.9	288
22	7.5	82.9	26.2
44	2.9	93.4	17.1
64	1.3	97.0	13.2
93	0.48	98.9	11.4

Note: From Lai (1979b).

[1] The initial concentration was 44 μg/ℓ.

[2] The elapsed time was 67 hr.

Solid phase. The oxidation of solid WP has been extensively studied by Van Wazer (1958). The mechanism attributed to this oxidation involves a branching-chain mechanism similar to the one of vapor phase oxidation. The rate of combustion is diffusion controlled. In soils or sediments where the partial pressure of oxygen is low, oxidation will be very slow and WP would be persistent (Spanggord et al. 1983).

Hydrolysis

WP reacts with water according to the reaction:

$$P_4 + 6H_2O \rightarrow 3H_3PO_2 + PH_3$$

The main product of hydrolysis is phosphine, PH_3 (Lai and Rosenblatt 1977). The other reaction product in the reaction is hypophosphorous acid. In kinetic studies conducted by Spanggord et al. (1985), the production of phosphine was inversely related to oxygen concentration, thus favoring hydrolysis as a transformation process in soils or in moist storage areas. This study confirmed that a small percentage of WP lost from aqueous environments is converted to phosphine. According to Lai and Rosenblatt (1977), this percentage is between 6 and 9 percent. Thus, hydrolysis reactions must directly compete with oxidation reactions. Hydrolysis is also pH dependent (see reactions discussed in the section on aqueous phase oxidation).

Biotransformation

Under aerobic conditions, biological transformation is expected to be minimal compared with the rate of oxidation. Results of biotransformation studies conducted by Spanggord et al. (1985) indicate that WP is not readily used by anaerobic aquatic bacteria. However, polyphosphates and cyclic metaphosphates, degradation products of WP, can be hydrolyzed by both water and soil microorganisms under both aerobic and anaerobic conditions. Biosorption of WP was found to be insignificant (Spanggord et al. 1985). These studies indicate that all of the WP smoke-transformation products appear to be susceptible to microbial transformation in soil and water, although phosphine (PH_3) was not studied because of its rapid off-gazing. Such results suggest that although microorganisms will not directly affect WP, they will play a major role in the transformation of breakdown products to orthophosphoric acid.

WP has been tested as a phosphate fertilizer by Bohn, Ma, and Haas (1970) and Rodzigues, Bohn, and Johnson (1972). Their results show that in neutral, calcareous, and limed soil, WP is quickly oxidized to phosphates and used effectively by plants. However, in acidic soil, the process is much slower.

Breakdown Products of WP

The breakdown products of WP discussed in this section will be phosphorus pentoxide (P_4O_{10}), phosphorus trioxide (P_4O_6), phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), phosphine (PH_3), and other oxides. This section will present how these breakdown products are produced and some of their properties.

Phosphorus pentoxide

Phosphorus pentoxide (P_4O_{10}), also known as phosphoric oxide, is the major breakdown product of WP combustion in the presence of excess air. The reaction is:

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

The P_4O_{10} is responsible for the dense white cloud generated during WP munitions burst. The P_4O_{10} cannot be further oxidized, but it will react with atmospheric moisture to form polyphosphorus acids. The major environmental transformation mechanism is hydrolysis (Table 9). The products of

Table 9
Summary of Environmental Fate of WP Smokes and Their Combustion Products

Material	Environmental Transformation	Environmental Fate
White phosphorus, P_4	$P_4 + 5O_2 \rightarrow$ combustion $\rightarrow P_4O_{10}$ P_4O_{10} + atmos, $H_2O \rightarrow 4\ H_3PO_4$ $P_4 + 3O_2 \rightarrow$ combustion $\rightarrow P_4O_6$ P_4O_6 + atmos, $H_2O \rightarrow 4\ H_3PO_3$	Aquatic and soil fate is oxidation to phosphate via lower oxides
Phosphorus pentoxide, P_4O_{10}	Reacts with atmospheric moisture to form polyphosphorus acids	Aquatic and soil deposition to phosphates and lower oxides
Phosphorus trioxide, P_4O_6	$P_4O_6 + H_2O$ vapor $\rightarrow 4\ H_3PO_3$	Forms H_3PO_4, PH_3, and phosphates
Orthophosphoric acid, H_3PO_4	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $pK_{A1} = 2.12$ $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ $pK_{A2} = 7.21$ $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $pK_{A3} = 12.32$	Aquatic and soil deposition formation of phosphate salts
Phosphine, PH_3	Oxidize to form oxy-acids of phosphorus	Oxidized or disassociated
Phosphorus acid, H_3PO_3	$H_3PO_3 \rightarrow$ heating, 250 - 275 °C $\rightarrow 3\ H_3PO_4 + PH_3$	Thermal decomposition to give H_3PO_4, H_2, PH_3, and red phosphorus. It will form salts such as ammonium phosphite.

Note: Yon, Wentsel, and Bane (1983); Sawyer, McCarthy, and Parkin (1994).

hydrolysis of P_4O_{10} are tetrameta-phosphoric acid (77 percent), tripolyphosphoric acid (15 percent), and a mixture of trimeta-, tetrapoly-, and orthophosphoric acids (Spanggord et al. 1983). The P_4O_{10} reacts with alcohol to yield organic phosphates. Both the vapor phase and solid phase hydrolysis reactions are oxygen diffusion limited. The P_4O_{10} is one of the most powerful dehydrating agents known. It will remove water from materials such as nitric and sulfuric acids and from certain organic molecules.

Phosphorus trioxide

When phosphorus is burned in an oxygen-deficient atmosphere, phosphorus trioxide (P_4O_6) is formed according to the reaction:

$$P_4 + 3O_2 \rightarrow P_4O_6$$

The P_4O_6 is a colorless liquid at room temperature with a boiling point of 175 °C. It is stable in oxygen environments at room temperature. It is thermally unstable at temperatures over 210 °C decomposing to red phosphorus and to other PO_x oxides. As in the case of P_4O_{10} (phosphorus pentoxide), the trioxide is rapidly hydrolyzed. According to Spanggord et al. (1983), P_4O_6 reacts with water, at low temperatures and in the presence of atmospheric moisture, to yield phosphorus acid (H_3PO_3) (Table 9). Phosphorus acid, when heated, will form phosphoric acid (H_3PO_4) and phosphine (PH_3).

Phosphoric acid

Phosphoric acid (H_3PO_4), also called orthophosphoric acid, is produced when phosphorus pentoxide is exhaustively hydrolyzed according to the reaction:

$$P_4O_{10} + atmos,H_2O \rightarrow 4\ H_3PO_4$$

It is a colorless solid at room temperature. As a pure material, the acid has no oxidizing properties below 350 °C. Reactions of H_3PO_4 are predominated by dehydration to pyrophosphoric acid ($H_4P_2O_7$) and reduction by metals. These reactions are significant only at elevated temperatures. The acid is tribasic, and the following equilibrium equations are known to occur (Sawyer, McCarthy, and Parkin 1994):

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad pK_{A1} = 2.12$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad pK_{A2} = 7.21$$

$$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-} \qquad pK_{A3} = 12.32$$

Phosphoric acid is a major by-product of the wet-fill production operations of WP munitions. In the soil, it is generally converted to inorganic or organic phosphates. The H_3PO_4 will react with bases in most environmental mediums to yield the phosphate salts. It attacks metals to form the metal phosphates. Ammonia reacts with H_3PO_4 to produce the ammonium salt which can be utilized by plants and other biota as a source of phosphorus. The major reaction of H_3PO_4 in aqueous systems is salt formation. The phosphate ion will become partitioned between the sediment and aqueous phase (Berkowitz et al. 1981). Once it is in the sediment phase, the sediment may serve as a phosphate source for the aquatic environment. Phosphates are also an important plant nutrient and are incorporated into the organic phase by plant uptake.

Phosphorus acid

Phosphorus acid (H_3PO_3) is formed from the combustion product, P_4O_6, reacting with water (Table 9). Pure phosphorus acid is a colorless solid. It is prepared by reacting phosphorus trichloride with water under vacuum. It decomposes thermally to phosphoric acid, hydrogen, phosphine, and red phosphorus. It will undergo several transformations in the environment which give H_3PO_4 and phosphite salts such as ammonium phosphite. The oxidation of phosphorus acid to phosphoric acid is slow:

$$4H_2(O_3PH) \rightarrow 3H_3PO_4 + PH_3 \qquad (heating\ at\ 250-275\ ^\circ C)$$

Phosphine

Phosphine (PH_3) will be produced during any phosphorus oxidation reaction where less than stoichiometric quantities of oxygen are available in the presence of water (Spanggord et al. 1983). Phosphine is an extremely toxic gas with a Maximum Permissible Concentration of 0.3 ppm for humans. It has a low-water solubility. Therefore, it is expected to be found in the vapors above phossy water and perhaps during WP munitions use. Phosphine is a colorless gas at room temperature. It does not spontaneously ignite in air. It is rapidly biologically degraded in wet soil. Phosphine is oxidized to form oxy-acids of phosphorus and water when an oxygen and phosphine mixture is ignited. Because the partial pressure of oxygen in the atmosphere is normally above 100 mm Hg, an explosive mixture will be formed only at very high phosphine pressures. Therefore, the oxidation reaction will only proceed at a rapid rate when high concentration of phosphine are present. Phosphine may persist in the atmospheric environment for weeks to months. It is not expected to accumulate in aqueous or soil environments. Eventually, it will be oxidized to oxy-phosphorus compounds.

Other oxides

Other WP oxidation products include linear polyoxoacids and cyclic polyphosphates. These are fully described by Spanggord et al. 1983. Other phosphorus oxides include hypophosphate, phosphite, and hypophosphite. These compounds are reported to be relatively nontoxic. Burrows and Dacre (1973) discuss some of the effects of these compounds on the mammalian and aquatic organisms. There appear to be no toxicity data of any kind for hypophosphate. Burrows et al. (1973) report that although polyphosphoric acid is a sequestering agent and might enhance the toxicities of any heavy metals in the water, it is readily biodegradable to orthophosphoric acid.

Phosphorus Deposition in Soils

The transformations of WP in soil are similar to the aquatic systems. Since WP is not very soluble in water, its mobility in soil systems is low. The rate is highly dependent on the available oxygen in the soil (Berkowitz et al. 1981). If solid WP is buried in soil, the rate of oxygen diffusion will determine the rate of WP transformation. Factors that affect the oxygen diffusion rate in soils are (a) the presence of a surface-oxide layer that builds up on a WP particle, (b) the surface area of the WP, and the depth at which the WP is buried (Spanggord et al. 1985). Spanggord et al. (1985) reports that for a 1-cm-diam piece of WP buried 12 cm in soil, its lifetime is expected to range from 10 years (in the absence of surface-oxide layer) to 10,000 years (in the presence of a surface-oxide layer). Berkowitz et al. (1981) also agree that WP can exist for long periods in oxygen-deprived sediments or soil.

Studies conducted by Van Voris et al. (1987) indicated that when WP is added to a soil, the equilibrium between aluminum oxides and silica ion is disrupted. Acidic conditions in the soil result from WP particulates. In their studies, only surface soils were considered since the deposition of WP particulates is typically a surface-loading phenomenon.

WP is predominantly oxidized to phosphates in surface sediments ranging from weeks to months. In soil systems, phosphates can be incorporated into biological systems by plant uptake. Also, inorganic mineral phosphates are formed. Soil phosphates may be transported to aquatic systems by soil transport and leaching processes (Van Voris et al. 1987).

Interaction of trace metals with phosphorus species can contribute to leachability and subsequent migration of those metals. Addition of polyphosphates to the soil promotes the dissolution of calcium, manganese, and zinc without forming stable complexes. This addition also promotes the dissolution of magnesium and iron, forming stable complexes which can then be leached into deeper soil horizons. Polyphosphates can also increase the soluble organic carbon content in the soil.

ate

Some mechanisms for phosphorus retention by soils are precipitation, adsorption, microbial immobilization, plant uptake, and occlusion. The major phosphoric species in soil are $H_2PO_4^-$ and its soluble metallic complexes. Phosphate sorption has been statistically correlated to pH, $CaCO_3$ content, particle-size distribution, extractable (active) iron and aluminum, and organic carbon (Van Voris et al. 1987).

Inorganic phosphorus in soil can be classified into functional phosphorus fractions. The three fractions are nonoccluded, occluded, and calcium-precipitated. The first fraction is associated with aluminum and iron oxide surfaces and is readily available to plants. The occluded fraction is associated with aluminum and iron oxide lattices and is not readily available to plants unless released by outside mechanisms. The calcium-precipitated fraction is not accessible to plants (Van Voris et al. 1987).

6 WP Studies at Military Installations

Distribution of WP Residues

A sediment or soil concentration of WP above which "cleanup" is required has not been determined to date. Unlike many groundwater contaminants that spread as a plume from a localized source, WP is generally distributed as discrete particles from detonation of WP projectiles (Figure 3). Walsh and Collins (1993) from CRREL conducted a study at Fort Drum to determine the spacial distribution of WP residue dispersed from an exploding mortar round by measuring the WP concentrations in soil at and around the point of impact. In the same study, they also examined the persistence of WP in an upland site and collected data on the WP particle sizes produced from an exploding mortar round. Their study is discussed in this section.

WP distribution study—procedure

Mortar smoke WP rounds (81-mm, M375A2 with point-detonating fuses, M524A6) were used for the test (Figure 2). The bursting area for the round is reported to be 20 m in diameter (Walsh and Collins 1993). To collect the material ejected when the round was exploded, aluminum pans containing 3 cm of water were placed at 5-m intervals out to 25 m along the north, east, south, and west axes from the mortar round. Five rounds were detonated electrically.

WP distribution study—observations

Walsh and Collins (1993) found that the crater produced by the exploding WP projectile was small compared with that produced by high-explosive projectiles. The crater was less than a half a meter in diameter and up to 20 cm deep. A burned area up to 2 m in diameter surrounded the crater. When the soil within each crater was disturbed, the soil ignited and burned for several minutes (Figure 5). This is attributed to WP reaction with air.

Figure 5. Fire produced when disturbing soil within an impact crater (Walsh and Collins 1993)

Within a 5-m radius of the craters, bright orange and black burn residue was sporadically observed on the soil surface.

WP distribution study—results and discussion

The median of the distributions of the WP particle lengths and widths was between 0.5 and 1 mm, respectively. A total of 45 particles were isolated, and the total mass, as determined by a GC-Nitrogen Phosphorus Detector, was 68.7 mg. The spacial concentration around the WP detonating point is presented in Figure 6.

Walsh and Collins (1993) found that WP driven into a soil from exploding mortar rounds can persist at high concentrations in an upland site for several months and perhaps years. They observed high concentrations of WP confined to the crater center or within an area of less than 50 cm in diameter. Walsh and Collins reported that the detection of WP along a transect is an indication that within a 25-m radius, there exists a small area of significantly higher WP concentration. Therefore, applying the results of this test to the site assessment at ERF, Walsh and Collins (1993) consider that choosing a WP concentration as a criterion for cleanup, specifically at ERF, is not practical. They concluded the following:

a. Screening of areas for WP contamination requires intensive sampling because of the relatively small area contaminated from each WP projectile.

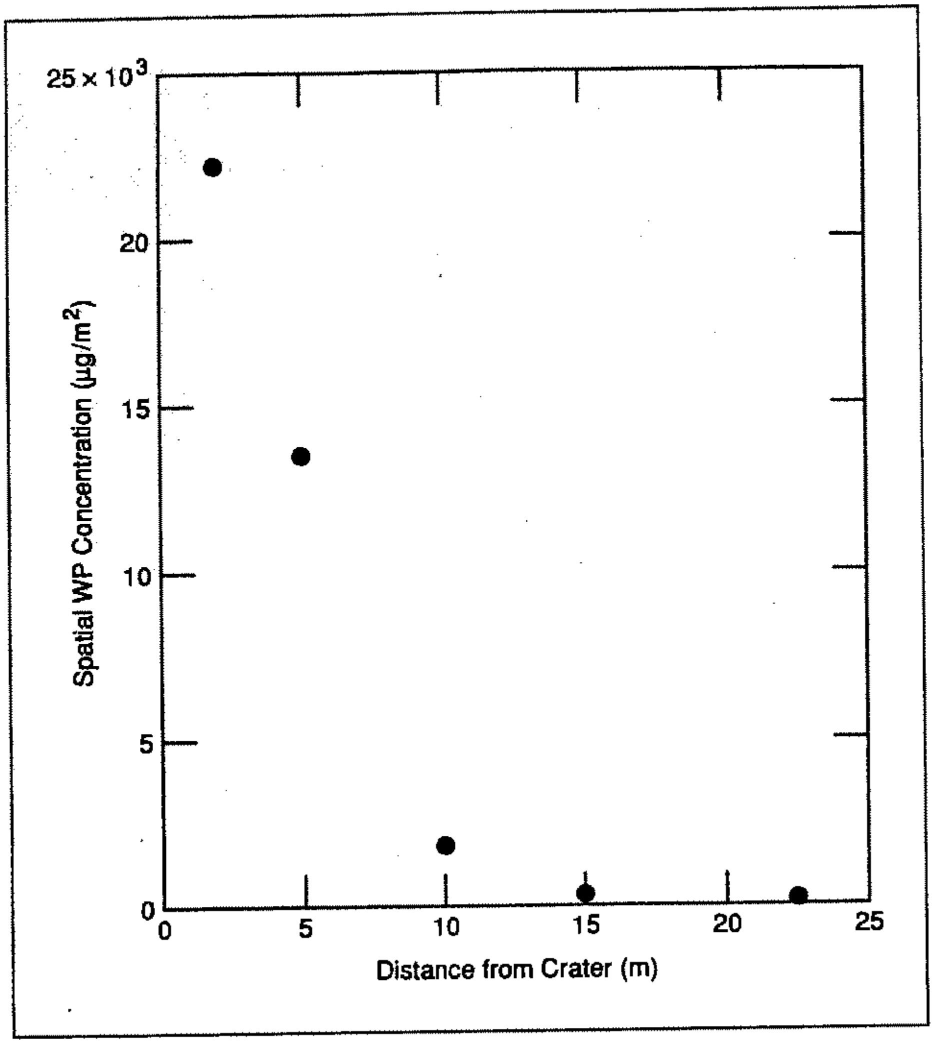

Figure 6. Spatial concentration of WP around detonation point (Walsh and Collins 1993)

b. Detection of WP at any concentration is evidence that a discrete area of significantly higher concentration may exist.

c. The discrete nature of the contamination precludes using any WP concentration as a criterion for cleanup.

Risk of WP Contamination at Several Military Installations

Simmers et al. (1993a-u) from WES evaluated the likelihood of WP contamination at 21 military installations. Their results are summarized in

Table 10. Each of these installations had been identified as a site where WP contamination might be present.

Table 10
Military Installations Studied by Simmers et al. (1993)

Installation	Number of Samples Where WP Was Detected per Total Samples Evaluated	Highest Reported WP Concentration mg/kg	Risk of WP Contamination
Fort McCoy	11/45	58.0	High
Yakima Training Center	3/27	430.0	High
Fort Bragg	7/90	0.10	High
Fort Riley	3/24	0.24	High
Fort Drum	11/45	0.023	High
Fort Campbell	2/48	1.30	Low
Fort Dix	1/36	0.003	Low
Fort Ord	1/18	0.00099	Low
Fort Pickett	0/33	<0.00096	Negligible
Fort Benning	0/48	<0.00096	Negligible
Fort Leonard Wood	0/18	<0.00178	Negligible
Fort Lewis	0/45	<0.00096	Negligible
Fort Chaffee	0/45	<0.00178	Negligible
Fort Gordon	0/24	<0.00096	Negligible
Fort Jackson	0/39	<0.00096	Negligible
Fort Hunter Liggett	0/33	<0.00096	Negligible
Fort Devens	0/21	<0.0014	Negligible
Fort Hood	0/27	<0.00096	Negligible
Fort Stewart	0/54	<0.00096	Negligible
Fort Sill	0/36	<0.0014	Negligible
Fort Meade	0/39	<0.0014	Negligible

At 5 of the 21 installations studied, Simmers et al. (1993a-u) determined the risk of WP contamination to be high. They reported a low risk of WP contamination for only 3 of the 21 installations studied. However, they recommended that the first eight installations in Table 10 may warrant a more detailed investigation for the risk of waterfowl poisoning from WP storage in wetlands. Simmers et al. (1993a-u) based their recommendations on the CRREL studies conducted by Walsh and Collins (1993) where they concluded that the detection of WP at any concentration is evidence that a discrete area of significantly higher concentration may exist.

7 Treatment Technologies

Introduction

Based on the literature reviewed, WP contamination present in wetlands sediments or soils and aqueous systems, as result of military uses of WP, is a significant but hard to estimate concern. A primary factor contributing to the contamination is that when WP is immersed in water, it ceases burning. WP is persistent in these systems and upon re-exposure to oxygen, will oxidize and may combust.

This chapter discusses several technologies being currently studied for treatment of contaminated sediments. Some of them are in conceptual stages of development and will require further study. The treatment effectiveness, adaptability, scale-up potential, and disadvantages of those technologies applied to the treatment of sediments is considered and discussed.

Aeration

Several studies have been conducted to relate the amount of DO to the degradation rate of WP. Lai (1979b) conducted a study to evaluate the degradation rate of WP in solutions by manipulating the amount of DO in the samples. In his study, two samples were exposed to limited air (closed system) and others to atmospheric conditions (open system). One of the samples in the closed system was exposed to daylight, and the other was kept in darkness. The degradation of WP in the open system was found to be much higher than that of the closed systems (Figure 7). The half-lives for the open and closed systems were reported to be 7.5 days and 11 days, respectively. The degradation rate of the open system appeared to follow first order reaction kinetics for up to 57 days. Such results indicate that WP is sensitive to air and light.

Lai (1979b) also studied the degradation rate in an aerated system. The air feed rate was 0.5 ℓ/min, and the DO concentration was maintained at 9 mg/ℓ. The temperature was 22 °C. The average half-life of WP reported was approximately 3 hr. The degradation rate decreased monotonically with time.

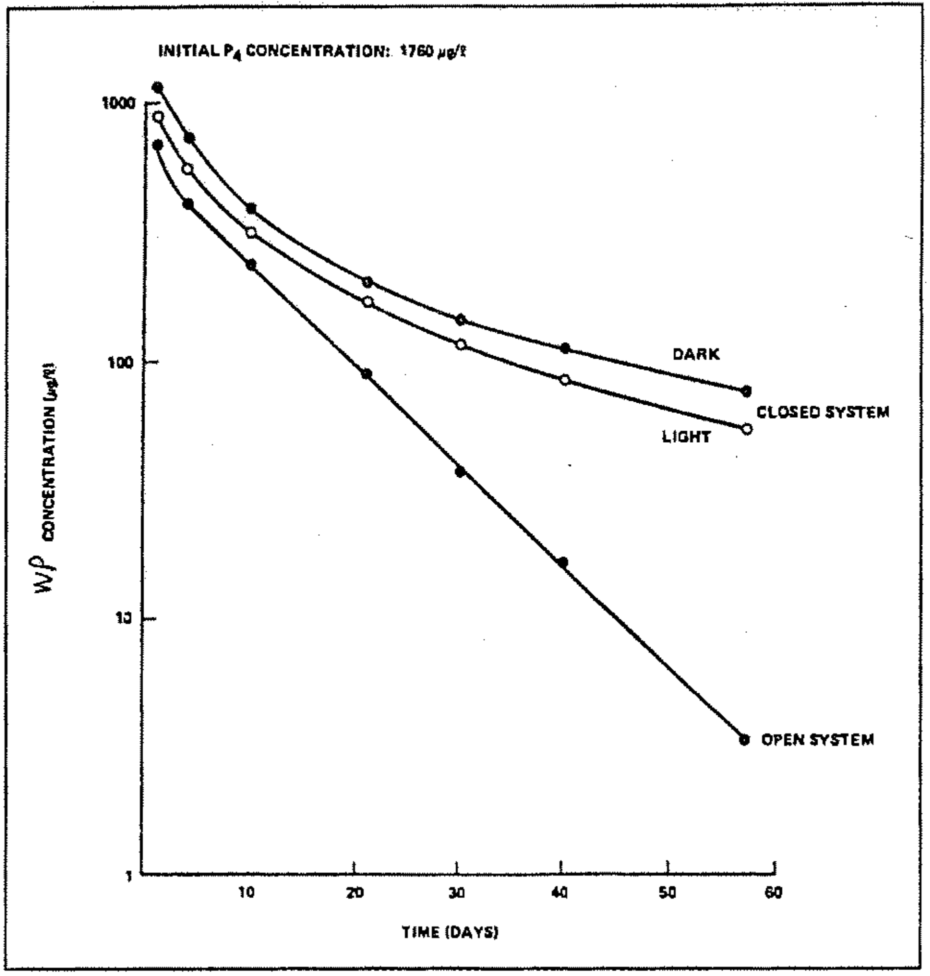

Figure 7. Degradation of WP in limited air systems (Lai 1981)

This study indicates that WP is rapidly oxidized to lower states of phosphorus in aerated waters.

Mixing as a mechanism to induce aeration was studied by Lai (1981). Lai (1981) conducted several studies evaluating the effects of certain parameters on WP release at the sediment/water interface. One of those parameters was the mixing intensity. His results demonstrated that WP release increased with increased agitation of the water (Figure 8). As shown in Figure 8, three conditions were studied: 60 rpm, 30 rpm, and 0 rpm. The release rate was 4 and 6 times higher for a system with mixing at 30 rpm and 60 rpm than without mixing, respectively. It can be observed from Figure 8 that the increased mixing was associated with an increase in the time required for the concentration of released WP to reach its maximum. Figure 8 reflects the combined effects of release and degradation rate.

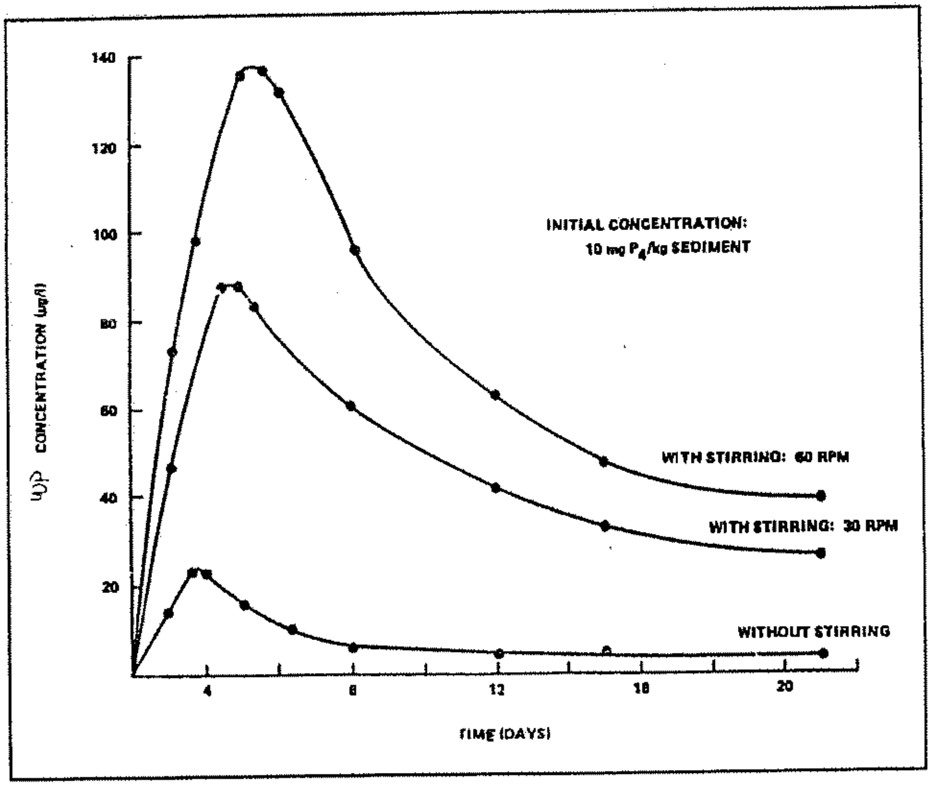

Figure 8. Release of WP from sediments when mixing is applied (Lai 1981)

Application to in situ treatment

Conceptually, an onsite aeration process would involve exposing the WP particles buried in the sediments and/or soils to oxygen. A mechanical aeration system could be used to increase the DO concentration in the sediment-water system. This would result in increasing the oxygen availability to the WP in the sediments, accelerating the degradation rate of the WP particles.

A mechanical aeration system would create a mixing process exposing the WP particles buried in the sediments to oxygen. An in situ mixing process or an in-vessel slurry mixing process could be used to distribute the WP stored in sediments. Treatment of WP in situ is expected to be slower due to buried WP. Such in situ processes would be dependent on the diffusion of oxygen into the sediment.

The mixing process would increase the diffusion rate of the air into the water. This would increase the oxygen available to the WP and, therefore, the oxidation rate would be increased. The WP would undergo rapid degradation through oxidation resulting from contact with DO in the water. The degradation products consist of nontoxic phosphorus species such as hypophosphorus acid, phosphorus acid, and phosphoric acid. In addition, this process can be combined with aeration.

Treatment effectiveness

Onsite aeration must consider the effective concentration of DO, matrix effects, temperature, and pH requirements to be applied for the treatment of WP. The oxygen demand of the sediments and all these factors require further study to determine if this treatment technology is feasible and acceptable for sediment or soil remediation. The oxidation rate of WP is proportional to the oxygen concentration to which WP is exposed. As previously discussed in the environmental fate section of this report (Chapter 5), the degradation rate of WP is also directly proportional to temperature and pH. The process may be scaled up using existing sediment handling and mechanical aeration equipment. Therefore, scale up should be readily achievable.

There is no information regarding full-scale mixing operations on sediments contaminated with WP. However, the experimental mixing data available on the release of WP from sediments seem to indicate that a mixing process can be adapted to treat WP-contaminated sediments. Onsite mixing processes must consider the effective mixing rate to use, the effective mixing time, and the matrix characteristics and effects. The mixing process involving undisturbed sediments and the slurry mixing process need to be evaluated under experimental conditions to determine the most effective and appropriate to the conditions for treatment.

In the case of slurry mixing, it would also be necessary to evaluate mixing depth effectiveness. The mixing process could require the determination of the optimum equilibrium concentration of water-to-sediment ratio, DO, and stirring rate for the system.

Potential disqualifiers

The principal concerns regarding application of the aeration process are as follows:

Lack of field application. Application of mechanical aeration or air diffusion, and mechanical agitation for in situ treatment of contaminated sediments with WP is purely conceptual at this stage. Research and development is warranted to evaluate the feasibility of applying this process to sediments.

Wetland alteration. The possibility of wetland alteration may be present. However, this alteration would have less magnitude than other techniques such as dredging, air-drying, and pond draining. If this treatment is applied, some wetlands functions may be altered. Wetland functions are physical, chemical, and biological processes or attributes of wetlands that are vital to the integrity of the wetland system (Adamus et al. 1991). Some of the functions that may be affected are flood flow alteration, sediment/toxicant retention, and nutrient removal/transformation among others. How these functions would be affected is beyond the scope of this report. However, they should be considered and studied for the implementation of this treatment technique.

Sediments characteristics. Depending on the sediment-water matrix, the kinetics of the process would probably differ from those observed under experimental conditions.

Lime Addition

Studies by Bohn, Ma, and Haas (1970) and Rodzigues, Bohn, and Johnson (1972) showed that in neutral, calcareous, and limed soil, WP is quickly oxidized to phosphates and used effectively by plants. For acid soil, the process was slow and phosphates were not available for plants for an extended period of time.

Application to onsite treatment

There are no experimental data to prove that this treatment technology can be used together with aeration and/or mixing for sediments contaminated with WP.

Treatment effectiveness

The effectiveness of lime treatment would be controlled by the soil-water matrix conditions. An evaluation of the conditions and properties of the sediment to be treated is necessary to determine the amount of lime required. It is expected that the lime addition would increase the pH of the sediments, increasing the oxidation rate of WP (see Table 7).

Potential disqualifiers

The disqualifiers in this situation would be the same as in aeration.

Chemical Oxidants

Lai (1979b) studied the effects of various oxidizing agents on the removal of WP from environmental waters. While all tested substances studied were effective in the removal of WP, ozone and sodium hypochlorite oxidants were the most effective (Table 11). In addition, sodium hypochlorite was the most rapid and inexpensive oxidant for use on the removal of elemental phosphorus in water when natural degradation was not possible.

Table 11
Reactions of WP With Various Substances[1,2,3]

Substance	Chemical Formula	Quantity	Residual WP Concentration, µg/ℓ
Nitric acid	HNO_3	1 N	5.7
Potassium hydroxide	KOH	1N	5.1
Zinc metal	Zn (20 mesh)	12.5 g/ℓ	3.2
Silver oxide	AgO	1.25 g/ℓ	0.28
Potassium permanganate	$KMnO_4$	125 mg/ℓ	0.20
Sodium hypochlorite	NaClO	375 mg/ℓ	0.01
Ozone	O_3	200 mg/hr 0.8%	0.01

Note: Lai (1979b).
[1] The initial WP concentration was 1,760 µg/ℓ.
[2] The volume of the solution was 0.4ℓ.
[3] The reaction time was 48 hr (For ozone, it was 6 hr).

Ozonation

According to Lai (1979b), ozone was capable of reducing the WP concentration below the detection limits during the test period (Table 11). According to studies by other investigators (Campbell 1977), ozone resulted in a 10-min half-life of WP. In 11 hr, the WP concentration was only slightly above the detection limits; after 24 hr of treatment with ozone, WP was undetectable.

Sodium hypochlorite

Because of its outstanding oxidizing power and low cost, sodium hypochlorite can be considered one of the best candidates for the treatment of phossy water. Kinetics studies of WP with sodium hypochlorite performed by Lai (1979b) show that the oxidation of WP is extremely rapid (Table 12). Within 10 min, the concentration was reduced to 0.048 µg/ℓ, which was about one ten thousandth its original concentration. This appears to be more effective than the oxidation of WP with ozone. It is believed that a dose of a few milligrams of hypochlorite per liter should be adequate for the complete oxidation of WP.

Table 12
Reaction Rate of WP With Sodium Hypochlorite[1,2]

Contact Time, hr	Residual WP Concentration, μg/ℓ
0.17	0.048
1	0.045
4	0.035
11	0.017
24	ND[3]

Note: Lai (1979b).
[1] Concentration of NaClO used was 250 mg/ℓ.
[2] The initial WP concentration was 510 μg/ℓ.
[3] ND = Not detected (P_4 < 0.01 μg/ℓ).

Treatment effectiveness

While the use of these strong oxidants is well established for wastewater treatment, they have never been used for WP-contaminated sediments. Therefore, this treatment technology will require further study to determine if performance is acceptable for contaminated sediments remediation. It will also be necessary to evaluate the effects of the oxidizing agents in the water-sediment environment. This technology can be combined with the mixing process to accelerate the degradation rate.

Potential disqualifiers

Determination of contaminated zones. WP contamination of sediments in wetlands is not localized. When WP munitions are deployed, the phosphorus breaks up into minute particles which are dispersed over a large area. Therefore, to avoid the unnecessary application of these chemicals to the natural environment, it will be necessary to determine first the contaminated zones.

A lack of field application history. There are many unanswered questions regarding the application of strong oxidizing agents to WP-contaminated sediments in natural environments. Treatment of WP-contaminated sediments with oxidizers is only conceptual at this stage. Research and experimental work is necessary to evaluate the feasibility of applying these processes to sediments.

Sediment-water matrix characteristics. Depending on the sediment-water matrix characteristics, the kinetics of this treatment technology would probably differ from those associated with wastewater treatment.

Costs. Chemical and handling cost could be considerably higher than those associated with wastewater treatment. Oxidizers are nonselective. All organic materials present in the soil will typically compete with the oxidizers. Therefore, large doses may be required for soils of high organic content, increasing the treatment costs.

Infrared Desorption Technology

Infrared Desorption Technology has been used by McLaren/Hart Environmental Engineering Corporation for soil remediation. The McLaren/Hart Infrared Desorption process employs a patented Infrared Vacuum (IRV-100) Low Temperature Thermal Desorption (LTTD) Unit for onsite treatment which remediates contaminated soil by using an infrared heating carriage (Figure 9). The design of the system consists of a 16-ft-long steel container with a base vacuum extraction chamber and a cover containing an infrared heat source. The base of the unit contains a series of well screens and steel tracks. The tracks allow the direct loading and unloading of soils, simplifying the batch treatment process. The contaminated soil is loaded into the vacuum chamber to a depth of 18 in., and then 3,000 cfm of air is drawn through the soil, creating a stripping effect and a vacuum gradient. Then, the infrared carriage is rolled into position over the container and produces hot air and radiant heat, which raises the temperature of the soil to 200 to 600 °F. An extraction fan pulls air downward through the soil, increasing the temperatures of the lower layers of soil. Another unit of the LTTD system is the IRVH-200, which consists of a high vacuum unit (moderate air flows and high vacuums) that is used to treat compounds with high boiling points.

In Ogden, UT, this system has been used for the treatment of WP-contaminated soil. During the remediation activity, the contaminated soil and debris were stockpiled and covered within a bermed and lined temporary storage cell. McLaren/Hart mobilized and set up two IRV-100 treatment units, ancillary emissions equipment, and support equipment in 3 days. The operating parameter identified by the demilitarization specialist was that the soil had to reach a uniform temperature thoroughly to 260 °F. One instance of auto ignition of the white phosphorus was detected inside the IRV-100 by the emission of a white, thick smoke plum through the exhaust stack. This condition was rapidly controlled with no worker injury.

Adaptation to onsite treatment

This technology was designed for onsite remedial processes.

IRV-100
System Specifications

Heat Transfer Method	Infrared Energy
Processing Capacity	20 - 30 tons/hour
Energy Input	1.5 mm BTU/ hour
Soil Discharge Temperature	150°F - 300°F
Pollution Control System	Cyclonal/Condenser/Carbon
Treatment Atmosphere	Aerobic
Operating Pressure	750 - 700 mm Hg
Target Contaminants	BTEX Volatile Organics Light Petroleum Products
Fuel	Propane/Natural Gas
System Space Requirements	60 x 100 (4 units)

IRV-100 UNIT

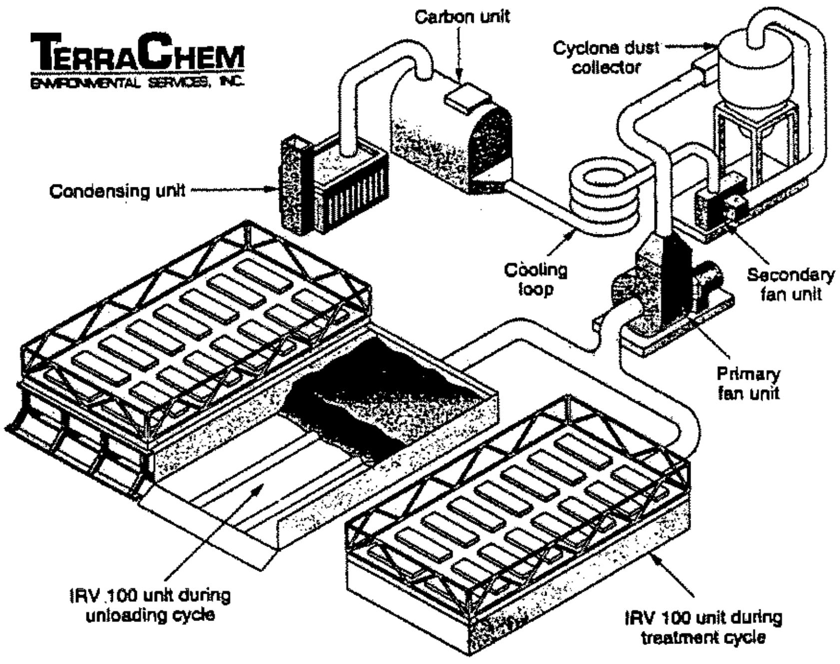

Figure 9. IRV-100 specifications end illustration (McLaren/Hart Environmental Engineering Corporation)

Treatment effectiveness

The LTTD system has proven to be effective in remediation WP-contaminated soil. The results of the remediation activity in Utah showed that the average treatment time for 107 five-yard treatment batches was 1 hr and 40 min. The treatment was completed in 4 days. The decontamination, equipment dismantling, and demobilization was complete in 2 days. Verification of the treatment and remediation was confirmed by feeding the treated soil and debris through a screening plant, thus exposing any nonignited white phosphorus.

With this technology, a volume from a hundred to thousands of tons of soil can be remediated depending on the principal contaminant to be treated. McLaren/Hart reported that a volume of 300 tons of WP-contaminated soil was treated using an IRHV-200 unit; the cost of the operation was $80K, $267/ton.

Potential disqualifiers

Release of toxic fumes. The concern that this treatment technology may present is the unplanned release of toxic gas. While the system is designed to operate under vacuum, WP might ignite inside the chamber and release a white thick smoke plum through the exhaust stack. This may present an employee hazard and a safety problem depending on the amount of WP ignited. This concern might be solved putting an air pollution treatment system at the end of the exhaust stack to avoid releases of toxic gases to the atmosphere.

Wetland alteration. The possibility of wetland alteration may be present if this treatment is applied. The wetland system and its functions may be affected. Some of the functions that may be affected are flood flow alteration, sediment stabilization, sediment/toxicant retention, and nutrient removal/transformation among others. How these functions would be affected is beyond the scope of this report. However, they should be considered and studied for the implementation of this treatment technique.

Air-Drying

During 1992, CRREL conducted an experiment to determine the effect of air-drying on WP concentration in sediments collected from some of the most highly contaminated sites at ERF. The moisture loss from these sediments resulted in a 99-percent removal of the WP after 2 weeks of air-drying at 20 °C in an environmental chamber (Racine et al. 1994). In this study, air-drying involves the excavation of contaminated sediment and then placing the sediment on a geotextile material to allow air-drying. When wet contaminated sediments were removed from ERF and allowed to air-dry, WP concentrations decreased to undetectable levels.

WP particles are persistent in saturated sediments. The studies conducted by CRREL indicate that air-drying is feasible by simply allowing the sediments to dry. The treatment will be potentially much more cost-effective than other treatment but it will be slow.

Pond Draining

CRREL demonstrated that WP particles were persistent at moisture contents at or above saturation. Pond draining technology may serve two functions: (a) it would eliminate the habitat for dabbling waterfowl, and (b) it would expose much of the WP-contaminated pond bottom sediment allowing for the in situ sublimation of WP particles.

CRREL studied the effectiveness of pond draining of contaminated shallow ponds in ERF for WP remediation (Racine et al. 1994 and 1995). The study was carried out in the Bread Truck (BT) pond at ERF. A siphon system consisting of 165 m of 6.1-cm rigid polyvinyl chloride plastic pipe was installed from the BT pond to a tidal gully north of the pond. Even though large areas of pond bottom sediment were exposed, they did not dry sufficiently to allow dissipation of any WP contamination. Although the siphon system lowered the pond water level faster than natural draining and evaporation, it did not lower the pond level below that which it would have attained without siphoning. Soil moisture sensors indicated that the sediments remained saturated throughout the period of study, summer 1994.

Application to onsite treatment

The CRREL treatability studies indicated that pond draining using a small-diameter siphon system could lower the water level faster than natural draining and evaporation. Artificial draining proved to be readily achievable.

Treatment effectiveness

The CRREL studies indicated that pond draining could be achieved by means of a drainage ditch. However, even though large areas of pond bottom sediments were exposed, they did not dry sufficiently to allow sublimation of WP particles. Collins suggested that the pond sediments were not exposed long enough throughout the period of study (Racine et al. 1995). He recommends that in order for pond draining to be a viable treatment option, water levels in a pond like BT have to be lowered as quickly and as far as possible after a flooding event to give the pond bottom sediments a long time to dry. This would require an active pumping system. Interactions of surface water runoff from adjacent areas may affect the length of time required to pump down the pond and the final achievable water level in the pond. A series of piezometers should be installed around the pond to monitor groundwater conditions during the pumping tests. Also, small cofferdams could isolate small areas at a time, if recontamination was not a problem.

Potential disqualifiers

The environmental conditions can affect the pond draining technology. Some ponds may undergo a seasonal drying and refilling cycle that depends on tidal action, river stage levels, and precipitation. The input of water from precipitation or tidal flooding must be controlled during drying.

Barriers

Since WP presents a major problem to waterfowl poisoning, another treatment technology that could be considered for use in remediation is the use of barriers. These barriers are comprised in part by geosynthetics, to prevent waterfowl from eating WP. This process can be considered for intermittent ponds where the natural sublimation of WP particles is occurring at a slower rate, but faster than those particles stored in the bottom sediments of permanent ponds.

Different kinds of barriers have been studied by CRREL. These are listed in the ERF study (Racine et al. 1994 and 1995). Geosynthetic barriers can effectively separate contaminated and uncontaminated soil, and they resist damage due to loading caused by large mammal traffic.

Another barrier studied by CRREL is the chemical hazing of ducks (Racine et al. 1994 and 1995). An encapsulated product containing a bird repellent, methyl anthranilate, was developed for the purpose of chemically hazing waterfowl from contaminated marshland. The chemical is encapsulated and spread onto the sediment of contaminated wetlands.

Racine et al. (1994 and 1995) also described other standard hazing methods. Up to 15 propane cannons were located around the open-water areas within a marsh. Visual scare devices like scarecrows and mylar tape were used. Electronic guards were also located, and they consisted of a siren and flashing strobe light, both of which activate automatically on 6- to 8-min intervals to deter waterfowl during hours of darkness.

Simple capping could be another barrier to apply. It could be less expensive and environmentally protective for a number of situations. Capping is the controlled placement of clean sediment over material considered contaminated to isolate it. Capping is a control measure currently used for contaminated dredged material disposal. As in any capping project, the procedure should be controlled and monitored.

Treatment effectiveness

The use of physical barriers as a remedial action would be effective in preventing waterfowl mortality due to the ingestion of WP. However, the saturated conditions of the contaminated bottom sediments would still preserve the WP particles, and geotextiles would prevent efficient drying if left in place for a long time. The method could be effective for intermittent or seasonal ponds where the sediments are exposed naturally to air. In such cases, the physical barriers should be removed during dry season to allow the WP concentration to decrease naturally and gradually. If a remediation technology is not feasible on a certain area, geosynthetic barriers may be considered as a permanent management alternative to prevent waterfowl mortality.

The use of chemical hazing and standard hazing methods studied by CRREL indicated a feeding rate decrease from waterfowl. However, these two methods are mainly temporary since there is no removal of WP particles from the sediment. Therefore, these barriers could be used temporarily to prevent waterfowl mortality until cleanup is achieved.

Potential disqualifiers

Wetland alteration. The possibility of wetland alteration may be present if barriers are used as a control measure to prevent waterfowl from WP intoxication. Some wetlands functions that may be affected are flood flow alteration, sediment stabilization, sediment/toxicant retention, and nutrient removal/transformation among others. How these functions would be affected is beyond the scope of this summary. However, they should be considered and studied for the implementation of this technique.

Waterfowl traffic. If capping is used as a barrier, a large waterfowl traffic could disturb and damage the cap. Therefore, the design life and the feasibility of a cap should be considered.

Dredging—Removal Technique

Dredging can be applied for contaminated areas which are constantly flooded, such as deeper ponded areas that do not allow natural drying of the soil and subsequent sublimation of the residual WP. For interconnected ponds over large areas, it would be impractical to address through pond draining. In this case, dredging may be appropriate. This technology is being studied at ERF (Racine et al. 1995). CRREL is studying remote control dredging, a small dredging operation, to remove sediments from contaminated ponded areas and treating the dredged material in an open-retention basin. The treatment method would be natural air-drying and sublimation of the WP. For small areas, a dredging operation could be quickly and efficiently conducted.

Treatment effectiveness

If remote control dredging can be achieved in certain ponds contaminated with WP, the dredged material can be collected in a diked area. Then, the sediment is allowed to air-dry so that the WP particles proceed to sublimation. Refer to the air-drying section for more information.

Potential disqualifiers

Overall cost. Dredging in an impact area presents many unique problems. A safety plan must be developed in addition to equipment selection. Safety concerns could significantly impact overall cost since special dredging will be required. Without supporting data, this is difficult to evaluate. Studies and a demonstration are currently being conducted by CRREL.

Presence of unexploded ordnance. A principal concern of a dredging operation in an impact area is the presence of unexploded ordnance which present a safety hazard. Remote-control dredging could be considered to address this issue.

8 Conclusions and Recommendations

An extensive literature search was conducted to identify the health risks associated with WP contamination, documented environmental effects, behavior and fate in the environment, and potentially applicable treatment technologies.

Results of this literature search indicate that WP contamination is generally restricted to the production of military smoke munitions as phossy water discharge to some impoundments or outfalls and to the use of incendiary rounds on training activities in wetland areas. The focus of this investigation was toward soil or sediment contamination resulting from training actions on impact areas. The purpose of this literature search was to identify potential remediation alternatives from such contamination.

The results of this effort indicate that information regarding remediation of WP in impact areas is very limited. Most studies focus on the fate and assessment of WP. The following paragraphs summarize the information covered.

From information currently available, it is difficult to identify the size of the WP soil and sediment contamination problem. It appears that WP soil and sediment contamination is limited to impact areas at fewer than 23 facilities of which ERF is the most studied. WP contamination is difficult to identify due to the particle nature of the contaminant or to the fact that it is dispersed over a large area. As a result, it is difficult to establish soil treatability goals if in fact such an approach is justified. While information to assess the environmental impact of WP contamination is incomplete, most historical research has focused on the impact of discrete particles on waterfowl or aquatic organisms that waterfowl may use as a feed source. According to this information, it appears that remediation alternatives must address the removal or destruction of WP particles.

Results of studies show that oxidation is an extremely important destruction process for WP and hydrolysis reactions will dominate the transformation of phosphorus oxides in the presence of moisture. WP undergoes degradation in aqueous solutions through oxidation with the DO. The degradation rate is also affected by pH and temperature. The studies conducted by Lai show that accumulated WP in sediments undergoes degradation, as in water, but at a slower rate. At the same time, part of the WP concentration can be released from the sediments back into the water. The release rate will depend on the DO concentration in the water, mixing, and temperature at the water-sediment interface. In addition to oxidation of WP through air exposure, chemical oxidation seems to be an effective means of WP destruction in aqueous systems. Air-drying also appears to be an effective destruction method for WP.

Some remediation alternatives may be achievable based on the result of the literature review. As result of this investigation, the following recommendations are presented:

a. The issue regarding WP contamination impact must be resolved. This involves the question of whether WP impact is limited to waterfowl.

b. Studies should be initiated to provide in situ remediation alternatives for WP.

c. Studies should be conducted to determine the effectiveness of oxidation alternatives for WP destruction in soil and sediments.

d. The cost-effectiveness of infrared technologies for WP treatment should be investigated.

e. There is a question of whether excavation techniques for WP in military impact areas are practical.

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13.ABSTRACT ***(Maximum 200 words)***

This document is a culmination of research from many different sources on the environmental effects and available treatment technologies of white phosphorus (WP). Health risks associated with WP exposure, environmental fate, and transformation products are also summarized.

WP is highly toxic and poisonous and spontaneously ignites in the presence of air. It is used in smoke-producing munitions by the U.S. military to create battlefield conditions. When WP munitions are deployed, they break up in little particles which disperse over a large area. When these particles come in contact with water, they cease burning. Then they settle and remain stored in the sediments. These particles are now available for aquatic organisms and waterfowl that feed from bottom sediments, and poisoning may result.

This report focuses on WP soil and sediment contamination due to its persistence in these environments. Most of the information sources found focused on WP water contamination and waterfowl poisoning. Limited information is available about remediation of WP in contaminated areas. However, technologies for removal of WP from soil and sediments are currently being studied. Some recommended technologies are only in the conceptual stage. Evaluation of these treatment technologies shows that the remediation alternatives must address the removal or destruction of WP particles. Oxidation and air-drying alternatives can be effective in removing WP particles from the soil and sediment.

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